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Sixth EC Natural Analogue Working Group Meeting

Proceedings of an international workshop held in Santa Fe, New Mexico, USA on 12-16 September 1994

Report

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Abstract

The sixth Natural Analogue Working Group meeting was held at Santa Fe, NM, USA on 12-16 September 1994 and was jointly organised by the Los Alamos National Laboratory and the European Commission.

About 50 participants from 13 countries and International Organisations (EC, IAEA) attended the meeting which was hosted by Los Alamos National Laboratory (USA) and co-sponsored by US-DOE, EC, LANL and US-NRC. Their support and cooperation are gratefully acknowledged.

The present proceedings include the scientific results of the 25 papers and some posters presented at the workshop which are devoted to (i) review the present status of the various national NA programmes, (ii) address the 'state-of-the-art' of several key issues in near field and far field processes and their importance to Performance Assessment (PA), (iii) arrive to a general consensus for each issue and (iv) provide guidelines as to the future importance of each issue in NA studies and their eventual use in PA and public relations.

The members of the NAWG Core Group summarised the main conclusions from the workshop and issued a statement outlining the present status of NA studies and future direction of NAWG.

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NAWG Core Group Statement

The 6th EC Natural Analogue Working Group (NAWG) Meeting at Sante Fe, USA (Sept. 12-16) was jointly organised by the European Commission (EC) and the Los Alamos National Laboratory. The meeting came at a time when natural analogue (NA) studies are well established in most national radioactive waste programmes. It is greatly encouraging that natural analogue data now play an important qualitative role in repository performance assessment (PA), for example their value in building confidence by demonstrating that important processes do occur, and by showing that these processes behave in a way predicted by models based on laboratory and *in situ* experiments. Less encouraging has been the very limited quantitative use of natural analogue data in performance assessment modelling. This is due to a number of factors, for example the complexity of natural systems contrasting with the oversimplistic modelling necessary for PA, the general limitation of NA studies to provide more rigorous boundary conditions for PA modelling, the difficulty encountered by PA modelling groups to address the complexity of natural system processes, and a general lack of integration of NA studies with specifically designed laboratory and *in situ* experiments.

With these reasons in mind, the Sante Fe meeting was organised to provide an opportunity: 1) to review the present status of the various national NA programmes, 2) to address the "state of the art" of several key issues of importance to PA, 3) to arrive at a general consensus for each issue, and 4) to provide suitable guidelines as to the future importance of each issue in NA studies and their eventual use in PA. It was hoped that for each issue an agreement would be reached stating whether adequate study has been carried out and whether adequate NA data were now available. This would finally put to rest some of the more well documented issues and allow future NA programmes to concentrate resources on other less well defined phenomena.

Achieving a consensus of opinion, however, proved difficult to realise; this showed that natural systems are still considered too complex when evaluating and comparing the validity of data from one site to another. Much of the data are site-specific and some national radwaste programmes feel the need to confirm the importance or otherwise of each process or phenomena which form an integral part of their respective disposal systems, irrespective of existing data describing similar processes or phenomena in other regions. The difficulties in comparing site-specific data may in part reflect different schools of thought, not uncommon within the earth sciences, or simply from the outset a more substantial co-ordinated geological and geochemical database is required from each analogue site to facilitate comparison.

In general, progress is being made to provide a more quantitative use of analogue data in PA; NA studies are becoming more structured to address PA issues, and consequently the integration of PA groups during the planning, execution and evaluation phases, should lead to greater use of analogue data in PA.

Within the Core Group there is now a feeling that the sphere of NA studies is expanding beyond the restricted influence of the NAWG, such that direct distribution of information and expertise is no longer maintained by informal contact and an official meeting once every two years. The Core Group* has decided to create an additional Scientific Liaison Group, still under the auspices of the EC, comprising active analogue and PA scientists representing each country currently engaged in radioactive waste studies. It is not envisaged to expand the Core Group as this would prove unwieldy. The Liaison Group will be invited to participate at the NAWG workshop meetings; this should improve information and data exchange considerably, and also ensure that NAs are suitably focussed on PA (e.g. with respect to licencing) and duplication of scientific studies minimised.

It is also proposed to increase the profile of NA studies within the scientific community at large. This will entail the promotion of NAs at geoscientific and geochemical conferences hitherto not approached. Furthermore, the role of analogues in other areas of hazardous environmental waste disposal (e.g. toxic wastes; mine tailings etc.) should be advertised to a much greater extent. A considerable amount of expertise within the nuclear waste sector can now be transferred to other areas of need. These topics will be included in the next NAWG workshop scheduled for 1996 in Switzerland. It is also planned to hold a 7th EU-NAWG meeting along similar lines to that in 1990 (linked to the Poços de Caldas Analogue Project) and 1992 (linked to the Alligator Rivers Analogue Project). This is scheduled for 1998/99 in France to coincide with the completion of the Oklo and Palmottu international analogue projects.

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* Core Group members were, until September 1994: Peter Airey (ANSTO, Australia), Russell Alexander (RWIG, Switzerland), Jan Cramer (AECL, Canada), David Curtis (Los Alamos, USA), Paul Hooker (BGS, UK), Linda Kovach (NRC, USA), Didier Louvat (CEA, France), Henning von Maravic (EC, Belgium, provides secretariat) and John Smellie (Conterra, Sweden, Chairman).

SUMMARY AND MAIN CONCLUSIONS OF THE WORKSHOP

Introduction

The Sante Fe NAWG workshop came at a time when natural analogue studies are well established in many national radioactive waste programmes. Much experience has been gained from the practical side, for example structuring natural analogue studies to performance assessment requirements, establishing field and laboratory protocols, the compilation, evaluation and conceptualisation of data, increasing public awareness/acceptability of disposal concepts etc., but experience in the final use of such data in repository performance assessments is still limited. The areas of limitation are due to a number of factors, for example the complexity of natural systems contrasting with the oversimplistic modelling necessary for performance assessment, the general limitation of natural analogue studies to provide more rigorous boundary conditions for performance assessment modelling, the difficulty encountered by performance assessment modelling groups to approach the complexity of natural systems, and a general lack of integration of natural analogue studies with specifically designed laboratory and *in situ* experiments.

The Sante Fe workshop was organised to provide an opportunity: 1) to review the present status of the various national analogue programmes, 2) to address the "state of the art" of several key issues of importance to repository performance, 3) to arrive at a general consensus for each issue, and 4) to provide suitable definitive guidelines as to the future importance of each issue in natural analogue studies and their eventual use in performance assessments. To arrive at a general consensus for each issue, the folllowing questions were posed:

* Are there sufficient data?
* What additional data, if any, are required, and why?
* Can such data be obtained from natural analogue studies?
* Are support data from laboratory and *in situ* studies adequate?

Key Issues Addressed

The key issues identified for discussion fell under the general headings of:

A. Near-field Processes and PA Implications

- Spent fuel dissolution
- Stability of clay-based buffer/backfill
- Canister stability
- Radiolysis
- Trace element migration

B. Far-field Processes and PA Implications

- The role of colloids
- Matrix diffusion
- *In situ* K_d values
- Geochemical transport modelling

C. Natural Analogues and PA

- Performance assessment and natural analogues
- Performance assessment and public relations

As mentioned above, the main objectives of the workshop were to address the present status of information available for each of the above issues, and to provide suitable guidelines as to their future use and importance in natural analogue studies related to repository performance assessment. It was hoped that for each issue a consensus would be achieved stating whether adequate study has been carried out and that enough analogue data were now available. This would finally put to rest some of the more well documented issues (e.g. matrix diffusion; the role of colloids etc.) and allow future analogue programmes to concentrate resources on other less well studied phenomena such as waste form stability or the role of microbes etc. Achieving a consensus of opinion, however, proved difficult to realise; this showed that natural geological systems are still considered too complex when trying to evaluate and compare the validity of data from one analogue site to another. Much of the data are site-specific and some national radwaste programmes feel the need to confirm the role of each process or phenomenon which forms an integral part of their respective disposal systems. The difficulties in comparing site-specific data may in part reflect different schools of thought, not uncommon within the earth sciences, or simply from the outset a more substantial co-ordinated geological and geochemical database is required from each analogue site to facilitate comparison.

Report Structure

Session 1 of the workshop dealing with the present status of the different national analogue studies is not addressed in this chapter, but a summary of each programme is presented in Tables 1a-c. Emphasis is put in summarising Sessions 2, 3 and 4 and presenting the main conclusions of the meeting. To facilitate this the following main headings are used: State of the Art; Available Data; Consensus; Future Direction.

A. NEAR-FIELD PROCESSES AND PA IMPLICATIONS

Spent Fuel Dissolution

To assess the potential dissolution rate of UO_2, which comprises spent fuel, the use of particular fission product concentrations within and near natural uranium occurrences was addressed.

I. State of the Art

Rates of UO_2 dissolution are estimated on the basis of the concentration of natural tracer nuclides in rock or rock pore water within or near uranium deposits; analogue sites investigated include Oklo (Africa), Cigar Lake (Canada) and Alligator Rivers (Australia). Technetium-99 in rock and iodine-129 in water are considered as tracer nuclides. At Peña Blanca (Mexico) the dissolution rate of the uranium minerals is not estimated on the basis of tracer nuclides, but by means of uranium removal by percolating water.

Uncertainties about the validity of models and parameters are significant, nevertheless results based on technetium-99 for Oklo (i.e. ruthenium-99 and other fission products traced back in time) and Cigar Lake (present *in situ* production) are surprisingly consistent. Iodine-129 results for Cigar Lake and Alligator Rivers are also somewhat consistent. Contrastingly, technetium-99 and iodine-129 data are not consistent since they provide dissolution rates that differ by about two orders of magnitude.

The inconsistency of the two sets of data was discussed extensively and various possible explanations reviewed.

II. Available Data

Technetium and iodine data are available from the above-mentioned analogue studies (exception Peña Blanca) of varying quantity and quality. Since the technetium, iodine and Peña Blanca data are based on different models and assumptions (e.g. intentionally conservative in the case of Peña Blanca), it is doubtful that the datasets can be considered uniform in respect to uncertainty and reliability. Consequently, can these data be used in PA? Despite uncertainties about the reliability of the data, there was a general belief that such data would improve understanding of UO_2 dissolution and increase confidence in PA.

Results from Cigar Lake uraninites showed (supported by uranium decay series and radiogenic lead data) both a good retention of the isotopes in the natural UO_2 matrix, and congruent dissolution of the matrix, at least over timescales of one million years. This supports the long-term stability of spent fuel under reducing groundwater conditions envisaged by, for example, the Canadian and Swedish disposal concepts. With reference to the Yucca Mountain site, USA, only the Peña Blanca analogue study was considered relevant. Here, the UO_2 dissolution rates suggested by data and assumptions about the geological history of the site resembled those obtained in the laboratory.

III. Consensus

General consensus was reached on several points:

- the models used to estimate UO_2 dissolution are probably oversimplified,
- the inconsistences existing between the technetium and iodine data need to be explained to allow their use in calculating dissolution rates in PA,
- the approach of using fission product data to quantify the release and, therefore, the dissolution rate of uranium minerals, is satisfactory, and
- it was considered worthwhile to continue this type of work at other well documented analogue sites.

IV. Future Direction

Future work was recommended within the following areas:

1. For the US programme, study of additional uranium deposits (or old mines) in a geological setting similar to that of Yucca Mountain and Peña Blanca.

2. Completed studies on uraninite from Oklo examined fission production in technetium; these data will now be compared to *in situ* production in the same uraninite.

3. Additional data of the type obtained from Oklo, Cigar Lake and Alligator Rivers should be obtained, coupled with rigorous testing of the model assumptions.

Stability of clay-based buffer/backfill

The long-term stability of bentonite clay as a backfill/buffer material emplaced around the canister has been the focus of analogue studies for some 10-15 years. Although not an important consideration for the US programme, bentonite is a critical engineered barrier component in most other disposal concepts.

I. State of the Art

Under excessively high temperatures and/or in contact with a dissolved source of potassium, montmorillonite, the dominant clay component of bentonite, breaks down to illite or mixed smectite/illite layers which drastically changes the physical and chemical character of the bentonite. To understand these changes and their repercussions on canister corrosion and potential radionuclide leakage from the waste package, bentonite, or worst case examples of illite-dominated clays, have been studied under different geological environments representing temperature ranges and groundwater conditions expected to be encountered in a repository during the long isolation times required for safe disposal of radioactive wastes. For example, there is a wealth of information on the range of smectite/illite stability derived from contact metamorphism of bentonite clay formations. Furthermore, studies of illite-type clays surrounding the uranium occurrences at Oklo and Cigar Lake have provided clear evidence of their radionuclide retention properties and, in the case of Cigar Lake and Dunarroba, Italy, their function as an effective barrier to groundwater flow. Clays, as an efficient filter of colloid material, has been indicated at Cigar Lake and Morro do Ferro, Brazil.

II. Available Data

Analogue studies have provided temperature and pressure boundary conditions for bentonite stability under repository conditions expected, for example, in the Canadian, Swedish and Finnish disposal concepts. These studies have supported laboratory results which have been used in PA. Equally, if not more important, the analogue observations show that illite clays, whilst theoretically are significantly inferior to the montmorillonite in bentonite, still provide an efficient hydraulic and chemical buffer to groundwater movement and radionuclide migration.

III. Consensus

There was consensus that enough data exist, from both natural analogue and laboratory studies, to show that illitisation of bentonite is not a major problem for PA. This being the case, there is no apparent need for further natural analogue studies of smectite-illite instability. There was some need, however, to gain greater understanding about the radionuclide retention capacity character of clays in general.

Of two additional bentonite topics discussed, cementation problems (due to heating) and rheological properties, there was some agreement that cementation of bentonite was a potential problem but no analogue studies had yet been identified. With reference to the latter problem, it was accepted that even though modelling of the long-term rheological properties of bentonite indicated that canister sinking would not be a problem, it was recommended that suitable analogues be sought to test model predictions. However, the behaviour of salt as an analogue to clay, for example, was rejected as inappropriate in this context.

IV. Future Direction

Additional studies in the above-mentioned problem areas were recommended:

> * canister sinking; further work would be useful, for example, a) barite nodules (as examples of dense objects) in bentonite to measure long-term creep aspects, and b) present-day monitoring of the SFR low- to intermediate-level radioactive waste facility in Sweden, to determine any sinking of the cementitious silo into the surrounding bentonite buffer.
>
> * cementation; one possibility is cementation of clays at the contact of intruded igneous rocks. In general the conditions are inappropriate (temperature too high; temperature gradient too high etc.), but a carefuly selected smple may be of use.
>
> * more clay studies on radionuclide retention properties (e.g. Oklo)

Canister Stability

The central issue of many disposal concepts is the long-term integrity of the metal waste canister; for example the Swedish, Swiss and Finnish repository safety analyses rely heavily on the stability of the canister. Natural analogue studies from anthropogenic sources, e.g. archaeological artefacts of metals, have been widely used to study potential canister materials. The presentation focussed on the behaviour of two materials, copper and steel, related to a high-level waste repository design.

I. State of the Art

Archaeological artefacts (and to a much lesser extent native metals) have long been studied as analogues to metal canister materials, particularly by Sweden and Switzerland, and more recently by Finland and the USA. Bronze/copper (Sweden; Finland) and iron (Switzerland; Japan) objects have provided analogue support for the various national repository PA concepts. The metal objects in question vary from iron nails dating back to Roman times to a bronze canon some hundreds of years old. One drawback is the large range of physico-chemical environments encountered, none of which accurately represent the deep, reducing groundwater conditions predicted to characterise a future repository. An exception to this is the on-going USA Santorini study in Greece where metal archaeological artefacts (i.e. bronze) of known age are embedded in unsaturated volcanic formations showing some similarity with the host volcanic rock environment at the Yucca Mountain repository site.

In addition to the direct integration of such analogue data in some performance asessments, some have also been used at "lower" levels of PA, for example in concept building.

Two other studies are currently on-going; examination of coexisting uraninite/copper at Cigar Lake, and the behaviour of iron artefacts (rail lines etc.) in salt mines in Germany.

II. Available Data

A considerable amount of analogue data are presently available and some have been directly used in PA; see referenced data in SKB-91 (copper) and Kristallin-1 (steel).
With regard to copper, corrosion rates used in PA (0.025-1.3 μm/a) were calculated from both recent and archaeological copper artefacts found in a wide range of wet/dry and oxic/anoxic environments which demonstrated the long-term durability of copper, consistent with thermodynamic considerations. Natural analogues for steel, which is a relatively recent technological alloy, are mostly limited to geological (native iron) or archaeological artefacts (e.g. Roman nails). These examples indicate corrosion times of anything from 10 000 to 250 000 a.

III. Consensus

The consensus appears to be that, with respect to iron and copper corrosion rate studies, enough is known to support the corrosion rates (laboratory and model derived) currently assumed in specific PA studies (e.g. SKB-91; Kristallin-1).

Nevertheless, it was noted that the Swedish Regulatory Inspection Board (SKI) have recently stated a desire for further studies (natural analogue or laboratory) on corrosion of canisters in case a specific process has been overlooked. This was generally doubted, but it was agreed that any future natural analogue studies should more directly address repository relevant materials (i.e. copper not bronze; steel not iron) in repository relevant environments (i.e. relevant groundwaters; appropriate pH/Eh conditions). In addition, any such work should also be focussed on producing clear, simple information of use in public relations (PR) issues.

IV. Future Direction

Several areas of future work were identified to further improve understanding of metal canister behaviour under repository conditions:

* structural integrity of the canister; no obvious natural analogue examples were identified even though this could be of great PA signficance. Doubt was expressed as to the likelihood of finding any examples of relevance,

* canister behaviour in a cementitious repository; presence of steel in old concrete was discussed, but this was considered of limited relevance because of generally oxic conditions. It was suggested that further effort be expended on identifying examples which are more repository relevant (e.g. anoxic pore waters),

* microbial action; little (or nothing) has been carried out in this area but there was general agreement that it was both important and possible to pursue. However, no specific suggestions were forthcoming,

* iron artefacts; in particular reference to the USA's radwaste programme, it was suggested that examination of iron artefacts under geological conditions similar to Yucca Mountain should be explored, especially in the light of the potential use of a steel "multipurpose containment vessel" at the site. It was pointed out that the Santorini site, although highly relevant, was too old (i.e. pre-iron age) to yield relevant material but that possibilities exist at other sites (e.g. Turkey), and

* geochemical effects of canister degradation; redox fronts produced during steel canister corrosion driven by radiolysis reactions were mentioned and it was noted that Nagra/SKB may be initiating studies of relevant analogues to further illustrate these phenomena.

Radiolysis

Radiolysis as a repository performance assessment issue may be important to disposal concepts where the composition of the metal canister is inadequate (e.g. copper) to buffer the outward propagation of a redox front (i.e. radiolysis products) from the waste package out into the host rock. In such a scenario the production of oxidants would greatly increase the dissolution of the waste form and subsequent transport of radionuclide material.

I. State of the Art

Knowledge is currently sufficient to allow relatively detailed description of possible chemical effects (e.g. H_2 generation and migration; development of redox fronts; alteration of organic matter; evolution of oxidising environments in the vicinity of radiation sources etc.). Quantification of these effects and their movement, however, remain problematic due to a lack of information from natural systems.

II. Available Data

Examples of radiation damage in natural materials (e.g. clays; salt) are available and well documented. Data supporting models of radiolysis effects, however, are less common. Although data exist that document the occurrence of oxidised regions in the vicinity of uranium and thorium concentrations, a variety of mechanisms can explain these occurrences. In addition, some locations that possess high uranium and/or thorium concentrations (e.g. Cigar Lake and Oklo) exhibit reducing conditions. Although this may be due to chemical effects associated with the presence of organic matter, the data remain problematic for models of radiolysis.

III. Consensus

There is a clear consensus that the available data are adequate to allow conclusions to be reached regarding the extent to which radiolysis may influence the chemistry of natural systems.

The importance of radiolysis in PA will vary depending on the disposal concept chosen. For many countries, radiolysis is of little consequence and of minimal interest. For others it figures prominantly in PA models. However, radiolysis effects are mainly considered for the waste form, not on the geological environmental conditions. Based on current data, these conditions are now being reconsidered.

The consensus reached from NA evidence is that the complexity of natural systems makes it difficult to obtain useful data on the effects of radiolysis, despite the fact that it must occur. If it is significant, the absence of clear signatures suggests that it is a second-order effect, often marked or overwhelmed by other geochemical processes.

IV. Future Direction

Effort would be best spent on laboratory studies to better quantify effects. Based on the results of such studies, natural analogue sites may then be selected and studied. For the present, natural analogue studies of radiolysis effects should be low in priority.

Trace Element Migration

So-called "blind" predictions, to test geochemical codes and thermodynamic databases used in PA, have been integrated into some of the major natural analogue studies (e.g Poços de Caldas, Cigar Lake). Chemical thermodynamic models provide two main types of data for PA purposes: a) solubilities of particular elements or radionuclides (this parameter places an important constraint on release rates from, e.g spent fuel), and b) speciation of such elements in solution (allows their transport properties to be estimated).

I. State of the Art

Current capabilities to predict radionuclide/trace element behaviour in groundwaters under repository-type conditions is limited. Current PA codes generally oversimplify chemistry and do not take into account common ion effects, coprecipitation-solid solution effects, or kinetic effects on precipitation of limiting solid phases. The ability to test predictions of trace element/radionuclide aqueous speciation is very limited, due to a paucity of field-based measurements.

II. Available Data

Data for determining aqueous speciation are very poor. Data for solid phases that limit solubilities are more common but need further refinement to establish links between coprecipitation/solid solution phases and water chemistry. There are indications that major components of the system may be coupled with specific element behaviour, but additional data are needed to quantitatively link the data to specific mineral occurrences.

Data on the kinetics of solid phase formation need to be obtained. Although a significant body of data is available, employing the data in model simulations has been inadequate.

III. Consensus

Resolution of discrepancies between PA calculations requires better and clearer communication about modelling approaches, specific models to be employed and techniques for model testing. "Blind" prediction modelling is an important tool, but must be used in a consistent fashion (e.g. common database) by everyone involved in each exercise.

Better and more thorough information from natural analogues needs to be obtained for aqueous species and on solid phase compositions. In some cases, clear identification of the limiting phase is not available and needs to be established. Sites where reaction kinetics can be measured also require to be considered and, together with thermodynamics, examined in the context of the timescales conceptualised for the different evolutionary phases of a repository, and what has been accomplished in the laboratory.

IV. Future Direction

* Obtain *in situ* measurements of aqueous species, kinetics, common ion effects and coprecipitation.

* Solid-solution properties of solids need to be incorporated in PA models.

* Develop better communication between PA and geochemical modellers.

B. FAR-FIELD PROCESSES AND PA IMPLICATIONS

The Role of Colloids

Colloids may be important as a transport mechanism for radionuclides from deep geological repositories, particularly into the far-field and ultimately to the accessible biosphere. Consequently, considerable effort has been devoted to this subject in natural analogue studies, where both sampling protocols and potential significance of colloids in transport mechanisms have been addressed.

I. State of the Art

Field studies show that colloids are always present in varying amounts in groundwater systems. Deep, geochemically stable natural groundwater environments tend to contain low concentrations of colloids, shallow natural aquifer systems (both geochemically stable and unstable types) are generally associated with greater concentrations, and geochemically disturbed sites are also characterised by greater colloid contents.

The presence of organic material reduces the physical stability of colloids and causes them to agglomerate, whereas the chemical stability of colloids is highly uncertain under changing environmental conditions. Colloids bind a variety of radionuclides, and the extent of binding appears to be inversely related to the radionuclide's solubility.

Analogue sites are useful in identifying the extent to which colloid transport is or could be an important process. Uranium or thorium/REE deposits such as Koongarra, Australia, Morro do Ferro, Brazil, and Cigar Lake, show evidence against radionuclide uptake and transport by colloidal material.

Although it is not yet possible to reliably predict the nature, stability and abundance of colloidal particles as a function of the chemical, hydrological and mineralogical properties in a range of subsurface environments, some general relationships are beginning to emerge.

II. Available Data

A considerable amount of data is available from natural disturbed and undisturbed geological systems and from anthropogenic analogue sites created by disposal of radionuclides or by nuclear detonations. Colloids are always present, their stability is variable under different hydrogeochemical and hydrodynamic conditions, and studies clearly indicate that radionuclides do associate with colloidal species (e.g. Cigar Lake, Koongarra, Morro do Ferro) where a much larger fraction of the less soluble thorium is apparent in comparison with only a few percent of uranium. REEs show an affinity for colloids that is intermediate between uranium and thorium, and sorption appears to be generally inversely related to solubility. There is some evidence that the more strongly adsorbed elements (e.g. Th, Pu) are not in equilibrium with the solution phase, and that the association of the radionuclide with colloids is not readily reversible. Data suggest evidence both for and against colloidal transport.

III. Consensus

Reliable sampling procedures are generally suitable for most natural environments; the main exception is deep sampling from fractured hostrocks where artefacts from drilling activities and from pumping fractures of low hydraulic conductivity may enhance the colloidal contents in the sample. Caution is required.

Field studies to date have not been successful in establishing the transport potential of colloids. Studies at Morro do Ferro and Cigar Lake, however, indicated that clays act as efficient barriers (i.e. filters) to colloid transport; this is important information for PA. Furthermore, colloidal contents in many deep crystalline rock environments are so low that they can be considered unimportant to PA.

IV. Future Direction

The focus for future work should consider colloid production at geochemical fronts, such as pH plumes (e.g. transuranic waste contained in a cemetitious repository design) and redox fronts (e.g. resulting from radiolysis reactions). In these cases colloidal materials may be added to the system, the behaviour of which is largely unknown. Priority should therefore be to establish the sources and transport of colloids in these settings. A further priority is to determine the relative importance of adsorption and desorption of natural colloids onto the host rock mineral surfaces with respect to the reversibility of sorption of radionuclides onto the same class of colloids.

Matrix Diffusion

Of several potential retardation mechanisms influencing far-field radionuclide transport in crystalline rock, matrix diffusion and sorption in the rock matrices is perhaps one of the most important. The effectiveness of the mechanism is dependent on the diffusion penetration depths into the rock from water-conducting fracture zones (e.g. dependent on rock porosity and diffusivity), and also the area of fracture planar surface in contact with the moving groundwater (i.e. flow-wetted surface).

I. State of the Art

Most PA transport codes are not sensitive to diffusion coefficients but rather to depths of interaction with rock and radionuclide, for example dispersion length increases with distance. Consequently, a considerable number of studies have been carried out during the last 10 years or so to quantify diffusion depths, mainly in crystalline rocks. Laboratory and field measurements of matrix diffusion have been performed using non-sorbing as well as sorbing species; ion migration in electric fields has been used to speed up the diffusion process and to cover longer distances. Diffusion experiments in rock samples under stresses similar to those at repository depth have been conducted in the laboratory, together with *in situ* diffusion experiments at great depths to closer simulate natural conditions. Natural analogue studies have also made a major contribution by measuring the diffusion depths of uranium series radionuclides into crystalline rock matrices over geological timescales more in line with the expected lifespan of a repository.

II. Available Data

Natural analogue studies have mostly focussed on radionuclide diffusion penetration depths in a variety of different hydrogeological environments. These data show that most penetrative depths range from 1mm to 50mm (values up to 50cm have also been mentioned); 10mm is suggested as a suitably conservative value. Greatest penetration usually correlates with increased alteration (i.e. greater porosity) adjacent to the fractures.

Few field data, however, exist at the moment to derive diffusivity coefficients; furthermore, those data available indicate a confusingly large range of values (10^{-19} to $10^{-10}m^2s^{-1}$). Currently, emphasis must still be put on laboratory-derived data for PA considerations, although these data should be regarded as non-conservative because of experimental artefacts.

Early PAs assumed either that diffusion extended through the granite matrix (Swedish KBS-3) or to a maximum of 1mm (Swiss Gewähr). More recently Sweden has used a laboratory-derived apparent diffusivity coefficient of $1.9 \cdot 10^{-17}m^2s^{-1}$ for uranium in granite. Comparison with analogue data using a simple diffusion model corresponded to diffusivities in the order of 10^{-18} to $10^{-16}m^2s^{-1}$, which was considered as supporting evidence to the use of laboratory-derived data.

III. Consensus

Realistic estimations of penetration depth and apparent diffusivity values are available for crystalline rock, and have illustrated the great potential of matrix diffusion as an efficient radionuclide retardation mechanism. Even though this is based on adequate generic analogue data, more systematic studies are desired. These studies, however, should be restricted to repository site-specific or analogue site-specific locations.

IV. Future Direction

Future repository site-specific or analogue site-specific studies of matrix diffusion should consider the following points:

1. Radionuclide profile measurements should be supported by detailed petrographic and geochemical studies, measured physical rock parameters (e.g. porosity, diffusivity, permeability etc.) and contact groundwater chemistry. Physical parameters have tended to be neglected, usually because of the sample size restrictions of the drillcore material. Large-scale specimens should be selected from underground excavations if available.

2. Fracture radionuclide profile measurements are required from "unaltered" water-conducting zones.

3. Many of the reported data derive from randomly selected fracture samples. Profiles should be systematically selected from oxidising through to reducing bedrock conditions.

4. Any additional diffusion experiments should be conducted under *in situ* conditions of highly stressed rock.

In situ K_d Values

The distribution of radionuclides between a solid phase (rock, clay, pure minerals etc.) and solution (groundwater, clay pore water, concrete porewater etc.) can be described by the sorption coefficient (K_d), and the K_d value is specific for the radionuclide, the solid and solution. It is generally conservative to simply assume that the sorption is reversible and that the measured K_d is an equilibrium value. Sorption of Cs and Sr (as examples of performance assessment interest) onto mineral phases is by ion exchange, and is strongly dependent on the ion exchange capacity of the mineral, on the concentration of the radionuclide in solution and on the concentration of other cations. Alternative mechanisms, however, control sorption of other important radionuclides, for example pH is a critical parameter for Pu and Am and redox conditions for U, Np and Tc. As a far-field retardation mechanism, sorption of radionuclides (i.e. surface sorption and, more importantly, diffusion/sorption into the rock matrix) along the flow-wetted surface is an important process in repository performance assessment. To date, performance assessments have depended solely on laboratory-derived K_d values. In situ K_d values would appear to be a more representative source of data; but do analogue studies offer this possibility?

I. State of the Art

Many analogue uranium decay series data are available and attempts have been made to use these data to derive K_d values. These attempts have shown that the definition of *in situ* K_d values by means of the natural decay series is extremely complex, despite the fact that current models are generally oversimplified. There is a consensus, however, that more could be made of the available field data if the model limitations were recognised and tested prior to their application to uranium series data sets. For example, differences in the $^{234}U/^{238}U$ activity ratios between the "sorbed" phase and the associated water immediately show that the K_d concept is inappropriate because K_d values should represent equilibrium between these two pools. Such differences may be explained by analytical inconsistences or by the nature of the retardation mechanism. Either way, sorption is not the only explanation and therefore doubt is cast on the validity of the *in situ* K_d concept. These uncertainties must be resolved before constructive progress can be made in the future use of natural analogues.

Whilst further development of sampling and analytical methods may help to resolve existing uncertainties, the mood within the area of performance assessment is less positive. First, the point that natural retardation processes need to be understood before radionuclide retardation around a repository can be accurately predicted, is refuted. For a start, the natural decay series radio(geo)chemistry is much more complex than that of many isotopes of interest to performance assessment (e.g. Cs). In addition, as most observations of natural decay series water-rock pairs represent one or two points in a potentially large matrix of mechanisms and processes, it is unrealistic to expect to be able to "understand" such a system. On the positive side, large, regional differences in aquifers could be recognised by collecting a few sets of uranium series data but that such results could, of course, be used only qualitatively.

The overall situation may not be quite as negative as suggested by the uranium decay series-derived data. Other analogue studies, which have focussed on, for example Cs, Rb, and REEs, have been making slow, but steady progress, and may yet provide important results.

II. Available Data

As inferred above, there are available data (e.g. Alligator Rivers), but many are not considered representative enough of the natural system to give dependable K_d values. This mostly reflects the sampling and analytical difficulties encountered using very small amounts of material, often fracture mineral coatings. Sequential leaching of these solid phases is fraught with difficulties and uncertainty. Furthermore, it is very difficult to guarantee that the water phase analysed has actually been in contact with the sorbing mineral assemblages. Consequently, the data have been more useful in testing assumptions of sorption models rather than deriving *in situ* K_d values to be used in performance assessment.

III. Consensus

The general consensus was that, although the current models are over-simplistic, it would be of academic interest to further examine *in situ* retardation (but not *in situ* K_d values) but that it would be unlikely to be of much use in a repository performance assessment. In addition, it was emphasised that all *in situ* K_d data reported to date were suspect and should be treated with caution and certainly not used directly for performance assessment purposes.

IV. Future Direction

Despite the present scepticism surrounding the derivation of *in situ* K_d values using natural analogue studies, further development within the most crucial areas of such studies, i.e. representative sampling, sample preparation and analysis, should still be encouraged, at least to provide qualitative support for laboratory-derived K_d values presently used in performance assessment.

Future progress may be monitored within the Alligator Rivers project where uranium series disequilibria have already been modelled for the solid phase. The next logical step is to model the water phase with the ultimate aim of correlating the two models, using the retardation factor as the grouped factor. The best retardation factor would then be compared with laboratory-derived K_d factors.

Geochemical Transport Modelling

Two topics were addressed under this general heading: "scientific" geochemical modelling of groundwater evolution in natural geological systems and "performance assessment" modelling of the potential transport of radionuclide material through the repository host rocks. In common is the complexity of the natural system to be simulated.

Geochemical modelling of groundwater evolution

The evolution of knowledge and increasing sophistication of modelling geochemical systems, together with the various types models, were outlined. Forward modelling tends to be too unconstrained whereas inverse modelling or the mass balance approach often suffers from a lack of sufficient data. Notable exceptions from analogue studies include Poços de Caldas, Cigar Lake, Needles Eye, UK, Stripa, Sweden and El Berrocal, Spain.

The limitations in geochemical modelling can be divided into two categories, the input data itself and human error. It is difficult to conduct an analysis of error propagation if data are missing; in its absence something like a probability distribution function is created. In addition, concepts or processes may be totally missing from models. The computerised model can be only as good as the conceptual model's ability to represent the natural system. The application of mathematics helps to quantify things, but whether it gets closer to understanding processes in nature, or to obtain a confident value, is questionable. Where good phase control and good thermodynamic data are available for some of the phases, it may be possible to estimate values for a remaining phase for which data are lacking.

Regarding spatial variability of geochemical parameters in natural systems, opinions differ as to whether geochemical variability is less important in sensitivity to performance assessment than is hydrological variability along flow paths. Some instances indicate that hydrogeology has a greater influence on geochemistry than *vice versa.*

Modelling kinetics is not as advanced as modelling thermodynamic equilibrium. This can be explained by complexities in the field which often indicate reaction rates slower than those in the laboratory. With regard to data from a fractured granitic environment, with a limited number of major ions in certain water-rock interactions, there exists guarded optimism that certain water-rock interactions can be modelled by considering kinetics.

Future Direction

1) Separate modelling teams should use forward and inverse approaches and compare results.

2) As hydrology may have a greater influence on geochemistry than *vice versa,* then the opportunity should be taken to couple thermal, mechanical, hydrologic, geochemical and geomicrobiological processes. Communication between these disciplines should also be encouraged as discoveries in one field may relate to, or explain, phenomena in another field.

Modelling uncertainities in performance assessment

Bias and uncertainty can be unwittingly incorporated into models if incorrect assumptions are made about the operating processes at a potential repository site, for example whether normally immobile thorium can be transported in colloidal form. Detailed examples were provided from analogue sites that characterised colloid transport in order to address issues which require greater focus.

The necessity in evaluating uncertainties in performance assessments was stressed and cited as an example where the results were flawed because an error introduced at the outset prejudiced all subsequent calculations. Initial assumptions which are not explicitly stated, for example that all iodine was previously released, results in a biased performance assessment at the end.

Natural systems are useful in testing uncertainties in models and parameters. The Poços de Caldas study was recommended as a good example in this respect, where all potentially significant processes were considered at the outset. Later, processes that are found to be inconsequential can be dismissed. The null hypothesis should be presented by stating what is known, what is assumed, and what will be tested. This will allow the evaluation of weakness in assumptions and uncertainties in the interpretations.

When evaluating parameters, examination of the reasonableness of each parameter should be included as well as variation in values and the form and shape of the probability distributed function. For example, a K_d for aqueous-solid partitioning should not be provided when most of the material is present in a colloidal phase. Studies were cited in which 99% of thorium appears as a colloidal phase. Furthermore, it should not be assumed that results of laboratory studies can be scaled up to obtain a similar result.

Future Direction

* Uncertainty in the conceptual model itself and in the parameter values should be separated. Uncertainty and bias should be examined at each stage, documenting alternative conceptualisations and associated assumptions.

* Natural analogues are increasingly being used in PA by contributing to scenario development as a means of dealing with bias and uncertainties in conceptual models. Evidence from analogues can contribute to the consideration of features, events and processes. This use of analogue data in scenario development will increase as more analogue data are published and more PA personnel are integrated into analogue programmes.

* In order to reduce uncertainties of scaling from laboratory to predicted field behaviour, more field-scale, well constrained analogue studies are recommended. With regard to colloid behaviour, this is currently being addressed in the Steenkampskraal Study, South Africa, where it is hoped to observe thorium colloids within a large scale natural environment.

C. NATURAL ANALOGUES AND PA

Performance Assessment and Natural Analogues

Of several possible topics, this review focussed on repository system design, providing input data to PA and testing models used in PA. The Cigar Lake analogue was cited as a good example of how repository design can be supported by field studies, for example the geometry and component geological parts of the Cigar Lake uranium occurrence, i.e. stable orebody, surrounding clay and location at repository depths etc., can be readily identified with, and lend credence to, a high-level waste repository design. Poor examples include the analogy of 2Ga old organic material from Oklo, which is thought to have preserved included uraninite, to the recommended use of bitumen as an isolating material to high-level spent fuel in present-day repository design. This exemplified the lack of background knowledge of nuclear waste disposal behind some analogue studies.

There is a danger, however, for reviewers to see things in terms of "black and white", all good or all bad treatment of the different analogue projects. Furthermore, while some aspects of NA studies provide fruitful results (either qualitative and in rare cases quantitative), at times the results have been reported in an irresponsible fashion. Managers of projects must be careful to eliminate exaggerated or unsubstantiated claims, as these could damaging to the credibility of the overall study.

Analogue studies and direct input to PA was discussed and examples given of successful and failed applications. Successful studies which have resulted in reliable numerical input to PA are few and generally refer to canister stability (e.g. corrosion rates derived from pitting studies of archaeological artefacts) and matrix diffusion penetrative depths in crystalline rocks by measuring naturally occurring radionuclides. Unsuccessful studies include the derivation of K_d sorption values from natural environments, where the practical difficulties of sequential leaching from different sorbing mineral phases are too great to give reliable results. Whilst a gloomy picture was painted, there was general support that future work should continue to try and solve these presently intractible problems; meanwhile PA models would have to continue to use laboratory-derived K_d values.

Testing of models used in PA, in particular the "blind prediction" approach, was addressed and good examples of studies were cited. Studies were also cited where PA-oriented was mismanaged by modelling groups who used non-representative models and insisted on using field-derived K_d values.

As an example of a successful performance assessment, the Swiss Kristallin-1 was presented in detail emphasising the integration of natural analogue studies at all stages of PA development. In contrast the DOE Yucca Mountain performance assessment was chosen as an example where natural analogues appeared to have been totally neglected.

Recommendations included:

1) Groups such as the NAWG should attempt to extract more PA-relevant information from natural analogue studies, and to provide specific guidelines to the involved groups as to how this can be accomplished.

2) The necessity for more integration of PA into natural analogue studies at all stages of their planning, execution and evaluation. Pressure should be put on the funding organisation for this to be officially accomplished.

3) The present lack of communication and dialogue between those working with natural analogues and PA must be addressed and a solution found. The establishment of a NA/PA interface group for each natural analogue study would be a constructive step forward.

4) National programmes must be focussed to the extent of having a reference disposal concept. Without this as a background framework, it is very difficult to plan natural analogue studies from a PA viewpoint at the outset.

Further comments were made from the floor specifically related to performance assessment issues and the USDOE programme. These speakers supported the need for greater integration between NA and PA, and greater need for guidelines as to how NA data can be incorporated into PA; where the uncertainties lie, what are the limitations of the models used, sensitivity analyses etc. It was generally agreed that the lack of integration could partly be explained by the unwieldy organisational structure existing in the USA, in comparison to the smaller European countries. Exceptions were presented, for example the USNRC Peña Blanca analogue study, where people from different scientific disciplines were brought together and meshed with PA groups. Consequently, attempts have been made to carry out PA modelling on some of the Peña Blanca data with variable success. This led to some feedback which helped steer the subsequent direction of the study to provide more useful data to the PA modellers.

Performance Assessment and Public Relations

Natural analogues are important as a public exercise since they serve to demonstrate to the general public the long-term reliability of a repository in an easily understandable fashion, generally not possible through a description of a performance or safety assessment. In fact, organisations such as SKB and Nagra have become more and more reliant on NAs as a method to gain public support for the deep geological disposal of radioactive wastes. As an example to illustrate the long-term isolation of clay material, it was emphasised that to physically handle near-perfectly preserved wood more than one million years old from Dunarobba, Italy, is a very persuasive argument for creating confidence and public acceptance in disposal concepts and design. Other examples include native copper and the 300 year old Swedish canon. Exposure of the public to natural analogues is also expected to aid eventual permission and licencing procedures necessary for repository construction and operation.

Information materials such as brochures and leaflets were described and their relevance to radioactive waste disposal illustrated. It was also underlined that analogues are not used to give the impression of "truth", rather to use them to create; a) the recognition of the most important processes and events, b) the timescales over which such processes and events are expected to occur, and c) an increase in confidence in the proposed solutions to disposal problems.

The presentation closed by viewing the natural analogue video, "Traces of the future", an internationally-funded cooperative project of eight organisations (AECL, Canada; European Commission; ENRESA, Spain; Nagra, Switzerland; ONDRAF/NIRAS, Belgium; SKB, Sweden; UK-NIREX, UK and the US DOE, USA) by Mircea Weiser and Chris Reppmann, Switzerland, produced under the management of Nagra.

Table 1a

Analogue Programme	Main Analogue studies	Investigated key processes
AECL - Canada	* Cigar Lake uranium deposit, Saskatchewan, Canada	- uranium ore stability - retardation and migration processes - RN migration due to colloids
NRC - USA	* Oklo uranium deposit, Gabon, Africa	- uranium ore degradation
	* Pena Blanca uranium deposit, Chihuahua, Mexico	- uranium ore degradation and mass transfer processes
	* Valles Caldera, SW from Santa Fe, NM, USA	- coupled heat and mass transfer processes
	* Santorini, Greece	- geochemical transport processes in an unsaturated environment
DOE - USA	* Taupo Volcanic Zone, New Zealand	- characterisation of the hydrogeology and geochemistry of an active geothermal system
	* Cigar Lake uranium deposit, Saskatchewan, Canada	- migration processes of Pu and Tc over long time frames
	* Uranium mineralisation in volcanic host rocks in Nevada and Oregon, USA	- characterisation of the long-term behaviour of the natural system
NAGRA - Switzerland	* Maqarin, hyperalkaline natural spring, Northern Jordan	- geochemical analogue for testing of solubility and speciation thermodynamic databases - migration of hyperalkaline fluids and reactions - role of colloids
	*Tono uranium deposit, SW of Tokyo, Japan	- solubility and speciation of trace metals in reducing groundwaters - radionuclide retardation in fractured sediments - colloid transport of radionuclides

Table 1b

Analogue Programme	Main Analogue studies	Investigated key processes
ANSTO- Australia	* Koongarra uranium deposit, Northern Territory, Australia	- sorption mechanisms of actinides on weathered schists
	* uranium mineralisation in granitoid occurrences in Western and Southern Australia	- migration and retardation mechanisms of radionuclides
	* Alligator Rivers Region - proposed new NEA/ASARR (Analogue Studies in the Alligator Rivers Region) project	- fracture flow mechanics - field sorption processes - radionuclide retardation on natural substances
SKB - Sweden	* Oklo uranium deposit, in particular the Bangombé near-surface reactor zone, Gabon, Africa	- uranium ore dissolution and mass transfer processes - characterisation of the geochemical/hydrological system - role of colloids, organics and microbes
	* Maqarin, hyperalkaline natural spring, Northern Jordan	- characterisation of the geochemical system - clay stability - role of microbes
	* Palmottu uranium deposit, SW Finland	- hydrogeological and hydrogeochemical characterisation - far field radionuclide mobilisation/transportation processes
	* Cigar Lake uranium deposit, Saskatchewan, Canada	- uranium ore stability - radiolysis - redox front - clay stability
Geological Survey - Finland	* Palmottu uranium deposite, SW Finland	- site characterisation - redox chemistry of U-rich groundwaters - matrix diffusion mechanism - glacial impact on hydrogeological regime (palaeohydrogeology)

Table 1c

Analogue Programme	Main Analogue studies	Investigated key processes
ENRESA - Spain EC contract n° FI2W/0080	* El Berrocal uranium-bearing granite, SW Toledo, Spain	- characterisation of natural radiouclide (U, Th) migration processes - predictive geochemical modelling
British programme	* El Berrocal uranium bearing granite, SW Toledo, Spain	- model testing for groundwater mixing - transport properties of colloidal materials in fractured crystalline rock - radionuclide migration processes - test specific downhole tools
	* Maqarin, hyperalkaline natural springs, Northern Jordan	- natural alkaline cementations conditions - fractured flow - rock matrix diffusion - colloids and radionuclide migration
CEA - France EC contract n° FI2W/0071	* Oklo uranium deposit including Bangombé near-surface reactor zone, Gabon, Africa	- source term - migration and retention processes - hydrothermal events - modelling of the recent and present day migration system
Univ. Rome - Italy EC contract n° FI2W/0121	* Fossil Forest of the Dunarobba Basin, Tiber Valley, Umbria, Italy	- characterisation of the geological, hydrogeological and geochemical processes - processes controlling the wood preservation
KfK-PTE - Germany	Presentation of the German approach for possible future 'natural analogue' studies for a repository in rock salt.	

INTRODUCTION

The value of natural analogues W. Miller (UK)

THE VALUE OF NATURAL ANALOGUES

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Abstract

Natural analogue studies provide information that is essential for proving the safety of a radioactive waste repository. Information may be provided to performance assessment modellers in a 'soft' format to guide model conceptualisation or in a 'hard' format to help validate models. In addition, analogues provide a tool for illustrating to a wide range of audiences the fundamental concepts and safety of a repository system. The value of natural analogues in these diverse roles is gaining recognition as more studies are completed. However, some issues warrant further investigation and a new generation of studies must be planned with the active participation of modellers. Some suggestions for these new studies are provided.

1 Introduction

Natural analogue studies are often seen as an essential component in building a credible safety case for radioactive waste disposal, although their value and application to performance assessment is sometimes unclear and often questioned by modellers. This paper represents a personal view of natural analogue studies: what they are, what they have achieved and where they are going. It is hoped that the views expressed herein will assist in the ongoing discussion of natural analogues and their application to performance assessment.

At the outset I must express my thanks to my four co-authors of 'The Book' (Miller, Alexander, Chapman, McKinley & Smellie, 1994) who gave me free reign to explore the subject but I should also add that they should not be held responsible for the views expressed here.

2 The definition of a natural analogue.

It is a paradox that most workers involved in natural analogue studies have an essential grasp of what they are about, yet a group of workers would be hard-pressed to agree on and commit to paper a clear and unequivocal definition of the term. Partly this is due to the ongoing evolution of the subject but also partly because different groups (both national and organisational) have similar though subtly different views on the matter.

In essence, a natural analogue study examines the occurrence of materials or processes similar to those found in, or caused by, a repository under conditions that are similar to those of the near or far-field environments. Furthermore, the occurrence should be investigated with the predetermined aim of developing or testing concepts and models for repository safety or with the aim of providing parameter values or their limits. This definition, although long, is still quite vague (correct!), especially concerning the necessary degree of 'similarity' but it does exclude studies aimed at obtaining information such as groundwater flow rates and patterns which should be considered under the banner of site characterisation. In a nutshell, a natural analogue study is one that provides information on the behaviour of a repository that is derived from one site but applicable to another: natural analogue derived information must, therefore, be *portable.*

3 *Natural analogues and performance assessment*

The application of natural analogues to performance assessment has often been discussed over the last decade although some would argue that no clear consensus understanding has been reached in this time. Performance assessment modellers sometimes pay little more than lip service to the value of natural analogues and, as indicated in the discussion that marked the end of the last NAWG meeting (McKinley 1994), explicit recognition of natural analogues is often absent from performance assessment documentation. Some observers may argue that there has been a dilemma facing natural analogue studies that can be expressed as:

> " Natural analogue studies provide information performance assessments cannot use: performance assessments require information natural analogues cannot measure."

Yet it is encouraging to see that this dilemma is slowly being resolved with modellers increasingly turning to natural analogue studies for model construction and validation. However, the value of natural analogues is far from universally accepted and consequently the level of interaction between natural analogue researchers and performance assessment modellers must be raised. This position was recognised by the NAWG Core Group in their statement to accompany the report of the last NAWG meeting (von Maravic & Smellie, 1994):

> "Although a working dialogue between natural analogue workers and performance assessors has been emphasised since the first NAWG meeting, . . . closer liaison is desired even today. It is fair to say that the gap has narrowed somewhat in the last seven years but it seems nevertheless that greater appreciation and respect from both groups is still required."

On the positive side, there are those who have recognised the value of natural analogues from an early stage. As an example, consider the list of critical processes which McCombie (1991) claimed then were better understood because of analogue studies:

- radionuclide release from UO_2 and glass waste forms,
- radionuclide solubility and speciation in aqueous solutions,
- redox front initiation and movement,
- radionuclide diffusion in clays,
- matrix diffusion in fractured media,
- particulate and colloidal transport of radionuclides, and
- smectite to illite transition in clays.

This list has continued to grow and several other issues could be added as a consequence of the results from natural analogue studies completed in the last few years. Such lists, however, may be a double-edged sword: yes, they are encouraging and we need to see recognition of our labours but there is a danger that these lists may be misinterpreted with some individuals concluding that these processes are now understood *fully.* This is not the case and, as with all studies of natural systems, our understanding of them needs to be compounded by repeat investigations at new sites to test the range of environments to which we may apply our developing conceptual models. Confidence can only be built slowly.

Returning to the discussion concerning the relationship between natural analogues and performance assessment, it is useful to consider how both aspects fit within the overall framework of geological disposal. The connections are shown in Figure 1 which represents a philosophical system of categorisation but a useful one because it demonstrates unequivocally that natural analogue studies are essential to all three aspects of performance assessment development, namely 'model construction', 'data acquisition', and 'model testing and validation.' Each of these aspects is unique in its requirement for natural analogue input as discussed below. However, before that discussion, it is important to recognise that two forms of natural analogue study exist, these are: (i) soft, qualitative and (ii) hard, quantitative. The recognition of these two types of study, and the consequent nature of the data, is gaining ground (Chapman & Grindrod, 1994). The distinction between the two is not a consequence of the environment or system under investigation but is a result of the methodology employed or, rather, what the researcher is hoping to find. An example of a soft, qualitative study would be one where the researcher is trying to establish the nature of those processes responsible for the degradation of uraninite within a certain environment. In contrast, an example of a hard, quantitative study would be one where the researcher is attempting to measure the rates of those same degradation processes. A little thought will indicate that the soft, qualitative form of investigation must precede the hard, quantitative form at any site: a process can not be quantified until it has been identified. This distinction must be understood to appreciate the level of natural analogue input in the three aspects of performance assessment development.

Model construction: It is clear that the development of many conceptual models of repository processes may proceed only on the back of a good understanding of how the natural environment operates. The development of a model ought to involve natural analogue studies, as it is only after close observation of natural systems that it is possible to make the necessary decisions regarding: (i) which processes to include, (ii) which processes are likely to be dominant and which of secondary importance, (iii) which process interactions to model, (iv) the scales (both spatial and temporal) with which the model should cope, and (v) whether the basic premises of a model are appropriate. It is clear, therefore, that model construction is the performance assessment end-point for the soft, qualitative form of natural analogue investigation. It should also be clear that this is a necessary procedure because it is the foundations upon which the entire performance assessment will be built. It is strange then, that examination of published performance assessments indicates that this aspect of natural analogue studies usually goes unacknowledged.

Data acquisition: The extraction of well-controlled parameter values for assessments is fundamentally very difficult when compared with laboratory data derivation due to the inherent complexity of natural systems. In fact, there are only a few examples of natural analogues providing quantitative data: the most important probably being matrix diffusion penetration depths. However, the analogue studies prove invaluable for providing bounding values to processes when laboratory techniques prove inadequate or inappropriate, *e.g.* for processes too slow to be observed in the laboratory. Clearly this is an example of the hard, quantitative form of natural analogue study.

Model testing and validation: This is an aspect which has recently grown considerably in importance, as models and databases used in performance assessment need to be validated for 'real' conditions. Thermodynamic solubility and speciation codes and databases have been extensively tested in a number of 'blind predictive modelling' exercises as part of a number of natural analogue studies, such as Oman, Jordan (Maqarin) and Poços de Caldas. The outcome from these exercises has been that, while the basic codes used appear adequate (provided the conceptual model of rock-water interactions in the system is appropriate), the databases used and the assumptions made by the modeller can cause errors in prediction. There appears to be scope for extending this approach to the testing of other types of model, particularly of system dynamics, rather than just static chemical equilibria. A limited attempt has been made on models of redox front movement, for example. Perhaps the most obvious target would be solute transport models where validation is currently based on short-term tracer migration tests. Again, this must be seen as an example of the hard, quantitative form of natural analogue study.

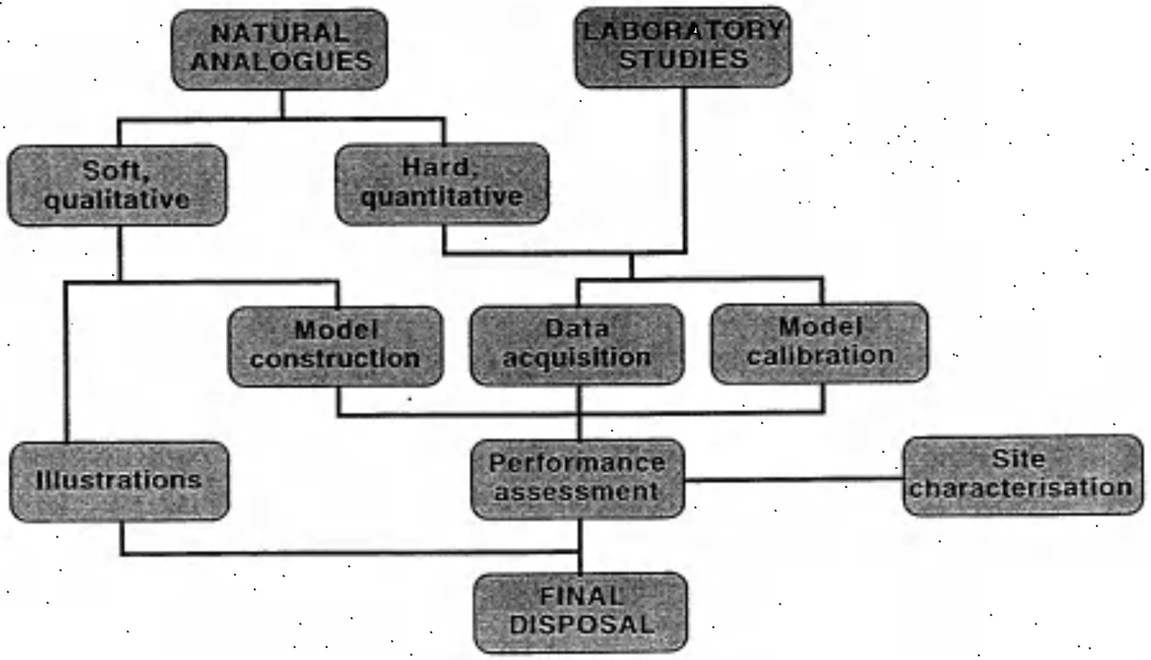

Figure 1: A model of the relationships and interdependencies between the various components necessary for a full safety case for a radioactive waste repository. Natural analogues provide key information for both the performance assessment and illustration aspects.

Figure 1 represents only one way to view the relationships between the various components of geological disposal. Although many of the implications of this diagram, and of the three aspects of a performance assessment, will be clear to individuals, it is hoped that by defining the relationships explicitly it will serve to end the debate about *should* natural analogues be used in performance assessment and focus attention on the question *how* to use them.

4 *Types of natural analogue studies*

There are many forms of natural analogue study of both the 'soft qualitative' and 'hard, quantitative' forms described earlier. However, it is convenient to divide natural analogue studies into those that are concerned with the behaviour of materials in the repository and those that are concerned with radionuclide release and transport processes. It should be recognised that this distinction is, in reality, somewhat blurred because often the behaviour of a material can affect directly the mobility of radionuclides in the near-field. An example of this would be the decomposition of organic materials in the waste (*e.g.* ion exchange resins) or in the engineered barriers themselves (*e.g.* bitumen), creating a wide range of complexing ligands that may adversely affect radionuclide speciation, solubility and thus mobility. Care must therefore be exercised by the analogue researcher to ensure that the implications of their work are fully evaluated.

Materials for which natural analogues have been sought and studied include: borosilicate glass, spent fuel, copper, steel, bentonite, cement and concrete, bitumen, cellulose, polymers and resins. These represent materials that may be present in the waste form, waste packaging or the buffers, backfills and seals. Usually, the aim of the studies is to both identify and quantify degradation processes because the stability and longevity of these materials are key parameters in guaranteeing the safety of a repository. There is no space here to review the many technical conclusions from these analogue studies and the reader is referred to Miller *et al.* (1994) for details.

Natural analogue studies concerned with radionuclide release and transport processes cover a wide range of issues that include: solubility and speciation, retardation mechanisms, matrix diffusion, radiolysis, redox front mechanisms, colloids, microbiological populations and gas generation. Studies are often focussed on naturally-occurring concentrations of U and/or REEs, or unusual physico-chemical environments (*e.g.* hyperalkaline springs). Such studies are hampered by the fact that many of the radionuclides found in the waste do not occur naturally. This problem is usually overcome by choosing naturally-occurring species with similar geochemical characteristics to the repository species: so called chemical analogues. Examples of chemical analogues are natural ^{226}Ra for waste ^{226}Ra, Th for Pu(IV), and U under oxidising conditions for Pu(VI). Great care must be exercised when choosing a chemical analogue because two species that display similar characteristics in one environment may behave very differently to each other under another set of conditions. A detailed review of the results from the many analogue studies focussed on release and transport processes cannot be given here and the reader is referred to Miller *et al.* (1994) for further information.

5 *Illustrative uses of natural analogues*

Natural analogues have a very important role, beyond their application to performance assessment, as providers of illustrative and sometimes non-technical information to a broad range of audiences. This aspect of their use is indicated on Figure 1. In some cases, this illustrative application takes the form of providing information to a wide public audience, with analogue studies being described in advertisements and promotional literature as simple comparisons between nature and the repository. This form of use of analogues in material for wide public dissemination has some value and should be encouraged, provided that the material used is relevant, informative and, above all, honest. However, the illustrative value of natural analogues extends well beyond this usage. There are many other types of audience, some of whom may be well-informed but non-expert technical peers, who may find the concepts and conclusions from a performance assessment credible only if provided with natural parallels for comparison. Such groups may include interested academic researchers familiar with the broad scientific subjects (*e.g.* geology or materials science) but not with the intricacies of performance assessment methodology, and politicians charged with the final decision making but who lack a technical training and who will need some form of 'everyday' proof of repository safety.

The need to supply easily digestible evidences that indicate geological disposal is a sound and credible technology should not be underestimated. No performance assessment can overcome a widespread anxiety concerning repository safety if no effort is made to explain the concepts in a language that is intelligible to all. However, we should not forget that even the assessment modellers require illustrations from natural analogues that indicate that the underlying theory is correct. The illustrative uses of natural analogue information derives from the soft, qualitative form of study. It is the identification of processes, the broad evaluation of material stability, and process rates and interaction that the qualitative study provides which are used in all forms of illustrative literature.

6 Studies of natural systems

Natural analogues are just one way in which natural systems can be examined to provide ways of assessing repository safety. Other ways include studies of natural elemental fluxes and palaeohydrogeology. In the former case, natural elemental fluxes, the concept is concerned with quantifying the natural fluxes of elements and isotopes and their associated health risks and comparing this to the predicted repository -derived fluxes and risks. In simple terms if the flux to the biosphere from the repository is not significant compared with the natural flux from the geosphere, then its radiological significance should not be of great or priority concern. Aside from the quantitative applications, one important illustrative use from such an analysis is simply that the performance assessment numbers are put into a natural, realistic context. In the latter case, palaeohydrogeology, the past hydrogeological regime at a site is reconstructed from evidence taken from the hydrogeochemical and isotopic signatures of the present-day groundwaters and the rock (fracture coating mineralogy), and the hydrogeological properties of the formation (Chapman & McEwen, 1992). At its simplest, palaeohydrogeology provides a test of our understanding of a site for if we cannot postdict the past behaviour of a site, can we claim to be able predict the future behaviour of the same site?

It is not claimed that studies of either geochemical fluxes or palaeohydrogeology are natural analogue studies. The definition provided earlier precludes this because the information gained from such studies is not easily incorporated into performance assessments and is not directly applicable, in a generic sense, between sites. However, there are links between natural analogue studies and other forms of natural system studies that should be recognised. At the simplest level, all these techniques challenge our ability to model adequately a natural system and can provide validatory tests of our model predictions. They also provide alternative but complementary techniques for assessing the suitability of a proposed repository site. What is lacking is a forum where natural analogue and natural system researchers can discuss together and learn from each other and, importantly, where natural system studies can be nurtured and encouraged in the way natural analogue studies were by the formation of the NAWG.

7 *Where to now?*

Any review of natural analogue studies would be incomplete without a discussion on the nature of studies that could or should be performed in the future. It may be heartening to the natural analogue community (although not, necessarily, to those organisations charged with the actual disposal of wastes) to hear that there are several areas in which further natural analogue studies are warranted in order to increase our knowledge of the repository system to a level sufficient to guarantee the validity of performance assessment models. The repository system considered here is the 'European' concept of disposal in a water-saturated environment: different specific conclusions may be reached for the 'US' concept for disposal in an unsaturated environment, although the general conclusion is still that further natural analogue studies are necessary to validate the US concept as well as the European (Pearcy & Murphy, 1991).

Given these requirements for further studies, it is likely that the following two types of natural analogue project will be seen in the future:

1) Large-scale multi-objective projects, probably centred on ore bodies or other geochemical anomalies rich in relevant elements, but in geological environments much closer to those of proposed repository sites and aimed at studying a range of geochemical transport processes.

2) Small-scale, issue or process-specific studies aimed at clarifying particular problems, probably being linked to individual national disposal programmes.

Issues that warrant further natural analogue investigation are those which: (i) have not yet been resolved completely (or with an acceptable level of uncertainty), (ii) are currently dealt with by making very conservative assumptions, or (iii) are so central to the safety case that any additional supporting information would be very valuable. Specific issues that may be considered for further natural analogue study are:

- longevity of the near-field chemical environment, *e.g.* efficiency of buffering reactions for Eh and pH,
- interactions of high pH plume with the host rock,
- rates of cellulose breakdown and nature of degradation products,
- solubility and speciation of radionuclides in various groundwater environments,
- sorption properties of engineered barrier corrosion products,
- irreversible sorption processes in the near and far-fields,
- site-specific matrix diffusion quantification, and
- evidence for long-distance (hundreds of metres) colloid transport in relevant rock formations.

With this list in mind it is possible to define the properties of a number of 'ideal' future analogue studies.

1 Archaeological studies of cementitious, wooden and metal artefacts that have been buried in saturated, reducing environments for known periods of time, where it is possible to examine the undisturbed surrounding soil in detail. This requires participation in the excavation of such materials, rather than simply access to artefacts after excavation.

2 Archaeological studies of metal mining or smelter wastes, preferably disposed of below the water table in a well or pit in clays or fractured rocks where the groundwater flow field can be reconstructed with confidence.

3 Any natural environment where groundwater chemistry is closely analogous to porewaters or groundwaters in some part of the repository system, and contains elevated concentrations of radionuclides and other relevant trace elements from a known source. For the purposes of equilibrium geochemical model testing, a very slow flowing to stagnant environment would be preferable.

4 Discrete zones, rich in relevant trace elements (*e.g.* uranium) in fractured rocks intersected by identifiable preferential groundwater flow paths to allow the definition of a source region and transport pathway and a study of sorption processes on fracture surface minerals.

5 A natural or anthropogenic trace element source in a geochemical environment favouring colloid production and allowing subsequent migration along a definable groundwater flow path in fractured crystalline or sedimentary rocks. The source might be a well which has been used for metallic and chemical waste disposal.

It is recommended that all future natural analogue studies should involve performance assessment modellers from a very early stage to ensure that the objectives of the study are consistent with the modelling requirements. That said, it is probable that future natural analogue studies will take the form of small, process-specific investigations or larger, multiobjective investigations that comprise a collaborative effort between organisations with similar disposal concepts and, thus, similar questions requiring answers.

8 Conclusions

Natural analogues studies have two clearly defined but distinctly different applications: (i) building and supporting performance assessments, and (ii) as qualitative illustrations of the concepts and safety of geological disposal. Both of these applications are essential for the presentation of a safety case: the performance assessment must meet licensing criteria and the illustrations must provide a framework against which the assessment predictions can be judged.

Performance assessments can be seen as comprising three components: model construction, data acquisition, and model testing and validation. Natural analogues are essential in all three components although recognition of their importance is often limited only to the last two. Natural analogue studies can broadly be separated into soft, qualitative and hard, quantitative forms. The former is concerned with identifying natural processes and their interactions, and the latter is concerned with fitting parameter values to processes. Consequently, the soft, qualitative form of analogue study provides input into the model construction component of the performance assessment. The hard, qualitative form of study provides input (together with laboratory investigations) into the data acquisition, and model testing and validation components of performance assessment.

The understanding of several key processes has been improved directly by natural analogue research although many topics can still be identified as requiring further investigation. Future natural analogue studies should be focussed on specific, well-defined performance assessment requirements. These studies may take the form of small process-specific investigations or comprise part of a larger, multiobjective investigations, probably as a international collaborative effort.

The dialogue between performance assessment modellers and natural analogue researchers is at a higher level than ever before however the value of natural analogues is still not universally accepted. Increasing acceptance of natural analogue-derived information can be achieved only by involving the modelling teams in the first stages of planning future natural analogue studies to ensure that the studies provide the information that is *actually needed* and not what the analogue researchers think *should be needed.*

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SESSION 1: PRESENTATION OF NATIONAL PROGRAMMES/PROJECTS

Chairpersons: E. Pearcy (USA), R. Ewing (USA)

-	Analog support for the Canadian concept for disposal of nuclear fuel waste	J. Cramer (CAN)
-	Natural analogues and performance assessment	P. Cloke et al. (USA)
-	Overview of the Swiss natural analogue programme, 1994	W.R. Alexander et al. (CH)
-	Natural analogue studies in Australia	P. Airey (AUS)
-	Swedish natural analogue programme	J. Smellie et al. (S)
-	Natural analogue studies in Finland	R. Blomqvist (FIN)
-	The El Berrocal project: an example of a natural system characterisation exercise	P. Hernán (E)
-	An overview of the British natural analogue programme	P. Hooker (UK)
-	The Oklo-natural analogue project: recent outcomes and applications of phase I programme	J. Carpéna et al. (F)
-	The Dunarobba Forest as natural analogue: analysis of the geoenvironmental factors controlling the wood preservation	S. Lombardi et al. (I)
-	Natural analogues for a repository in rock salt, the German approach	W. Steininger (D)

ANALOG SUPPORT FOR THE CANADIAN CONCEPT FOR DISPOSAL OF NUCLEAR FUEL WASTE

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ABSTRACT

The assessment of the long-term safety and performance of the concept for disposal of nuclear fuel waste is a unique and challenging undertaking, because predictions have to be made for time periods in the range of 10^4 to 10^6 a into the future. The data used for the assessment modelling is in large part based on observations from short-term laboratory and field experiments. Natural analogs can give a reference for the environmental and safety assessment of the concept, providing both useful data and a qualitative illustration of the interaction of processes and materials in complex natural systems.

The available natural analog information has been reviewed with particular emphasis on the disposal of used CANDU (CANada Deuterium Uranium) fuel. The review is broken down into sections pertaining to the major components of the disposal system: the vault, the geosphere and the biosphere. Specific examples are given for each. In addition, information from the Cigar Lake uranium deposit, a natural system that contains a number of features and processes similar to those in the disposal concept, is used to illustrate and support the Environmental Impact Statement for the Canadian concept.

1. Introduction

AECL Research (AECL), with support from Ontario Hydro under auspices of the Candu Owners Group, has assessed a concept for the safe disposal of nuclear fuel waste in Canada (AECL 1994). The disposal concept is to place nuclear fuel waste in corrosion-resistant containers and emplace the containers with sealing materials in an engineered vault at depths of 500 to 1000 m in plutonic rock of the Canadian Shield. Humans and the environment would be protected from contaminants in the waste by several barriers: the waste itself, the container, the sealing materials, and the rock. This disposal concept permits a great deal of flexibility in its implementation, which means that a wide range of circumstances could be accommodated. The safety of nuclear fuel waste disposal in Canada is regulated by guidelines issued by the Atomic Energy Control Board (AECB 1987), which require quantitative predictions for up to 10^4 a and qualitative predictions (or reasoned arguments) for performance thereafter.

In accordance with the 1981 Joint Statement of the governments of Canada and Ontario, no specific site for disposal of nuclear fuel waste is proposed at this time. Thus in developing and assessing the disposal concept an illustrative "reference" disposal system was defined and assessed. This "reference" disposal system illustrates what the major elements of a disposal system, including the geosphere and biosphere, might be like. Although it is hypothetical, it is based on information derived from extensive laboratory and field research. Many of the assumptions made are conservative, that is, they would tend to overestimate adverse effects. The components and designs chosen are not presented as ones that are being recommended but rather as ones that illustrate a technically feasible way of implementing the disposal concept.

The development of the disposal concept and the research towards assessing the safety of the concept are based on knowledge and understanding of the materials and processes involved. This knowledge and understanding provide both the qualitative (conceptual models) and quantitative (databases) input to the assessment of the disposal concept. The assessment models, being the mathematical representations of the knowledge and understanding of the disposal system, are needed to calculate the long-term predictions on the performance of the disposal system and, thus, to assess the future safety and environmental impacts.

The conceptual models and databases are products of laboratory and field research programs, such as the Canadian Nuclear Fuel Waste Management Program (CNFWMP). However, laboratory and field experiments are, by necessity, carried out over relatively short periods of time. Therefore, additional information and data are required to provide confidence in the safety of the disposal concept and in the predictions from assessment models when extrapolating to time periods of thousands-to-millions of years.

Studies of natural analogs provide important information for evaluating and improving our knowledge and understanding of the disposal concept. Improved conceptual models and databases, in turn, result in better assessment models, enhancing the level of confidence in the safety predictions from these models. In addition, analogs can be valuable illustrative tools when consulting on the disposal concept with the non-expert and the public.

2. Use of analog information

No natural system exists that is analogous to a complete disposal system. Because the disposal of used nuclear fuel involves the emplacement of a large volume of UO_2-based waste deep inside a natural rock formation, the comparison with certain large and ancient uranium-ore deposits is tempting. The obvious absence of engineered components in a natural uranium deposit, such as the container and cement-based seals, and the absence of thermal and radiation fields from the waste, however, preclude a direct comparison with a disposal vault. On the other hand, the long-term stability of a UO_2-based ore in a similar, but less ideal, system provides information that is important feedback to the disposal objective of long-term isolation of UO_2-based fuel waste. Thus, carefully selected natural systems may be studied for processes expected to occur in a disposal system. For instance, a natural uranium deposit may be studied for the processes and materials controlling the long-term UO_2 stability and the migration of radionuclides from the ore. But the long-term performance of other materials and processes, such as container corrosion and concrete stability, require the study of separate analogs.

Analog information is primarily qualitative or, at best, semiquantitative, because data are obtained by reconstructing the natural system's long and often complex history. The results and conclusions from an analog study are seldom unambiguous, because it is impossible to obtain 100% certainty for the values of all the parameters in such reconstructions. For instance, the study of an analog system can provide the present-day hydrogeological framework for water-rock interaction processes, but it may be impossible to know exactly how this framework evolved over the past 10^4 to 10^6 a. Similarly, a reaction rate measured for a certain geochemical process in an analog system may only be matched with an experimentally obtained value if one can be absolutely sure that the process in the natural system was not affected by an event that has eluded detection. For this reason an analog cannot be used for direct validation of a mathematical code for safety assessment. Analog information must rather be used to revise and refine our knowledge and understanding, as reflected in the conceptual models and databases, and, thus, can increase the confidence in the validity of the code and its predictions.

The following points illustrate the use of analog information in the environmental and safety assessment of the Canadian disposal concept:

- FEEDBACK on conceptual models
  Comparison of analog information with that of the conceptual models, such as the composition of the disposal system or subsystem(s) and the processes occuring therein. This provides feedback on the reality and boundary conditions of the conceptual models and on the input to the assessment code: for instance, the importance and role of certain materials and processes in radionuclide migration, such as colloids, organics and microbes, can be obtained from the study of natural analog systems.

- FEEDBACK on laboratory data
  For instance, the applicability over long periods of time of mineral dissolution and corrosion rates obtained from laboratory experiments can be evaluated by comparing them with rates obtained from the study of natural dissolution and corrosion in geological or archeological systems.

- TEST tools used in assessment models
  For instance, solubility/speciation codes and their thermodynamic databases, sorption K_d-database, etc., are tools used in assessment codes. The quality of such tools can be evaluated through application in analogous natural systems by, for example, comparing 'blind' predictions of certain parameter values from a code with actual measured values from the natural system.

- TEST actual assessment models
  For instance, submodels of an overall assessment model, such as a fuel-dissolution model or mass-transport model, can be evaluated through application in appropriate natural systems.

- FEEDBACK to concept design
  For instance, studies of thermal alteration of bentonite in analogous natural systems provide feedback to design parameters of the disposal concept regarding the maximum thermal regime in the vault if bentonite alteration must be minimized. Similarly, redox buffering/control in analogous natural systems provides feedback on the conceptual model for redox control in the buffer surrounding the waste package.

- SUPPORT reasoned arguments
  Information on natural processes occurring over time periods of $>10^4$ a, such as glaciation, erosion and tectonic evolution, is used to develop reasoned arguments for the safety assessment of the disposal concept beyond the required 10^4 a time frame.

- PROVIDE education information
  Natural systems and processes are valuable tools for educating the public and non-experts on the disposal concept and on the approach to making long-term predictions, thereby building confidence in our understanding and knowledge behind the safety assessment.

During the past decade, the evolution of the CNFWMP has led to a better understanding and focus of the role of natural analogs in the environmental and safety assessment of the Canadian disposal concept. Whereas early on the analog information was dominantly qualitative, the more recent analog studies focussed on well-constrained systems capable of providing more specific and quantitative feedback.

AECL has produced a report reviewing the body of analog information for many aspects of the Canadian disposal concept (Cramer 1994). This EIS-supporting document includes particular reference to the case study for used nuclear fuel in granite, as described in the EIS (AECL 1994) and the nine primary reference documents. A second report (Cramer and Smellie 1994), published jointly with the Swedish Nuclear Fuel and Waste Management Company (SKB), provides a comprehensive record of the AECL/SKB analog studies carried out on the Cigar Lake uranium deposit.

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NATURAL ANALOGUES AND PERFORMANCE ASSESSMENT

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ABSTRACT

This paper presents a number of general data types needed for performance assessment of the potential high level nuclear waste repository at Yucca Mountain, NV. These include hydrology (e.g., fluxes through a breached waste package and to the accessible environment), geochemistry (e.g., water composition and changes thereto due to corrosion and waste dissolution; radionuclide solubilities), the engineered barrier system (e.g., rates and times of container failure; degradation of concrete), the source term, and disruptive scenarios. Comparison of some characteristics of two natural analogue studies supported by the U. S. Department of Energy (USDOE), specifically the Taupo Volcanic Zone (New Zealand) and Cigar Lake (Canada), against these needs identified eight categories of analogous data obtainable from the former and five from the latter. The paper also takes note of six uranium districts in Nevada and Oregon that may serve as natural analogue sites specific to the U.S. disposal concept. Each of these sites possesses the potential to provide insights concerning the long term behavior of the natural system in relation to a few characteristics and data needs. The characteristics that pertain to performance at Yucca Mountain differ from site to site, and largely do not overlap. This paper presents one way of evaluating the potential applicability of studies at a specific site to performance assessment.

I. Introduction

This paper provides a brief synopsis of the kinds of information needed by performance assessment and compares them with the types of information potentially available from two natural analogue studies currently supported by the U. S. Department of Energy (USDOE). Comparisons are made between the potential repository site at Yucca Mountain, Nevada, and the Taupo Volcanic Zone in New Zealand (Ellis and Mahon, 1977) and between Yucca Mountain and the Cigar Lake uranium deposit (Goodwin et al., 1989) in Canada. The first analogue site, the Taupo Volcanic Zone, has broad relevance to conditions expected at Yucca Mountain, if a repository is constructed and waste emplaced. The rock types are largely the same, the hydrothermal conditions (actual vis-a-vis expected) bear a close resemblance to one another, and at least some engineered materials in use in New Zealand are similar to materials that may be used in a potential repository at Yucca Mountain. The second comparison, with Cigar Lake, indicates that a few of the processes that occurred at Cigar Lake resemble those required for performance assessments at Yucca Mountain, although in many other respects the sites aren't analogous. Principally, this analogue is potentially valuable to performance assessment because it may cast light on the migration processes for plutonium and technetium under specific environmental conditions.

2. Data Needs for Performance Assessment

Performance assessments conducted for the Yucca Mountain Site Characterization Project (YMP) have included parameters on hydrology, geochemistry, waste package, source term, and various aspects of disruptive scenarios. Hydrologic parameters included the rate of water influx into a waste package, the percentage of waste packages wetted in the anticipated unsaturated environment, and the rate of advective or diffusive water transport away from a waste package. Examples of geochemical parameters include the composition of water contacting a waste package and changes that occur after such contact. At this generalized level of detail, approximately twenty parameters were identified for comparison with data that might be supplied through the study of natural or anthropogenic analogues, as illustrated in Table 1.

3. Useful Natural Analogues

Table 2 provides a brief comparison of some characteristics of the Taupo Volcanic Zone and Yucca Mountain. As illustrated in Table 3, the correspondence between the parameters needed by performance assessment, generalized in Table 1, with characteristics listed in Table 2 is not exact, thereby ruling out direct analogies between hydrologic processes active in the Taupo Volcanic Zone in New Zealand and the potential repository at Yucca Mountain. The Taupo system lacks a localized heat source to correspond to waste packages emplaced in a repository. However, hydrological codes are planned to be adapted to create a computational model for the Taupo system and comparisons can then be made with actual observations; this would help to bolster confidence in the methodology used to construct the models, and the capabilities and applicability of the codes. On the other hand, many direct parallels exist in respect to geochemistry. These include the composition of the water in the two systems, as unaffected by man-made materials; modification of the water chemistry due to corrosion of steel (emplaced in steam wells at the geothermal power plant in New Zealand); and rock alteration, which is related to transport and retardation of radionuclides. In addition, studies of the corrosion of metals and concretes that have been installed in the geothermal power systems relate to performance assessment parameters needed to evaluate the engineered barriers. The Taupo Volcanic Zone may be the only locality where scientists have conducted extensive prior investigations of an active geothermal system (i.e. where geothermal power is produced) in the same kinds of rocks as Yucca Mountain, thus providing a unique opportunity to compare hydrology, geochemistry, and the behavior of engineered materials.

Table 1. Information Types Needed for a Potential Yucca Mountain Repository System Performance Assessment

HYDROLOGY

- Rate of water influx into or past waste package
- Percentage of waste package wetted or filled with water
- Rate of water flux from and away from waste package
- Rate of water transport from waste packages to the accessible environment
- Rate of gas movement to the accessible environment

GEOCHEMISTRY

- Composition of water contacting waste packages
- Changes in water composition from corrosion of container
- Changes in water composition due to interaction with the waste (including radiolysis), concrete, etc.
- Solubility of radionuclides in altered water
- Transport/retardation of dissolved radionuclides to the accessible environment
- Transport of gaseous radionuclides to the accessible environment

ENGINEERED BARRIER SYSTEM

- Rates of all types of container corrosion
- Time dependent distribution of container failures
- Release rates of radionuclides from the waste to water or gas
- Degradation of other engineered materials, e.g. concrete

SOURCE TERM

- Release rate of radionuclides into the host rock

DISRUPTIVE SCENARIOS

- Volcanic intrusion
- Human intrusion
- Faulting
- Climate change
- Others

Table 2. Hydrothermal Systems in the Taupo Volcanic Zone, New Zealand (A U.S. Department of Energy Natural Analogue Site)

New Zealand Site	Yucca Mountain Repository
Welded rhyolitic tuff	Welded rhyolitic tuff
Zeolitic rock alteration	Zeolitic rock alteration
Partially saturated	Partially saturated
Temperatures up to ~300°C	Temperatures up to ~250°C
Natural hydrothermal system	Man-made hydrothermal system

Table 3. Taupo Volcanic Zone Vis-a--Vis Yucca Mountain Performance Assessment Needs

Taupo Volcanic Zone	Yucca Mountain	Suitable Analogue
HYDROLOGY		
Saturated and unsaturated zones in welded tuffs mixed with fine grained sedimentary rocks, extensive hydrothermal alteration	Unsaturated zone in welded tuff, alteration probable following waste emplacement	Yes
GEOCHEMISTRY		
Water Composition:		
Variably reducing and oxidizing, concentrations determined by tuffs primarily	Oxidizing, concentrations determined by tuffs	Yes
Composition Changes due to Container Corrosion:		
No container, but steel and other metals have been emplaced	Container present	Yes, to some degree
Composition Changes due to Interaction with Waste:		
No analogue of waste present	UO_2 present in waste, high level of radioactivity from other radionuclides, radiolysis likely	No

Table 3. Taupo Volcanic Zone Vis-a--Vis Yucca Mountain Performance Assessment Needs (Continued)

Taupo Volcanic Zone	Yucca Mountain	Suitable Analogue
Composition Changes due to interaction with engineered materials:		
Concretes and metals present	Concretes and metals will be part of a repository, if built	Yes
Radionuclide Solubility:		
Radionuclide concentrations too low	"Insoluble" radionuclides expected to be at saturation	No
Transport of Dissolved Radionuclides:		
Radionuclide concentrations very low, but behavior of several can be assessed through U and Th series disequilibria	Pu, Tc, etc. present in significant concentrations, temperature will rise after waste emplacement	Yes
Transport of Gaseous Radionuclides:		
Radionuclide concentrations very low, but transport of Rn and CO_2 could be studied	Gas phase present	Yes

Table 3. Taupo Volcanic Zone Vis-a--Vis Yucca Mountain Performance Assessment Needs (Continued)

Taupo Volcanic Zone	Yucca Mountain	Suitable Analogue
ENGINEERED BARRIER SYSTEM		
Container Corrosion and Failure:		
No container present, but metals are	Container present	Yes, to some degree
Release of Radionuclides to Water:		
Radionuclide concentrations too low	Radionuclides released inside a container which may produce reducing conditions, reducing filler may be added. Intense radiation	No
Degradation of Other Engineered Materials, e.g. Concrete:		
Concretes and metal reinforcements emplaced in producing geothermal field	Concretes and steel reinforcements will be part of a repository, if built	Yes
SOURCE TERM		
Radionuclide Release into Host Rock:		
Radionuclide concentrations too low	Some type of backfill may be added around the container, but not bentonite. Hydrothermal activity may alter host rock, most likely to zeolites	No

Table 4 provides this same type of analysis for the Cigar Lake natural analogue site. Particularly in respect to this analogue, it is important to bear in mind the emphasis on process and reasoning, not on an exact match of characteristics between an analogue and a repository site. Cigar Lake provides a rare opportunity to assess the migration of Pu and Tc over very long time frames. At only a very few places in the world do these elements exist as natural deposits in sufficiently high concentrations to study their migration. Consequently, despite the poor match of most characteristics, particularly the oxidation state of the near field environment, between this site and the potential U. S. repository, Cigar Lake still constitutes a valuable analogue for processes important to the assessment of performance at Yucca Mountain.

As noted by Miller et al. (1994), the U.S. high-level waste disposal concept differs significantly from the disposal concepts being considered in other nations' programs in that it involves disposal in siliceous volcanic rock in the unsaturated zone. Therefore, the U. S. programs have made an effort to find analogue sites, including the Taupo Volcanic Zone, that allow study of processes in analogous rock types and unsaturated conditions. U.S. Nuclear Regulatory Commission (NRC) sponsored survey of potential geochemical analogues by Pearcy and Murphy (1991), described the Peña Blanca site in Chihuahua, Mexico, site as one potentially useful analogue; it is now being studied under NRC sponsorship. It contains a hydrothermal uranium ore deposit in unsaturated rhyolitic ignimbrites, and allows the study of the migration of material from almost completely oxidized ore. Pearcy et al. (1993) made a deliberately conservative and preliminary estimate of UO_2 oxidation rate limits based on observations of uraninite transformation and assumptions about how long one of the Peña Blanca ore deposits has been above the water table. The rates suggested by the data and assumptions about Peña Blanca geologic history resembled those obtained in the laboratory by Grambow et al. (1990). Evidence also exists for fracture flow and transport, and for matrix diffusion at the site; these data invite further study and quantification.

Pearcy and Murphy (1991) suggested that uranium occurrences in volcanic rocks in Nevada would be less directly comparable analogues to a potential repository at Yucca Mountain than Peña Blanca. However, Castor and Henry (written communication, 1993) argue that although Peña Blanca would constitute an excellent analogue for Yucca Mountain, it does not contain the zeolites and smectite minerals thought, potentially, to play a significant role in retarding radionuclide transport at Yucca Mountain. Castor and Henry, on behalf of the Nevada Bureau of Mines and Geology, submitted a proposal to the Yucca Mountain Site Characterization Office to study several occurrences of uranium minerals in volcanic host rocks in Nevada and Oregon. Analyses of the available data, in much the same fashion as here illustrated for the Cigar Lake and Taupo Volcanic Zone, will likely narrow the number of potential sites accompanying the proposal (see map in Figure 1 and site characteristics in Table 5). Some of these sites may be studied, through exploration and testing, especially during the confirmation phase of the high-level waste disposal program (i.e., during construction and operation) prior to final closure. The NRC's Part 60 of Chapter 10 of the Code of Federal Regulations (10 CFR Part 60) prescribes a confirmation phase, including a program of field and laboratory studies. These studies will provide "Performance Confirmation" information for inclusion in the license amendments required to receive and emplace waste, and for final closure. The idea is to select analogue sites that potentially can supply data for different and mutually exclusive

Table 4. Cigar Lake Vis-a-Vis Yucca Mountain Performance Assessment Needs

Cigar Lake	Yucca Mountain	Suitable Analogue
HYDROLOGY		
Saturated zone in sedimentary rocks, altered near ore	Unsaturated zone in welded tuff	No
GEOCHEMISTRY		
Water Composition:		
Reducing, concentrations determined by sediments	Oxidizing, concentrations determined by tuffs	Possibly, if fillers or backfill used at Yucca Mt.
Composition Changes due to Container Corrosion:		
No container	Container present	No
Composition Changes due to Interaction with Waste:		
UO_2 abundantly present, may be radiolysis effects	UO_2 present in waste, high level of radioactivity from other radionuclides, radiolysis likely	Yes, if radiolysis significant at Cigar Lake

Table 4. Cigar Lake Vis-a-Vis Yucca Mountain Performance Assessment Needs (Continued)

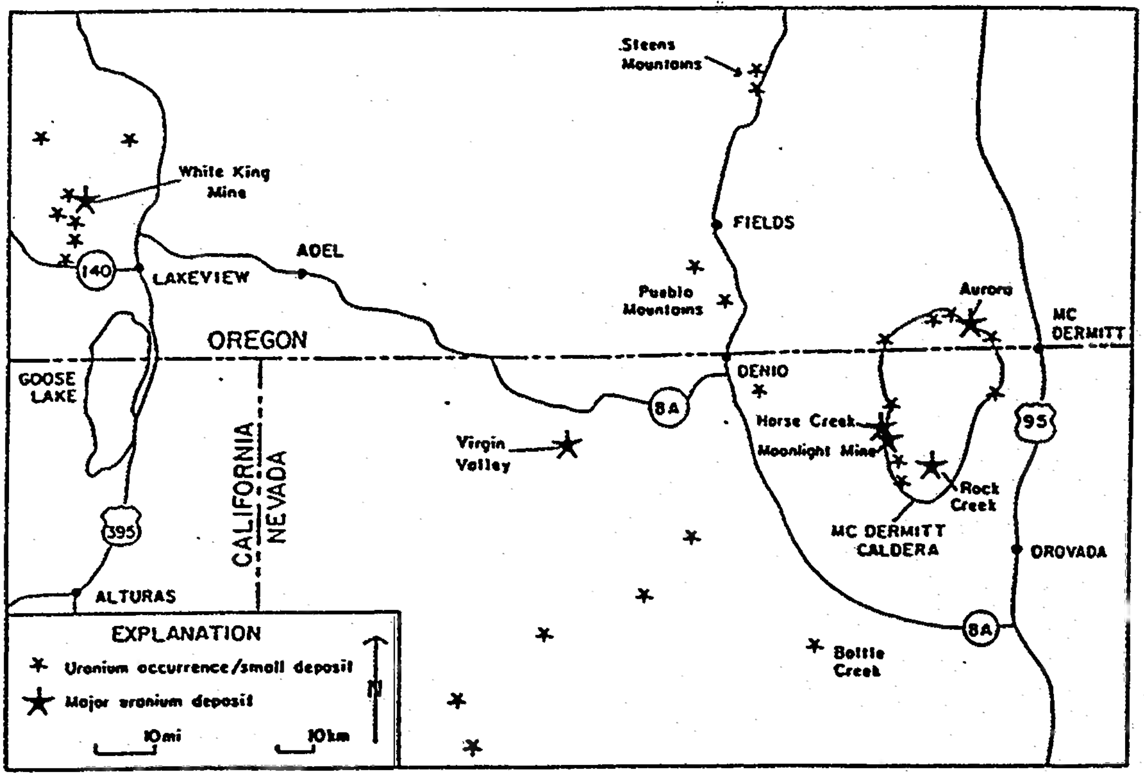
Cigar Lake	Yucca Mountain	Suitable Analogue
Composition Changes due to interaction with engineered materials:		
Concretes and metals present	Concretes and metals will be part of a repository, if built	Yes
Radionuclide Solubility:		
Radionuclide concentrations too low, except for U and possibly Th	"Insoluble" radionuclides expected to be at saturation	Not for radionuclides of most concern
Transport of Dissolved Radionuclides:		
Pu, Tc, and other radionuclides of greatest concern are present; migration processes can be studied at somewhat elevated temperature	Pu, Tc, etc. present in significant concentrations, temperature will rise after waste emplacement	Yes, to aid in understanding processes*
Transport of Gaseous Radionuclides:		
No gas phase present	Gas phase present	No

* Insights to processes may be obtained even though conditions differ; may serve as an "end-member".

Table 4. Cigar Lake Vis-a-Vis Yucca Mountain Performance Assessment Needs (Continued)

Cigar Lake	Yucca Mountain	Suitable Analogue
ENGINEERED BARRIER SYSTEM		
Container Corrosion and Failure:		
No container present	Container present	No
Release of Radionuclides to Water:		
Radionuclides of concern released under reducing conditions in presence of a radiation field	Radionuclides released inside a container which may produce reducing conditions, reducing filler may be added. Intense radiation	Possibly to probably
Degradation of Other Engineered Materials, e.g. Concrete:		
No concrete of engineered materials present	Concretes and steel reinforcements will be part of a repository, if built	No
SOURCE TERM		
Radionuclide Release into Host Rock:		
No container or corrosion products, clay alteration zone around ore	Some type of backfill may be added around the container, but not bentonite. Hydrothermal activity may alter host rock, most likely to zeolites	Probably not

Figure 1. Uranium Deposits and Occurrences in Northwestern Nevada and Southeastern Oregon. (Written Communication, Castor and Henry, 1993)



parameters and processes. For processes particularly vital to performance, such as the interaction of unsaturated zone flux and geochemistry, it may be useful to study several analogues that allow a rough response surface to be constructed that can then be compared with similar response surfaces created through modeling. This is expected to assist in building confidence in performance assessment model applications over very long time periods.

4. Use of Natural Analogues in Performance Assessment

In 10 CFR Part 60, the NRC suggested the use of natural analogues as part of the studies needed to provide a supporting technical basis for models used in system performance assessments. Specifically, the regulation states an expectation that "Analyses and models ... shall be supported using an appropriate combination of such methods as field tests, in situ tests, laboratory tests which are representative of field conditions, monitoring data, and natural analog studies." Subpart F of 10 CFR Part 60 describes the "performance confirmation period" and suggests that activities to support the technical basis of analyses and models continue from the time of site-characterization to the time of permanent closure. Thus, the obligation to continue to perform confirmatory studies well into the next century provides the opportunity to study several additional well selected additional natural analogue sites in detail.

Table 5. Characteristics of Uranium Deposits in Northwestern Nevada and Southeastern Oregon (After Written Communication, Castor and Henry, 1993)

AREA	HOST ROCK							
Subarea or deposit	**Near-Field**	**Far-Field**	**Mineral Assemblage**					**Age (Ma)**
			Glass	**Devit**	**Zeolite**	**Clay**	**Other**	
McDermitt Caldera Moonlight mine - Horse Creek	Ash-Flow Tuff, Mafic-Felsic Flow rock, Intr. Rhyolite	Peralkaline Ash-Flow Tuff	P	P	?	P	Adularia	15 to 16
Thacker Pass	Peralkaline Ash-flow Tuff	Peralkaline Ash-Flow Tuff	N	P	P	?	Adularia	15 to 16
Montana Mountains and Bull Basin	Bedded Tuff, Volc. Sed. Rock, Ash-Flow Tuff	Peralkaline Ash-Flow Tuff	?	P	P	P	Carbonate	?
Aurora	Andesite, Ash-Flow Tuff	Bedded Tuff, Volc. Sed. Rock, Ash-Flow Tuff	P	P	?	P		15 to 16
Opalite mine	Sinter, Bedded Tuff, Volc. Sed. Rock	Ash-Flow Tuff	N	P	?	P	Adularia	15 or less
Bretz mine	Andesite, Ash- flow Tuff, Volc. Sed. Rock	Bedded Tuff, Ash-Flow Tuff	P	P	?	?		<15 to 16
Cottonwood Creek	Bedded Tuff, Volc. Sed. Rock	Bedded Tuff, Ash-Flow Tuff	?	P	P	?	Opal	15 or less
McDermitt mine	Volc. Sed. Rock	Volc. Sed. Rock, Ash-Flow Tuff	N	P	P	P		15 to 16
Virgin Valley	Bedded Tuff, Volc. Sed. Rock, Rhyolite Flow Rock	Bedded Tuff, Volc. Sed. Rock, Rhyolite Flow Rock	P	P	P	P	Opal	14

Abbreviations:
Devit. = devitrification products, Spls. = samples, P = present, R = reported, N = not present, ? = no data, Mod. = moderate, Intr. = intrusive, Volc. = volcanogenic, Sed. = sedimentary, Rhy. = rhyolite, Subhoriz. = subhorizontal

Table 5. Characteristics of Uranium Deposits in Northwestern Nevada and Southeastern Oregon (After Written Communication Castor and Henry, 1993) (Continued)

AREA	HOST ROCK							
Subarea or deposit	Near-Field	Far-Field	Mineral Assemblage					Age (Ma)
			Glass	Devit	Zeolite	Clay	Other	
Bottle Creek	Ash-Flow Tuff, Volc. Sed. Rock	Ash-Flow Tuff	P	P	?	P	Epidote, Sericite	?
Southern Washoe County Pyramid district	Ash-Flow Tuff, Bedded Tuff, Mafic dike rock	Ash-Flow Tuff, Bedded Tuff	?	P	?	P		20 to 30
Dogskin Mountain	Ash-Flow Tuff	Ash-Flow Tuff	?	P	?	P		20 to 30
Petersen Mountain	Ash-Flow Tuff	Ash-Flow Tuff	?	P	?	P		20 to 30
Lakeview White King Mine	Intrusive Rhy., Bedded Tuff, Mafic Flow Rock	Bedded Tuff, Mafic Flow Rock	N	P	?	P	Adularia	6 to 7
Lucky Lass Mine	Bedded Tuff, Mafic Dike Rock	Bedded Tuff	P	P	?	P		?
Steens Mountain	Ash-Flow Tuff or Felsic Flow	Ash-Flow Tuff or Felsic Flow	?	P	?	?		?
Yucca Mountain	Ash-Flow Tuff	Ash-Flow Tuff, Bedded Tuff	P	P	P	P		12 to 14

Abbreviations:
Devit. = devitrification products, Spls. = samples, P = present, R = reported, N = not present, ? = no data, Mod. = moderate, Intr. = intrusive, Volc. = volcanogenic, Sed. = sedimentary, Rhy. = rhyolite, Subhoriz. = subhorizontal

Table 5. Characteristics of Uranium Deposits in Northwestern Nevada and Southeastern Oregon (After Written Communication, Castor and Henry, 1993) (Continued)

AREA	STRUCTURAL AND HYDROLOGIC CHARACTERISTICS				
Subarea or deposit	General	Faulting	Faulting Density	Relative Permeability	Hydrologic Regime
McDermitt Caldera Moonlight mine - Horse Creek	Caldera ring Fracture zone	Intense	Intense (?)	?	Vadose and Saturated
Thacker Pass	Subhoriz. Strata	Mod.	?	High (?)	?
Montana Mountains and Bull Basin	Subhoriz. Strata	Mod.	?	?	?
Aurora	Subhoriz. Strata	Mod.	?	Locally High	?
Opalite mine	Subhoriz. Strata	?	?	Locally High	?
Bretz mine	Caldera Ring Fracture Zone, Subhoriz. Strata	Intense (?)	Intense (?)	High (?)	?
Cottonwood Creek	Subhoriz. Strata	?	?	?	?
McDermitt mine	Subhoriz. Strata	Mod.	?	?	?
Virgin Valley	Subhoriz. Strata	Mod.	?	Locally High	?
Bottle Creek	Caldera Wall(?)	Mod.	?	?	?
Southern Washoe County Pyramid district	Discordant Dike, Subhoriz. Strata	Mod.	Mod. (?)	?	?
Dogskin Mountain	Subhoriz. Strata	?	?	?	?
Petersen Mountain	Subhoriz. Strata	?	?	?	?
Lakeview White King Mine	Rhy. Instustion in Bedded Tuff	Mod.	?	?	Mainly Saturated
Lucky Lass Mine	Shallowly Dipping Strata	?	?	High (?)	Mainly Saturated
Steens Mountain	Shallowly Dipping Strata	?	?	?	?
Yucca Mountain	Subhoriz. Strata	Mod.	Mod.	Low to Mod.	Vadose

Abbreviations:
Devit. = devitrification products, Spls. = samples, P = present, R = reported, N = not present, ? = no data, Mod. = moderate, Intr. = intrusive, Volc. = volcanogenic, Sed. = sedimentary, Rhy. = rhyolite, Subhoriz. = subhorizontal

Table 5. Characteristics of Uranium Deposits in Northwestern Nevada and Southeastern Oregon (After Written Communication, Castor and Henry, 1993) (Continued)

AREA	URANIUM MINERALIZATION						
		U Minerals					
Subarea or deposit	Geometry	6+	4+	Other	Gangue Minerals	Chemistry	Age (Ma)
McDermitt Caldera							?
Moonlight mine - Horse Creek	Vein	P	R	U+4 in Zircon	Quartz, Fluorite, Sulfides	Ag, As, Au, Br, Cu, F, Hg, Mo, Sb, Sn, W, Yb, Zn, Zr	
Thacker Pass	Stratabound, Veins	P	?	U+4 in Zircon	?	As, Au, F, Hg, Mo, Sb, Sn, W, Y, Zn, Zr	?
Montana Mountains and Bull Basin	Hot Spring	?	?	U+4 in Zircon	?	As, Hg, Li, Mo, Sb, Th, Y, Zn, Zr	?
Aurora	Stratabound	P	R	?	Sulfides	Ag, As, F, Hg, La, Mo, Sb, Sn, W, Y	?
Opalite mine	Hot Spring	?	?	?	Sulfides, Chalcedony	As, Au, Cu, Hg, Mo, Pb, Sb, Sn, W, Y, Zr	?
Bretz mine	Hot Spring, Veins, Stratabound	P	?	?	Sulfides, Chalcedony	Ag, As, Au, P, Hg, Mo, Pb, Sb, Sn, W, Y, Zn, Zr	?
Cottonwood Creek	Stratabound	?	?	?	Sulfides, Chalcedony	As, F, Hg, Li, Mo, Sb	?
McDermitt mine	Stratabound, Hot Spring	?	?	Organic	Sulfides, Chalcedony	As, Cl, Hg, I, Sb, Th	15 to 3
Virgin Valley	Stratabound, Hot Spring	P	?	Opal, Organic	Opal, Mn Oxides, Sulfides	As, Hg, Mo, Sb, W	2 to 3
Bottle Creek	Veins, Shear Zones	P	?	?	Opal, Celadonite	As, F, Hg, Mo, Sb	?
Southern Washoe County							
Pyramid district	Stratabound, Dike Contacts	P	?	Opal, Organic	Fe Oxides, Mn Oxides	Pb, Sb, Zn	?
Dogskin Mountain	Stratabound Fracture Zone	P	?	Organic	?	?	?
Petersen Mountain	Fracture Zone	P	?	Organic	?	?	?
Lakeview							?
White King Mine	Irregular	P	R	?	Sulfides	Ag, As,Hg, Mo, Pb, W, Y, Zn	
Lucky Lass Mine	?	?	?	?	?	Ag, As, Mo, Pb, Y, Zn	?
Steens Mountain	Breccia Veins	?	?	?	?	As, Ba, Hg, Mo	?
Yucca Mountain							

Abbreviations:
Devit. = devitrification products, Spls. = samples, P = present, R = reported, N = not present, ? = no data, Mod. = moderate, Intr. = intrusive, Volc. = volcanogenic, Sed. = sedimentary, Rhy. = rhyolite, Subhoriz. = subhorizontal

Andrews et al. (1994) and Wilson et al. (1994) outlined several areas in current system performance assessments of Yucca Mountain that are technically weak. These weak areas include waste package materials behavior; water availability and likely water contact modes; thermal perturbations and their potentially permanent effects on water flux in the unsaturated zone and on geochemistry, radionuclide dissolution rates, radionuclide solubilities, groundwater flow paths and fluxes toward the accessible environment; geochemistry of flowpaths over long times; and radionuclide migration characteristics along flow paths. It should be remembered, however, that current performance assessments are still preliminary: design and materials testing and selection are in progress, site characterization is in progress, thermal tests are planned and in progress, and laboratory testing of materials and processes is ongoing.

Probably suitable natural analogues will supply a number of qualitative and quantitative insights, e.g., the likely effects of the thermal perturbation to the unsaturated rock, the likely rate of dissolution of the spent fuel waste form, the likely range of groundwater fluxes onto the waste packages, and likely radionuclide solubilities and retardation behaviors. Observations of a number of uranium occurrences in unsaturated volcanic rock under differing climatic conditions may set bounds on the rates at which some of these important processes proceed in comparable natural settings, providing some estimate can be made of the geologic history of the analogue sites. This carries particular importance in addressing issues of scale: There will be no opportunity to observe flux in unsaturated volcanic rock that has properties comparable to those Yucca Mountain rock under a range of climatic change scenario conditions. Furthermore, no opportunity will exist to observe the dissolution of spent fuel under expected conditions, or to observe the migration of sorbing radionuclides under expected flux conditions over distances of more than a few meters. Yet, predictions of these processes need to be made. The role of natural analogues is to provide supporting information that allows a determination of the reasonableness of these predictions. Laboratory and field tests that are accelerated to allow meaningful observations in short times may or may not yield realistic results for predicting the progress of very long term processes in natural settings. It is likely that accelerated testing, since it purposely manipulates conditions to enhance rates, would lead to overpredictions of long term behavior under milder conditions. Natural analogues may provide a particularly suitable check on these types of predictions, although, as noted in Miller et al. (1994), it is also possible to misinterpret or overstate the results of natural analogue work.

Miller et al. (1994) discussed the status of international natural analogue efforts and natural analogue information in published performance assessments. They concluded that to date performance assessments have used natural analogue information very little. One reason for this limited use arises from the difficulty inherent in comparing model results with those from natural analogue studies. Miller et al. (1994) identified three areas wherein natural analogue information could be most useful in supporting performance assessment: (1) conceptual model construction (qualitative), (2) data acquisition as an adjunct to laboratory testing (quantitative), and (3) model testing (qualitative and quantitative). This last area potentially may carry the most significant benefit for the U. S. Program. It corresponds to the use of natural analogues explicitly mentioned in the applicable regulations (i.e. 10 CFR Part 60) in conjunction with providing technical support for performance models required in the Safety Analysis Report and with supporting a finding of reasonable assurance of meeting performance objectives.

5. Summary

The analyses of the Taupo Volcanic Zone, New Zealand, and Cigar Lake, Canada, natural analogue systems which are presented in this paper illustrate a method of evaluating the potential usefulness of specific natural analogue studies for assisting performance assessments. These two sites are active natural analogue sites for different reasons. As Tables 2 and 3 showed, the Taupo Volcanic zone promises to provide information on processes directly relatable to the expected Yucca Mountain near field environment. On the other hand, as indicated by Table 4, the Cigar Lake site is not geologically analogous to Yucca Mountain, but is still useful in terms of allowing prototype testing of characterization techniques and providing a rare opportunity to study natural Pu and Tc migration over long times.

The paper mentions the Peña Blanca, Mexico, natural analogue site and several uranium occurrences in volcanic rocks in Nevada and Oregon. These sites are being evaluated as potential analogues for processes that may be important to the performance of a potential Yucca Mountain repository. The Peña Blanca, Mexico, natural analogue site is currently being studied under sponsorship of the U.S. Nuclear Regulatory Commission. A more detailed site evaluation, based on existing literature and data, of the Nevada and Oregon uranium occurrences is being carried out by the Nevada Bureau of Mines and Geology under Department of Energy funding.

Many aspects of an individual analogue site may not supply required data, but other aspects at the same site may. Thus, a broad base of support for long-term performance assessments will require several different analogue sites, each emphasizing different processes for which an understanding of long-term behavior is needed. As noted above, each of the analogue sites discussed can potentially supply data for different and mutually exclusive parameters and processes. A suitable selection of sites should provide natural analogues for many processes important to performance assessment, and can thereby assist in building confidence in model applications over very long time periods.

Several long range planning efforts are now including limited natural analogue work that is to be carried out to support the License Application that allows repository construction, and more extensive natural analogue work that is to be carried out thereafter, to support the License Application amendment to receive and possess waste. The idea is that as risk goes up, so does confidence in the safety evaluations that support the License Application and its scheduled amendments. However, natural analogues are not a panacea for the uncertainty that will always exist in projections of system behavior into the far future. It seems unlikely that analogues can be found for all processes. For example, it seems unlikely that an analogue will be found for the degree of wetting of a waste package in an unsaturated zone environment.

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OVERVIEW OF THE SWISS NATURAL ANALOGUE PROGRAMME, 1994.

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Introduction

The aims of the Swiss natural analogue programme are currently dictated by the two "P"s, Performance Assessment (PA) and Public Relations (PR). In the PA field, it is the function of the natural analogue programme to:

- identify potential problem areas in the conceptual models of safety analysts
- investigate specific repository design problems identified by performance assessors
- test the various models (transport, geochemical, engineering, biological *etc.*) which are an integral part of any repository performance assessment.

In the PR arena, the analogue programme is expected to:

- provide clear, simple examples of repository related processes for general (and not just "specialist") consumption
- produce convincing arguments for repository safety based on clear observations from the natural environment. Note that `clear`may not necessarily be a quantitative example, rather illustrative.

The above aims are met through the involvement of Nagra in a suite of natural analogue projects, many of which are carried out in collaboration with other national radwaste organisations. Currently, Nagra is involved in:

- a study of a cementitious repository analogue at Maqarin, northern Jordan (along with SKB and UKNirex)
- a new joint study of radionuclide retardation in sediments with PNC as part of their Tono natural analogue project
- an examination of matrix diffusion in fractured sediments in Switzerland which have been identified as potential repository host formations
- analysis of elemental entrapment in the vicinity of redox fronts
- various projects of relevance to PR (detailed later)

Each project will now be discussed, with an explanation of the points of concern/interest to the two "P"s.

The Maqarin Project

The current design concepts for a low and intermediate level waste (L/ILW) repository in Switzerland envisage the use of several million tonnes of cement and concrete. The hyperalkaline conditions in the cementitious materials are believed to ensure low solubility of most radionuclides of interest plus the highly porous nature of the concrete will maximise sorption in the near-field. However, there is a paucity of data on the overall behaviour of cementitious systems, especially on the long-term evolution of the material, and so Nagra has been looking at natural analogues of the hyperalkaline cementitious near-field to supplement the data.

A first step was taken with the Nagra/UKNirex study of alkaline groundwaters in Oman (see Nagra,1987, for details) and the work has been carried on through the present Maqarin study. The Maqarin system is a particularly apt analogue of a cementitious system as the source of the hyperalkaline groundwaters (pH values of up to 12.9 have been recorded) are natural cement minerals, produced by the *in situ* combustion (*ie* thermal metamorphism) and subsequent rehydration of organic-rich clay biomicrites (see Nagra,1992, for details).

The project has now been running since 1989, first with Nagra, UKNirex and Ontario Hydro and latterly with SKB replacing the Canadians. Nagra's interests (the viewpoints of UKNirex and SKB are discussed elsewhere in these proceedings by Hooker et al. and Smellie, respectively) include:

-testing of a new Nagra PA thermodynamic database (TDB). The aim has been to produce one, quality assured, TDB to serve as a fixed reference point for Nagra's geochemical calculations. This is necessary because of the normal (inevitable?) habit which modellers have of "tweaking" their TDBs, thus ensuring that the PA calculations are fully traceable. This work has led to the scrapping of an earlier (tweaked!!) Nagra TDB (see Nagra,1992) and assisted in the development of the new TDB (partly through an intercomparison with other databases; see Nagra,1992). Here, the work indicated the use of inappropriate data for a couple of elements of interest to a L/ILW repository PA (especially Se) and has indicated weaknesses in the database for others, such as U (see Alexander et al.,1992; Khoury et al.,1992 and Nagra,1994a, for details). In addition, the work has provided excellent "hands-on" training for both PA modellers and the compilers of the new TDB (see Pate et al.,1994, for discussion).

-potential interaction of hyperalkaline cement leachates with the repository host formation. Obviously such leachates are not in equilibrium with the repository host rock and both modelling studies and short term laboratory studies suggest that the leachates may significantly alter those properties of the host formation for which it was originally chosen (such as high retardation capacity, low groundwater fluxes, matrix diffusion *etc.*). At the Maqarin site, such leachate/host rock interactions can be studied where the cement-buffered hyperalkaline groundwaters meet the non-metamorphosed host rock. Preliminary results (Milodowski et al.,1992; Nagra,1994a; Tweed and Milodowski,1994) indicate that the host rock does indeed undergo significant alteration, but the full implications to a repository PA are not yet clear as the rock also appears to have a large buffer capacity and the rock matrix remains accessible to trace elements in the groundwater. Further work is planned on this problem in 1994-1995.

-testing a new Nagra PA microbiology code (EMMA). The code has been produced with the intention providing upper estimates of microbiological populations in particular repository designs and assessing the likely impact of changes in the design to *in situ* microbial production (and all that implies to the repository PA; see McKinley and Hagenlocher,1994, for details). In this project, the code testing was carried out by first assessing the viability of bacteria under hyperalkaline conditions and then taking this work further to produce a detailed test case for EMMA and other such codes (see Coombs et al.,1994; West et al.,1994).

-defining the significance of colloidal material under hyperalkaline conditions. Colloid production at the cementitious near-field/far-field interface could have serious consequences for a repository PA, especially if the colloids, which are likely to be very stable under hyperalkaline conditions, were to take up radionuclides irreversibly. The Maqarin site offers an unique opportunity to study both the production of colloids at the near-field/far-field interface (*ie* the metamorphosed/unmetamorphosed rock boundary) and their subsequent behaviour as they move downstream into both the disturbed and undisturbed far-field (*ie* the unmetamorphosed host rock).

The two phases of work so far carried out at Maqarin have produced invaluable insights into a hyperalkaline environment and it is the intention to do more work in 1994-1995, in a third phase of study involving Nagra, UKNirex, SKB and UKHMIP. The results of this will be discussed at the 7th NAWG workshop!

The Tono Project

The Tono deposit is the largest sediment hosted U ore body in Japan and has been studied in detail by PNC for several years (see Seo and Yoshida,1994, for an overview). The Tono ore body is hosted by Tertiary fluvio-lacustrine and tuffaceous sediments unconformably overlying a Cretaceous granite. The U mineralisation is several hundred metres wide, two to three kilometres long and a few metres thick and contains at least one significant fracture zone. PNC have studied the Tono site for several years and, since July 1994, Nagra has been collaborating with PNC on several aspects of this natural analogue study and are addressing the following PA problems (as above, these represent Nagra`s viewpoint; PNC`s work is discussed by Yoshida et al., in these proceedings).

-solubility and speciation of trace metals in strongly reducing groundwaters. This work is complementary to that on-going in the Maqarin project on TDB testing and development, but with the emphasis on "undisturbed" far-field conditions. Preliminary data suggest that the Tono site is particularly apt for such studies as the groundwater fluxes in and around the ore body appear to be low, suggesting long residence time, hopefully leading to near equilibrium conditions in the groundwater system. As in the Maqarin project, a suite of safety relevant trace elements will be examined with a view to further test and improve the current Nagra PA TDB under relevant repository far-field conditions. A significant part of the study will be examining the redox buffer capacity of the groundwater/rock system and assessing the impact of the ore body on the overall groundwater redox state.

-radionuclide retardation in fractured sediments. The sediments hosting the Tono deposit show similarities to one of the formations identified as a potential repository host formation in Switzerland and, as such, offer an excellent analogue to retardation mechanisms in the repository far-field. It is hoped to build upon the extensive studies by PNC on radionuclide retention in the porous rock matrix at the Tono site (*eg* Yoshida,1994) and examine both localised retardation in specific flow structures along with regional retardation of U at the site.

-colloidal enhanced transport of radionuclides. CEA (France) and PNC are currently characterising colloidal populations in the Tono ore body and it is hoped that the work can be expanded to include Nagra in the future. Again, as in the Maqarin project, the aim is to produce a realistic test case for Nagra`s colloid transport code. In effect, the Tono site offers possibilities to study colloid related, far-field radionuclide transport not dissimilar to that of the Cigar Lake deposit (see the review of Cramer, these proceedings) with the advantage that the site is probably less disturbed than Cigar Lake.

It is hoped that the results of the above work also can be presented at the 7th NAWG workshop.

Matrix Diffusion In Fractured Sediments

Matrix diffusion is acknowledged to be an important redardation mechanism in the geosphere (see the review by Neretnieks, these proceedings) and the process has been extensively studied in crystalline rocks in general and in the potential crystalline host rock for a Swiss high-level waste (HLW) repository in particular (see Alexander,1993). However, little information exists in the literature on matrix diffusion in sediments and so, in addition to the planned work on the topic in the Tono project, Nagra is studying the mechanism in two potential sedimentary host rocks in Switzerland. The results to date indicate significant capacity for radionuclide retardation due to diffusion into/sorption within secondary porosity in both formations.

In the Opalinus Clay, a potential HLW repository host rock, the mechanism is clearly operating, at least at relatively shallow depths in the formation (Mazurek et al.,1994). In the Palfris Formation, Nagra`s preferred option for a L/ILW repository host rock, it is interesting to note that matrix diffusion is indicated even in those horizons where the water conducting fractures are coated by fracture minerals (mainly calcite). If this can be confirmed (the work is still on-going), it would represent a significant improvement in the predicted far-field radionuclide retention capability as, in the recent performance assessment for the site, pessimistic scenarios ignore retardation in the rock matrix due to presumed "sealing" of fracture surfaces.

Trace Element Entrapment At Redox Fronts

The current design for a HLW repository in Switzerland envisages the use of massive steel containers for the waste. A likely consequence of this concept is the formation of a redox front in the repository near-field, between the oxidised radionuclides leaching from the waste and the surrounding, reduced bentonite porewaters or host formation groundwaters (see the review of Hofmann, these proceedings, for further details). It has been noted that this redox front could act as an additional barrier to radionuclides released from the waste as redox fronts are known to present highly effective traps for certain trace elements, as can be clearly seen in uranium role front deposits, for example.

Regardless of the existence of many redox controlled ore deposits, there is actually a paucity of quantitative data on precisely which trace elements are normally retarded (by sorption, co-precipitation, redox control *etc*) in the vicinity of redox fronts and, of equal importance, the efficiency of the retardation process (see Hofmann,1994). Consequently, the two Swiss HLW performance assessments carried out to date (Nagra,1985,1994b) have chosen to omit redox front controlled retardation in the near-field, something which is arguably over-conservative and the question of including redox front retardation is now being reconsidered. The measured concentrations of a range of trace elements around the redox fronts at Pocos de Caldos was used to show that this effect could be potentially significant (Nagra,1993), but it appears that the analytical data used in this case are suspect (Hofmann, pers. comm.).

A review of available data on analogous trace element retardation in the vicinity of redox fronts is in preparation (Hofmann,1994) and the preliminary findings currently are being used to seek support for further, more detailed, examination of the process under repository analogous conditions.

Public Relations

Nagra were among the earliest proponents of the use of natural analogues for PR purposes, although recently it is probably SKB who have used the medium to the greatest effect. However, the present atmosphere of public distrust of nuclear power and radwaste disposal, coupled to Nagra`s plans to licence a L/ILW repository this century, have prompted Nagra to increase emphasis on the use of natural analogues in PR. As was stated in the introduction, the aim is to use clear examples from nature to explain, for example, complex repository design concepts.

More specifically, it is Nagra`s belief that reference to natural analogues can go a considerable way to indicate to non-specialists that the whole concept of safely disposing of waste for archaeological and geological time periods is not completely absurd. In this instance, it is possible that qualitative examples will carry more weight with the public (*eg* the simple fact that the Oklo reactors still exist after 2000 million years) than detailed reports on TDB development, for example. It is thus important to keep this in sight and not simply reject out of hand all qualitative natural analogue studies as useless.

Recently, Nagra has been active in the PR field via:

-the production of a special issue of the Nagra Bulletin (Informiert), a glossy periodical intended to keep the Swiss and interested international public informed on various Nagra projects, milestones *etc*, exclusively devoted to the Pocos de Caldos natural analogue project (Nagra,1993).

-initiating, managing and co-funding an internationally produced video on waste disposal and the role of natural analogues (Nagra,1994c; see also Lindqvist, these proceedings).

-the production of three books (Chapman and McKinley,1987; Chapman et al.,1993; Miller et al.,1994) and several newspaper and magazine articles (*eg* Chapman and McKinley,1990) intended to bring the use of natural analogues in waste disposal to a wider specialist audience.

It is felt that these projects have been successful enough to warrant further forays into the PR field and, in the first instance, it is hoped to produce a series of short videos (based on the internationally co-funded video mentioned above) for presentation specifically to Swiss audiences. Here, each video will be accompanied by a speaker who will discuss the topics covered with small groups in schools, social clubs *etc.* Where possible, a "PR factor" will be built into future natural analogue projects as a matter of routine.

Summary

This short overview has attempted to cover some of the PA and PR related questions currently vexing the Nagra natural analogue programme. In summary, the desired performance of a repository system will be displayed (to regulators and the public) by models which describe that system. It is Nagra`s view that it is only through the careful combination of evidence from both short-term, well constrained laboratory experiments and long-term, loosely constrained, but realistic, natural analogues can the models themselves be shown to be appropriate and their results demonstrated to be reasonable.

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NATURAL ANALOGUE STUDIES IN AUSTRALIA

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ABSTRACT

Early natural analogue work in Australia centred on the USNRC funded study *Radionuclide Migration around Uranium Ore Bodies - Analogue of Radioactive Waste Repositories*. This investigation preceded the NEA coordinated Alligator Rivers Analogue Project and a separate analogue study of the mechanism of far field radionuclide retardation by three Australian granites. ANSTO is currently participating in a systematic assessment of surface complexation models for the sorption of actinides on weathered schists in the vicinity of the Koongarra uranium deposit. Reference is also made to analogue studies designed to evaluate the impact of radiation damage on the mineral components of *synroc* and tailored ceramics. Finally comments are made on the technical and policy environment underlying ANSTO support for the proposed NEA/ASARR (Analogue Studies in the Alligator Rivers Region) Project.

Early analogue studies

Following the realisation that the Oklo deposit in Gabon was an excellent analogue of the very long term post closure behaviour of high level radioactive waste repositories (eg Curtis *et al* 1989), attention was turned to other uranium ore bodies. The USNRC funded study *Radionuclide Migration around Uranium Ore bodies - Analogue of Radioactive Waste Repositories* was directed towards identifying processes of potential significance over long time scales to a far-field behaviour of a high level waste repository (Airey *et al* 1986). Initially, the work encompassed the four major ore deposits in the Alligator Rivers Region of the Northern Territory; in the final stages of the project, all work was focussed on Koongarra (Figure 1). Four main themes were developed:

1) Stationary phase Particular emphasis was placed on the development of sequential extraction schemes for the study of the distribution of uranium series on identified mineral phases within the host rock;

2) Groundwater and colloids Previous groundwater investigations were extended to include D/H, ^{14}C, $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ as well as trace elements and tritium. Colloids were separated in this and in a separate UKDoE funded study (Ivanovich et al).

3) Fission products (I-129), transuranics (Pu-239) and Chlorine-36. Preliminary work was carried out to extend the analogue to fission products and transuranic elements. Groundwater samples were collected for ^{129}I, ^{36}Cl and ^{239}Pu and chemical procedures were developed to separate environmental levels of ^{36}Cl and ^{129}I from host rock. This aspect of the project was implemented by the University of Arizona (Tuscon) and the University of Rochester (NY).

4) Modelling An open system uranium model was developed to describe the gross features of the ore deposits. Initially it was used to model the rate of advance of the weathering front and then extended to the multiphase system defined on the basis of the sequential extraction measurements referred to above.

Alligator Rivers Analogue Project (ARAP)

Extension of the analogue work through the OECD Nuclear Energy Agency (NEA) was agreed in 1987 (Duerden, 1992). Funding was provided by the organisations listed in Table 1 to support an extensive research team. The overall aim of the study was:

> To contribute to the production of reliable and realistic models for radionuclide migration within geological environments relevant to the assessment of the safety of radioactive waste repositories, and
>
> To develop methods of validation of models using a combination of laboratory and field data associated with the Koongarra uranium deposit.

The study was directed towards understanding the evolution of the secondary uranium mineralisation and the distribution of radionuclides within the dispersion fan. The drillcore programs resulted in the development of substantial drillcore and groundwater databases for all distinctive geological units in the vicinity of Koongarra. It was therefore possible to test various aspects of radionuclide solubility/speciation calculations, of surface complexation models and of theoretical models for the formation of various zones of specific secondary uranium minerals.

Because of the large amount of systematic work undertaken at Koongarra, a holistic approach to the natural analogue was possible. A basis existed for outlining not only the interrelationships between the laboratory, field and natural analogue but also the adaption of natural analogue methodology to the assessment of proposed repository sites. In the following, processes are listed in a broadly decreasing time frame:

1) Evolution of the structural geology of the area and the deposition of the primary ore (1870 to 1600 My);

2) Development of the weathered profile following rapid erosion of the schist overlying the orebody during the Pleistocene (up to 2 My), leading to significant changes of uranium and thorium retardation factors;

3) Evolution of the dispersion fan (The results of transport modelling suggests 0.5 to 3 My with a median range 1 to 1.5 My.);

4) Formation and redistribution of the transuranic element ^{239}Pu, and the fission products ^{129}I and ^{99}Tc (The time scales (say 0.01 to 3My) represent those of the formation of the source uranium (refer 3 above), the hydrogeochemistry and the half life of the isotopes.);

5) Formation and distribution of the uranium series nuclides within the minerals of the weathered host rock - uranium (^{234}U/^{238}U, 0.05 to 1 My), thorium- 230 (0.01 to 0.3 My) and radium isotopes and daughters (days to thousands of years); and

6) Groundwater transport.

About 15 mathematical models were developed to describe the above processes. The modelling of the evolution of the secondary mineralisation (process 3) involved a level of complexity similar to modelling an overall repository system. An understanding of the scope and limitations of different concepts and models was obtained using a methodology similar to that in a joint SKI/SKB scenario development project.

Processes 1, 2 and 3 apply specifically to Koongarra, although insights obtained on the time dependent retardation processes are widely applicable, and the data bases obtained during the work can be applied generally to model testing. Process 4 is applicable to any analogue designed around a uranium deposit. Processes 5 and 6 can be studied in any setting and may be used to contribute to repository site evaluation.

Other far field analogue studies

A study of three granitic rocks as natural analogues of radionuclide retardation in the far field of a HLW repository was undertaken within the framework of a wider investigation of the interaction between *synroc*, water and granite during leaching under simulated repository conditions (Guthrie 1989, 1990). Drillcore samples to at least 1000m through three granitoids were investigated, namely, the Coles Bay Granite, Tasmania, the Kambalda Granodiorite, Western Australia, and the basement granite in the vicinity of the Olympic Dam copper and uranium mineralisation in South Australia.

Extensive fission track micromapping clearly indicated marked increases of uranium concentrations associated with alteration minerals, particularly iron and titanium oxides and hydroxides and clays. Samples of Coles Bay granite to depths of 963m were studied. With one exception, all samples showed $^{234}U/^{238}U$ secular equilibria. However the overwhelming majority of $^{230}Th/^{234}U$ ratios were in excess of 2, regardless of the mineralogy, the degree of alteration or the fracture density indicating clear evidence for the loss of uranium over the past 1M years.

The uranium series disequilibria within the Kambalda granodiorite indicated an overall gain in uranium over the past 1M years. The close association of the uranium with the secondary mineralisation suggested that the accumulation mechanism might involve either coprecipitation or sorption following secondary mineral precipitation. In the Roxby Downs samples, there is evidence for a complex series of mobilisation events. Near the top of the drillcore (450 to 550m) was evidence for accumulation of uranium from groundwater enriched in ^{234}U. At lower depths (to 800m) the systematic increase in $^{230}Th/^{234}U$ indicated a net leaching of uranium.

The precipitation of iron and titanium oxides and hydroxides in cracks and fissures contributes to the mechanism of radionuclide retardation. The study is a good example of the applicability of the natural analogue approach to the prediction of the potential migration pathways of radionuclides in the far field of a waste repository.

More generally the investigation confirmed that uranium series nuclides provide useful information on the long term migration of actinides and their geochemical analogues even in the absence of uranium anomalies (Airey and Ivanovich,1986). They are therefore potentially useful in the process of site selection and evaluation.

Current projects

Application of Surface Complexation Modelling to Natural Mineral Assemblages: Issues for Low Level nuclear Waste Disposal

A component of this USNRC funded project is being implemented through the USGS, the University of New South Wales and ANSTO. The aim of the investigation is to extend ARAP initiated surface complexation studies of U(VI) onto complex natural substrates. The initial stage involves extending the range of reference minerals and natural substrates considered in batch studies, including combinations of reference materials. To further elucidate the role of iron minerals in the natural environment, transformation (aging) experiments with synthetic ferrihydrite containing adsorbed natural uranium were undertaken (Payne *et al* 1994). The ferrihydrite was partially converted to crystalline forms such as hematite and goethite leading to a substantially reduced ability of the samples to adsorb ^{236}U from solution. Some of the adsorbed uranium was irreversibly incorporated into the mineral structure during the transformation process. Thus iron oxide transformations have a complex effect on uranium mobility. Whilst transformations provide a mechanism for immobilisation by incorporation into the solid, the transformed solid has less ability to sorb uranium directly from the solution.

The work will be extended to include the assessment of field partitioning information in the light of laboratory results and the implementation of column studies. Separate initiatives could involve a phenomenological approach (perhaps involving Neural Network Analysis, NNA) to predicting complex sorption behaviour on field samples on the basis of limited data.

Retention of Actinides in Natural Pyrochlores and Zirconolites

It was pointed out by Lumkin *et al* (1994) that natural analogue minerals provide a means of assessing the long term performance of actinide phases in high level nuclear waste forms including *synroc*and tailored ceramics. The authors illustrated the value of natural analogue approach to the near field in a study of the radiation damage and geochemical alteration effects in the minerals pyrochlore and zirconolite with particular reference to the behaviour of actinides and their daughter products. It was concluded that for periods of less than 10^8 years, the pyrochlore and zirconolites in nuclear waste ceramics will be rendered aperiodic at a decay dose of ~ 10^{16} α/mg at ambient temperatures. In *synroc,* the authors indicated that zirconolite would sustain this dose in 10^3-10^5 years depending primarily on he waste loading and the actinide element partitioning. They further pointed out that the principal effects of alpha decay damage are volume expansion and microfracturing providing potential pathways for fluids; however the extent to which microfracturing occurs is a function of grain size. Fine grained ($< 1\mu m$) nuclear waste ceramics are designed to accommodate volume expansion without significant expansion.

Future of natural analogue research

Moves towards a national radioactive waste repository

In 1992, the Australian Department of Primary Industry and Energy issued a Discussion Paper *A Radioactive Waste Repository for Australia: Methods for Choosing the Right Site* through the National Resource Information Centre. The report noted that total amount of radioactive waste was 3300 m^3 (including 1950 m^3 of contaminated soil) and was accumulating at the rate of 50 to 60 m^3 per year. Spent fuel from the HIFAR research reactor is not regarded as part of Australia's radioactive waste inventory, and the total does not include mining wastes which are normally disposed of at the mine site. The discussion paper emphasises that the development and management of a low level repository will be in accordance with the requirements of the National Health and Medical Research Council *Code of Practice for the Near Surface Disposal of Radioactive Waste in Australia* (1993).

The first phase of the study involved the development and use of an open and objective approach to site selection. A geographical information system was used to assemble continental-scale information which was classified according to suitability criteria and processed to show how suitable areas for locating a radioactive waste repository can be identified. A report was issued for public comment. In the second phase of the study, the selection method was once again applied to the identification of a number of suitable areas at the regional scale. Phase 3 will involve detailed field investigations to identify suitable sites. The natural analogue approach will very likely contribute to this phase. Western Australia has independently decided to dispose of its own low level waste at Mt Walton East near Kalgoorlie.

In 1993 a wide ranging Research Reactor Review was commissioned to assess whether Australia has a need for a new Research Reactor (1993). Issues associated with the future of spent fuel from HIFAR research reactor were canvassed. Australia also has a relatively small volume of intermediate level waste which will need to be disposed of in a geologic facility. Analogue studies may be directly applicable to site selection and performance assessment of such a facility.

Analogue Studies in the Alligator Rivers Region (ASARR)

Previous analogue studies in the in the Alligator Rivers Region have been part of the process of regulatory model validation. Validation is the process of reducing the uncertainty, increasing confidence and understanding, and ensuring that all relevant processes have been considered in a way that errs on the side of safety ie regulatory conservatism (P Duerden, private communication). Several complex phenomena and processes and several previously unrecognised phenomena were identified during the course of the ARAP investigations. The new project ASARR has been designed to continue the process of validation especially in areas such as fracture flow mechanics, field sorption processes and radionuclide retardation on natural substrates. These studies will provide a basis for distinguishing, from a regulatory perspective, what is conservative based upon knowledge of complex coupled natural system behaviour.

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Table 1. ARAP Agreement Funding Organisations

ARAP Agreement Signatories	
Participants	
Australian Nuclear Science and Technology Organisation	(ANSTO)
Japan Atomic Energy Research Institute	(JAERI)
Swedish Nuclear Power Inspectorate	(SKI)
UK Department of the Environment	(UKDoE)
US Nuclear Regulatory Commission	(USNRC)
ARAP Associate Participant	
Power Reactor and Nuclear Fuel Development Corporation of Japan	(PNC)
Additional Support	
US Department of Energy	(USDOE)
Central Research Institute for Electric Power Industry, Japan	(CRIEPI)

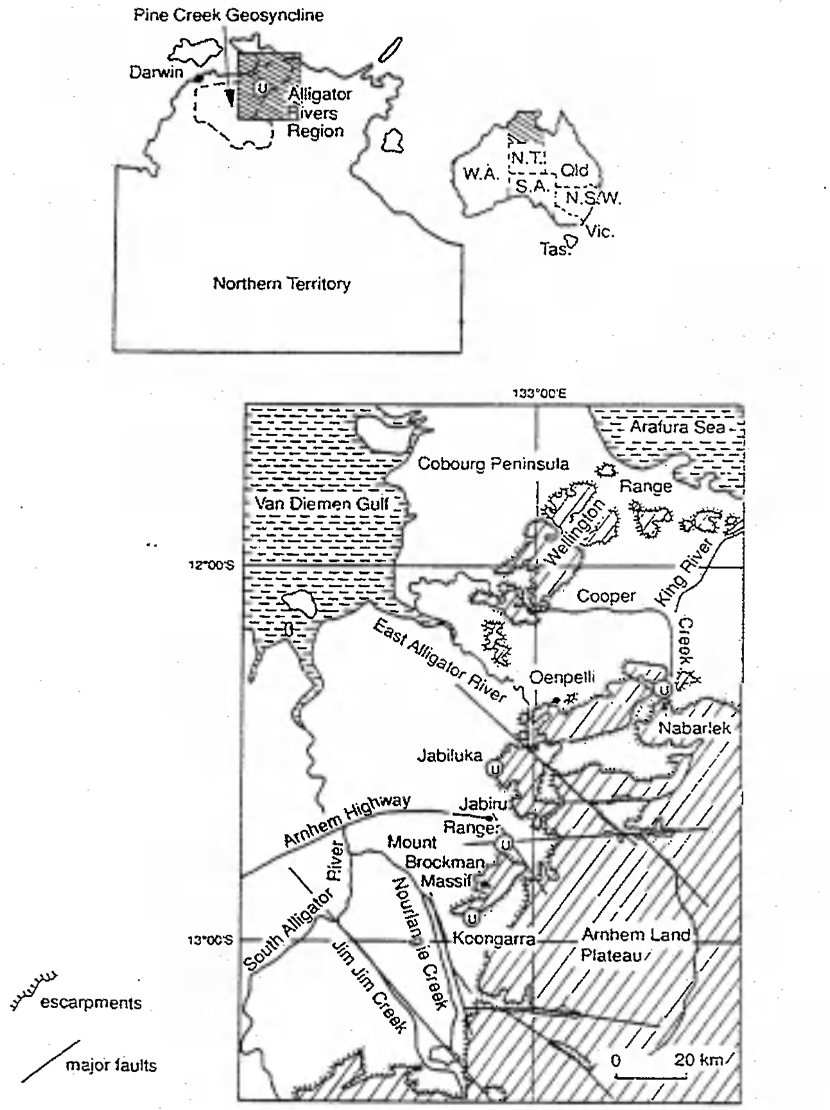

FIGURE 1 Location map showing the four uranium deposits in the Alligator Rivers Region, the sandstone escarpment and major faults (Snelling, ARAP Vol. 2, adapted from Needham and Stuart Smith, 1976).

6TH CEC NATURAL ANALOGUE WORKING GROUP MEETING

SWEDISH NATURAL ANALOGUE PROGRAMME

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Abstract

The present Swedish natural analogue programme falls into two main categories: a) participation in international large-scale analogue studies, and b) applying existing natural analogue data to repository performance assessments. The former includes the Oklo natural reactor in Gabon as an analogue to high-level spent fuel, and the Maqarin high alkaline groundwaters in Jordan as an analogue to a repository disposal facility for low- to intermediate-level waste. The Palmottu analogue study in Finland is also of interest because of the similarity of bedrock and climatic conditions, both past and present. Existing analogue data, which are presently being re-evaluated to further assess the long-term performance of a high-level waste repository, include the Cigar Lake study in Canada.

Swedish interests in the Oklo project are given, in particular the Bangombé near-surface reactor zone, and a brief account of the Maqarin study in Jordan is presented. In both cases emphasis are focussed on repository performance assessment issues of relevance to the Swedish disposal concepts. Analogue examples of direct and indirect use in performance assessment have been chosen from existing Cigar Lake analogue data; these are briefly described and their applicability to performance assessment underlined.

1. Introduction

The usefulness of natural analogue studies in the Swedish radioactive waste programme has long been recognised by the Swedish Nuclear Fuel and Waste Management Company (SKB). Initial interest in natural analogue studies began in the late 1970's, evolving from small-scale, strictly focussed process-oriented studies such as bentonite stability (Pusch, 1983), uraninite stability (Smellie and Rosholt, 1984), matrix diffusion (Smellie et al., 1986) and copper corrosion (Hallberg et al., 1988), to participation in major international analogue studies such as Poços de Caldas, Brazil (Chapman et al., 1992), Cigar Lake, Canada (Cramer and Smellie, 1994 a,b), and more recently at Maqarin, Jordan (Alexander et al., 1992) and Oklo, Gabon (Toulhoat et al., 1994).

For the earlier SKB performance assessments (KBS-1 on vitrified waste; KBS-2 and KBS-3 on spent fuel), the use of analogue data have been mostly concerned with the near-field environment, for example, the stability of the copper canister and the bentonite overpack. For the most recent SKB performance assessment, SKB-91, the analogue issues considered also included some far-field data (Karlsson et al., 1994). In general, however, the use of analogue data has been limited. This is partly due to the qualitative nature of the data produced and also to the reluctance of the performance assessors to recognise the complexity of the systems to be modelled.

These problems are presently being addressed; in collaboration with the Finnish Power Company (TVO) a first step was made to evaluate the importance of natural analogues and geological systems to repository performance assessment (Brandberg et al., 1993). This study attempted to judge the usefulness of the analogue data in performance assessment and to make recommendations that might improve both the focussing of future analogue/geological system studies and the appropriateness of present performance models. Work in progress includes a re-evaluation of some of the Cigar Lake analogue data in the light of Swedish performance assessment requirements.

In common with other national radioactive waste programmes, the one area of natural analogue studies were significant progress has been made is that of public awareness and understanding.

2. On-going International Analogue Studies

Active Swedish participation in large-scale analogue studies includes the Oklo natural reactor, Gabon, and the Maqarin high alkaline groundwaters, Jordan; in the Palmottu analogue study, Finland, SKB are present in an advisory/observer capacity.

2.1 Oklo Natural Reactor, Gabon

The Oklo Analogue Project is jointly funded by the Commission of the European Communities (CEC) and the Commissariat à l'Energie Atomique (CEA) and organised and co-ordinated by the CEA (IPSN). SKB's participation is through direct collaboration with the CEA.

Site Description

Details of the Oklo uranium deposits and associated reactor zones are given elsewhere in these proceedings (Louvat, 1994). In brief, uranium mineralisation resulted in early Proterozoic times from a partial mobilisation of uranium from uranium-bearing conglomeratic/sandstone placer deposits, initially derived from the erosion of the Challu massif of Archean age. These form the basal deposits of the Francevillian Sedimentary Series, contained within the Franceville Basin. The uranium became mainly concentrated in organic-rich pelites which form a distinct marker horizon between underlying sandstones and the overlying series of intercalated pelites and limestones. As a whole, the Francevillian sediments are well preserved, having undergone very little regional metamorphism during the last 2 Ga or so.

The reactor zones, which date to around 2 Ga, formed under fortuitous geochemical, isotopic and hydrogeological conditions such that nuclear criticality was achieved which lasted anything from 0.5 to 0.8 Ma at maximum temperatures of 450 °C. The reactions were terminated when the ^{235}U concentration and the amount of water were reduced as the porosity became progressively sealed through hydrothermally-induced argillisation of the surrounding sandstones. Today the reactor zones are well preserved and are characterised by high concentrations of uranium (20-60% U), mostly uraninite, closely related to ^{235}U depletion of up to 0.265% of the total U, and fission products whose end-member isotopic compositions are very different from those of the natural elements. The reactor zones are usually, but not always, surrounded by a clay halo (illite + Mg-Al chlorite adjacent to the core, becoming more Fe-rich towards the surrounding normal sediments); quartz is normally absent. Reactor zones are present at Oklo, Okelobondo and Bangombé, the two last-mentioned sites being located immediately SSW of Oklo and 30 km SSW of Oklo respectively, along the same strike and in association with the same pelitic marker horizon. Because of the relatively unperturbed nature of the Bangombé reactor environment, Swedish interests have been mainly focussed at this site.

The Bangombé uranium deposit and reactor zone are located near the surface (11-12 m depth) and within the saturated zone (groundwater levels are at a maximum of 4-6 m above the reactor) of a fairly well-defined run-off area on the Lekoni River. The reactor zone is located in a groundwater discharge area, the discharging waters originating from precipitation recharge on a major plateau to the south-west. A series of strategic boreholes have been drilled to intercept the groundwater flow path from recharge to discharge points through the reactor zone. Sections of the boreholes have been isolated with single or double inflated packer systems allowing hydraulic testing of the borehole sections and precise groundwater sampling immediately below, within and above the reactor zone. Details of the planning strategy, drilling, hydraulic testing and groundwater sampling of the boreholes are given in Smellie and Winberg (1992), Smellie et al. (1993), Blanc (Ed.) (1993) and Winberg and Smellie (1993). An overview of the Bangombé study, including initial results and discussion of the groundwater chemistry, is given by Toulhoat et al. (1994) and also in these proceedings (Louvat, 1994); preliminary details of the mineralogy, trace element geochemistry and isotope geochemistry of the reactor zone and host rock environment are summarised and edited by Gauthier-Lafaye (1994).

The Natural Analogue and Performance Assessment Implications

The Bangombé site offers the potential to study the interaction of ambient groundwaters with a fossil reactor zone located at the interface between oxidising and reducing groundwater conditions. This is closely analogous to the scenario of canister penetration in the presence of groundwater whereupon the spent fuel (reactor zone) is exposed to marginally oxidising redox conditions (radiolysis reactions) resulting in radionuclide mobilisation (fuel dissolution) and dispersion (near-field transport) into the surrounding sediments (far-field transport).

As the Bangombé study has not been completed, no attempt has yet been made to evaluate available data in the light of repository performance assessment. However, the programme of study has been closely planned with performance assessment implications in mind. As listed by Smellie et al. (1993), the advantages of the Bangombé site over the other Oklo/Okelobondo sites include:

* the mineralisation/reactor zone is located in the saturated zone near the surface

* groundwater flow patterns within and around the reactor zone should be relatively easily modelled and quantified by drilling and testing a series of short boreholes terminating above, within and below the reactor zone

* groundwaters (and colloids, organics and microbes) can be collected from isolated borehole sections below, within and above the reactor zone

* the groundwaters can be directly related to the bedrock core mineralogy and geochemistry at the sampling points

The close integration of groundwater and bedrock sampling to a well characterised hydrogeological environment provides the opportunity of satisfying some of the performance assessment (PA) criteria of interest to SKB. For example (Smellie et al., 1993; Karlsson, 1994):

1) To study the extent, if any, of uranium ore dissolution in a near-surface discharging, probably marginally oxidising groundwater environment
(*Status: partly completed*)

PA: spent fuel stability (redox; leaching; matrix release)

2) To study the influence of a downward penetrating weathering redox front in the near-vicinity of the reactor zone
(*Status: planned*)

PA: modelling near-field radiolysis/redox front propagation

3) To study the extent, if any, of secondary radionuclide/actinide dispersions either above or below the reactor zone
(*Status: partly completed*)

PA: modelling the near- to far-field radionuclide mobilisation/retardation; influence of the clay layer in shielding the reactor zone; co-precipitation

4) To provide a detailed mineralogical and groundwater geochemical database to evaluate water/rock interactions
(*Status: almost complete*)

PA: radionuclide solubility and speciation; testing of geochemical codes and thermodynamic databases

5) To provide well-constrained chemical and hydrogeological boundary parameters
(*Status: almost complete*)

PA: far-field coupled chemical mass transport modelling of radionuclides

6) Characterise the nature of colloids, organics and microbes in groundwaters within and around the reactor zone area
(*Status: partly completed*)

PA: potential role of colloids, organics and microbes in near- to far-field radionuclide dispersion

7) The nature of kerogen in the reactor zone under recent or near-surface groundwater conditions
(*Status: planned*)

PA: stability of kerogen; some similarity with bitumen (oxidation; leaching; microbial effects)

A thorough appraisal of all analytical data and their application to performance assessment issues is expected to be completed during 1995.

2.2 Maqarin, Jordan

The highly alkaline springs of the Maqarin area of NW Jordan are currently being investigated as part of an international project testing models used in repository performance assessment of low- to intermediate-level radioactive waste repositories. The Maqarin area provides a rock-groundwater system which is an ideal natural analogue of a cemetitious repository in a sedimentary host rock (Khoury et al., 1992; Alexander et al., 1992). Phase I of the project (1989-1991) was jointly funded by the Swiss National Cooperative for Radioactive Waste Management (Nagra), Ontario

Hydro and UK Nirex Ltd.; Phase II (1991-1993) was funded by Nagra, UK Nirex and SKB, and Phase III, scheduled for 1993-1995, will be funded by Nagra, UK Nirex, SKB and Her Majesty's Inspectorate of Pollution (UK HMIP).

Site Description

Geologically, the site area comprises late Cretaceous marls and bituminous limestones (i.e. Bituminous Marl Formation) overlain by Tertiary chalks and limestones followed by Pleistocene alkali basalts (no longer present at Maqarin) and Recent sediments forming poorly sorted slope wash and wadi fill materials and residual soil. Travertines, stalactites and stalagmites are common around springs and seepages (Khoury et al., 1992). The bituminous rocks are biomicrites (calcite + quartz, dolomite, apatite, pyrite and clays such as illite, kaolinite and illite/smectite mixed layers) with organic contents between 15-20% TOC and sulphate up to 12% SO_3; trace elements (including U) are mostly adsorbed by the organic material. The organic material is not bitumen, but probably more akin to kerogene.

The Bituminous Marls have commonly undergone spontaneous conbustion (>1000°C) resulting in widespread thermal metamorphic reactions. The chemistry of the hyperalkaline groundwaters (up to pH 12.5) results from the interaction of normal aquifer waters (pH 7-8) with these thermally metamorphosed marls. Subsequent hydration of this high temperature mineral assemblage formed portlandite, ettringite, thaumasite and numerous other cement minerals.

During Phases I and II of the project groundwater and rock samples were collected from an exploration adit and from various seepage localities. Natural springs in the near-vicinity of the Maqarin area were also sampled to establish the input source groundwater term. In situ measurements of pH, Eh and temperature were made and subsequent analysis of major and trace element ions and environmental isotopes. Regarding trace element studies, the main focus has been on U, Th, Ra, Se, Pb, Ni, Se and Sn, i.e. those elements considered important for performance assessments. Samples for microbial and organic material studies were also taken.

An important outcome of the Phase I and II studies was the definition of two geochemically distinct discharge zones (Eastern Spring and Western Spring areas), which may be analogous to early and later stage evolution of cement pore waters. Alternatively, some mixing of Eastern Spring-type groundwaters with deeper groundwaters from the Amman Formation within the reaction zones may also be presently contributing to the observed hydrochemistry of the Western Springs. A conceptual model of groundwater flow in the Maqarin area, based on published data, resulted from the Phase II programme. However, further investigation is necessary to define the local flow-paths specific to these discharge zones. Geochemical characterization of the recharge to these two systems is important in order to model the evolution of groundwater chemistry up-gradient, within and down-gradient of a repository. Further, an assessment of the age relationships between these two systems will be important.

In order to achieve these goals, three new boreholes have been drilled as part of the Phase III field activities; two of these have been completed using single inflatable packer systems (Western Springs and Railway Cutting sites). The third hole at Wadi Sidjin is restricted to a PVC stand-pipe as only the bottom metre of the borehole is conducting. Groundwater compositions from the new boreholes, including trace element compositions and isotopic data, will be required, to refine the detection of a variety of trace species and safety relevant trace elements from the western spring localities (to compare with the eastern springs), including Al, Si, Fe, Pd, Sr, Ba, Ra, U, Th and Co. Enhanced definition of the aqueous geochemistry should further improve the validation of speciation codes.

The Natural Analogue and Performance Assessment Implications

Available data (Khoury et al., 1992; Alexander et al., 1992; Tweed and Milodowski, 1994) have shown the Maqarin site to be a most interesting and relevant analogue for early and later stage leachate discharge from the near-field environment of a low- to intermediate-level cementitious repository for radioactive waste. Maqarin is unique in that it consists of high pH groundwaters in near equilibrium with naturally occurring cement minerals.

One of the major objectives of the study has been to make blind calculations of trace element solubilities (i.e. by calculating saturation indices at an assumed solute concentration of $1 \cdot 10^{-6}$ g/l) and speciation in the alkaline waters, and subsequently to compare the results of the various modelling teams by employing different models and thermodynamical data bases normally used in performance assessment (Alexander et al., 1992). Modelling was also extended to test coupled flow-transport codes in the hyperalkaline environment and to test a microbiological code developed to predict the influence of microbiological activity in a repository near-field.

The main performance assessment interests of the Swedish programme in the Maqarin analogue study (Phase III) are:

* Establishing the origin, chemistry and flow paths of the Western Spring waters using hydrogeological, hydrogeochemical and isotopic data (*Status: partly completed*)

PA: Testing coupled flow/transport codes employed in assessing the long-term evolution of a repository (near- to far-field dispersion of high pH plume with associated radionuclides and other trace elements)

- * Petrographical and mineral chemical studies of textures and mineral phases resulting from hyperalkaline (pH 13.5) water/rock interactions
  (*Status: mostly completed*)

  PA: Testing solid phase models to examine radionuclide solubilities with respect to mineral solid solutions (near-field dissolution and migration/retardation of radionuclides and other trace elements)

- * Petrographical and mineral chemical studies of clay phases in the presence of hyperaklaline fluids
  (*Status: partly completed*)

  PA: Establish geochemical controls on clay stability (analogue to bentonite stability in a high pH environment; near-field)

- * Petrographical and mineral chemical studies of kerogen phases in the presence of hyperalkaline fluids
  (*Status: planned*)

  PA: Establish geochemical stability of kerogen compounds (analogous to hydrocarbon compounds in a high pH environment; near-field)

- * Characterise the types of colloids, microbes and organics present in hyperalkaline groundwaters
  (*Status: planned*)

  PA: The role of colloids, microbes and organics in radionuclide (and other trace element) transport under high pH conditions (far-field dispersion)

Samples for the clay and kerogen stability studies are being studied from present-day water/rock interaction zones at Maqarin (young end-member stage) and compared with samples from similar geological strata in Central Jordan where fossil reactions (final end-member stage) have been preserved. This provides a suitable time-scale in which to set such reactions in the perspective of repository evolution.

A thorough appraisal of all analytical data and their application to performance assessment is expected to be completed during 1995.

2. 3 Palmottu, Finland

SKB have interest in the Palmottu Analogue Project, Finland, summarised by Blomqvist (1994; these proceedings), because of the similarity in climatic, hydrogeological, hydrogeochemical and bedrock conditions. Swedish participation is mostly limited to an advisory and observer status, although specific areas of the programme have been directly supported economically. These include downhole radar, downhole flow meter measurements and hydrogeological interpretation to help derive the 3D geometry of the bedrock fracture system conducting groundwaters (Carlsten, S., 1993; Andersson, 1994)

In terms of potential application to Swedish repository performance assessments, the following two major areas have been considered (Smellie, 1991; Brandberg et al., 1993):

* *Near-field Spent Fuel Solubility/Dissolution*

- geochemical modelling of ore dissolution (uranium solubility/speciation).
- geochemical modelling of additional trace elements present in solution considered important in safety disposal (e.g. Th, Tc, Pu, Cu, Mo, As, Cs, Sr etc.)

* *Far-field Radionuclide Mobilisation/Transportation.*

- the effects of groundwater redox chemistry on the dissolution and transportation of radionuclides (and other trace elements)
- the role of colloid/organic material on the uptake and transportation of radionuclides
- the role of microbes on the groundwater redox chemistry
- the role of fracture mineralogy (e.g. $Fe_{(III)}$-bearing phases) on the groundwater redox chemistry
- the role of fracture mineralogy on radionuclide mobility (e.g. sorption processes)
- the role of matrix diffusion in the uptake of radionuclides

3. Re-appraisal and Application of Existing Analogue Data from Cigar Lake

Large-scale analogue studies normally generate large volumes of analytical data and substantial time and effort is normally spent in the compilation, evaluation and modelling of these data to understand the nature and geochemical evolution of the sites under investigation. This is, of-course, quite essential, but unfortunately a full appraisal of these data with respect to repository performance assessment generally tends to be frustratingly inadequate. Of many possible reasons, a lack of time due to meeting reporting deadlines ranks high in the list. In order to address this situation, the Swedish programme is allocating time and resources to re-evaluate some of the existing analogue data in an attempt to derive full benefit for their performance assessments. The area in question is Cigar Lake, Canada, summarised and described by Cramer and Smellie (1994 a,b) and Cramer (1994; these proceedings). The SKB re-appraisal focusses on three main areas: a) origin of the uranium ore deposit, b) near-field related issues, and c) far-field related issues. Re-appraisal has been structured to allow direct comparison and integration of each study area (where possible) with relevant components of a Swedish repository system.

3.1 Site Description

The Cigar Lake uranium deposit is mostly comprised of uraninite and pitchblende with subordinate coffinite and has been dated to 1.3 Ga (Cumming and Krstic, 1992). The deposit is characterised by a series of hydrothermal alteration haloes geometrically arranged around the orebody, decreasing in intensity with increasing distance from the ore surface. These haloes comprise a clay-rich zone (mainly illite) of varying thickness (up to 12 m) immediately surrounding the orebody and mostly derived from the hydrothermal alteration of the host sandstones. The clay grades outwards into altered, friable sandstones and finally to the main Lower Sandstone unit; a highly silaceous horizon (quartz cap) occurs at the interface between the altered sandstone and the competent host sandstones. In addition to these major lithological differences, hydrothermal mineralogical alteration (e.g. illitisation) extends to the bedrock surface. Furthermore, geochemical haloes of some trace element concentrations (e.g. U, Cu, Ni, Mo etc.) have also been superimposed on the host sandstones (Bruneton, 1987).

The primary uranium minerals, uraninite (UO_2) and coffinite ($USiO_4$), precipitated coeval with the hydrothermal dissolution of quartz and alteration of the host rocks, both in the overlying sandstone and the pelitic basement.

3.2 Origin of the Uranium Deposit

Work has been in progress for some time to model: 1) interaction of basement hydrothermal fluids with the basement rock formations (e.g. Shi et al., 1993), and 2) interaction of these fluids with the overlying sandstone formations characterised by a uranium-rich aqueous phase (e.g. Shi et al., 1994). If the correct boundary conditions are chosen, it should be possible to predict the hydrothermal alteration mineralogy in the basement rocks underlying the uranium deposit, and in the overlying sandstones. It should then be possible to compare with the present-day mineralogy/geochemistry, thus determining any large-scale changes (i.e. mineralogical; chemical mass balance) that may have occurred since uranium emplacement, and that may even be occurring to-day under ambient groundwater conditions. This information has direct performance assessment relevance when:

- modelling the potential mass transport of radionuclides from the uranium deposit (near-field) to the sandstone host rock (far-field)
- modelling the significance of the redox zone (haematite concentrations) characteristically located at or near the massive ore/clay boundary (i.e.

radiolysis vs. hydrothermal origin of the oxidants)

* explaining the relative absence of massive uranium concentrations at the Close Lake deposit, which is located close to, and shares a similar geometry and hydrogeological environment to that of Cigar Lake. Does this mean that different basement geochemical conditions have precluded the initial deposition of large amounts of uranium, or, has the uranium been present and then subsequently removed?

3.3 Near-field Issues

Five performance issues have been identified directly related to the near-field: canister stability, radiolysis, stability of UO_2, redox front and clay stability.

Canister Stability

Mineralogical studies of the massive uranium ore body have occasionally revealed small amounts of native copper. Some additional work is being conducted to further characterise these occurrences and their relationship with the UO_2; this may provide some additional information on the potential stability of a copper canister in a repository situation.

Radiolysis

Taken collectively, results from Cigar Lake support the fact that radiolytic oxidation in the near-field of exposed nuclear fuel, within the concept of an underground repository, cannot be ruled out. However, the net changes are considerably overestimated by models currently used for performance assessment. The presence of some oxidation of uranium in the ore body indicates that the UO_2 in spent fuel may not necessarily consume all the oxidants generated (Karlsson et al., 1994).

In order to further test the robustness of the PA models, a collective effort is being made to re-interpret the significance of radiolysis in Cigar Lake and derive additional data for this purpose. This approach focusses on achieving a balance between a re-appraisal of existing data, new theoretical calculations (e.g. Jansson et al., 1994) and actual observations from the uranium deposit. The various components are as follows:

1) Re-appraisal of existing radiolysis product calculations

2) Calculation of the geometrical dose distribution (α,β,γ) from UO_2 particles to the groundwater phase

3) Calculation of radiolysis reactions in the solid UO_2 phases comprising the uranium ore body

4) Direct observational evidence of radiolysis in the ore body; quantification and interpretation (e.g. what evidence is there of radiolysis breakdown products such as H_2, O_2 etc. which may be contributing to the presence of Fe-oxyhydroxides, SO_4 etc?)

Stability of UO_2 (spent fuel dissolution)

Continuation of modelling geochemical conditions at the Cigar Lake site and comparing with dissolution models - mainly matrix stability of UO_2. In further collaboration with AECL, the current Electrochemical Model for Radiolytic Oxidation of Spent Fuel will be quantitatively tested against observations from the Cigar Lake uraniium deposit.

Redox Front

The presence of the so-called "redox front" at the massive ore/clay interface still remains an enigma; is it the result of radiolysis (past and/or present) or an artefact of some hydrothermal phase in the geological past? To test the latter theory, the geochemistry across the ore/clay interface at Cigar Lake will be compared to "similar" redox occurrences in other mineralisations of the Athabasca Basin. Is it possible to thermodynamically model the "redox front"?

Clay Stability

One important conclusion from the Cigar Lake study was that mass transport of radionuclides from the uranium deposit is not occurring on a major scale, and the primary reason for this is the existence of the clay halo which, even though comprised of illite, has effectively shielded the ore body hydrologically, in addition to acting as an efficient buffer to geochemical reactions and release processes. Consequently, these modelling predictions supported the integrity of the bentonite overpack under reducing groundwater repository conditions.

To further test the "shielding" capacity of the massive clay surrounding the ore body, several questions have been posed and are in the process of being answered. These include:

- has illite formation been the primary reaction at Cigar Lake?; need we have a smectite to illite transformation at Cigar Lake?
- is it possible that in all practicality illite has been a successful buffer since ore emplacement?
- has the shielding/buffering effect of the massive clay been more a function of thickness (up to 30 m in places) rather than due solely to the physical properties of illite?

3.4 Far-field Issues

Far-field processes constituted a major part of the Cigar Lake study, and each area of investigation is being considered by the present re-appraisal.

Hydrogeology

Re-appraisal of the hydrogeological understanding of the Cigar Lake system; usefulness of the 2D and 3D models employed?; has the heterogeneity of the system been adequately addressed?

Coupled Hydrogeology/hydrogeochemistry

Has this been adequately addressed?; is there room for improvement?

Palaeohydrogeology

Address those boundary parameters (e.g. porosity) useful in interpretating the origin and evolution of the ore body.

Mass Transport Modelling

Refinement of existing models in the light of improved understanding of key processes (e.g. the importance of radiolysis) and better defined mineralogy and geochemistry of the uranium deposit.

Colloids, Organics and Microbes

Role played by these species in radionuclide transport; comparison with other characterised areas of differing hydrogeology and hydrogeochemistry.

4. Natural Analogues and Public Awareness

SKB recognises the importance of public acceptance of their disposal concepts, and this acceptance has been greatly facilitated by using natural analogue studies. Consequently, considerable effort has been channelled into presenting natural analogues to the public, internationally through collaboration with other organisations (e.g. the natural analogue video: "Traces of the Future" managed by Nagra), and domestically, for example, through SKB's travelling floating exhibition housed on the M/S Sigyn.

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NATURAL ANALOGUE STUDIES IN FINLAND

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1. Introduction

Recent activity within the Finnish publicly financed natural analogue programme has focused on three major targets:

(1) Migration of uranium in crystalline bedrock, based on data from the uranium deposit at Palmottu, SW Finland: The Palmottu Natural Analogue Project.

(2) Palaeohydrogeology of glaciated areas based on geochemistry of groundwaters and fracture infilling. The target is to try to establish the degree of change of hydrogeological regimes during a glacial cycle.

(3) Studies related to stability of native iron and copper as analogues to radioactive wastes' canister materials.

As the third topic will be covered by another report, this report will only discuss the two first topics.

2. The Palmottu Natural Analogue Project

Palmottu is one of the study sites where a natural uranium deposit and its surroundings are studied in order to improve the scientific basis for assessing the long-term performance of nuclear waste isolation. The Palmottu U-Th deposit is hosted by Precambrian crystalline bedrock, mainly migmatitic mica gneiss, granite and pegmatite. Part of the granitic and pegmatitic veins act as the host for the primary uranium-bearing mineral uraninite (UO_{2+x}), frequently surrounded by a later rim of coffinite and other uranium silicates. The mineralized ore zones extend from close-to-surface oxidative conditions to low-Eh conditions at depths exceeding 300 m.

The Palmottu Analogue Project was launched as a national analogue project in 1988. The first phase consisted mainly of background data compilation and the development of research methodology, and was completed at the end of 1991. The present publicly financed 3-year phase of the study commenced in 1992 and is scheduled for completion in late 1994 (Blomqvist *et al.*, 1994a).

The general target of the second study phase is to obtain a sound knowledge of the factors affecting mobilization and retardation of U in crystalline bedrock (Fig. 1). Fundamental tasks include studies on uranium minerals (Ruskeeniemi *et al.*, 1994), fracture infilling and fissure characterization (Ruskeeniemi and Vesterinen, 1991, Lindberg, 1994), hydrogeochemistry (Blomqvist *et al.*, 1994b) and geochemistry of dissolved uranium (Suutarinen *et al.*, 1991). Major emphasis has been placed on studying retardation behaviour of uranium in water-conducting fractures (Suksi *et al.*, 1992, 1994; Rasilainen and Suksi, 1993, 1994). The role of uranium in buffering the redox conditions of groundwater, even though still controversial, is of great potential importance for radionuclide mobility around a repository (Ahonen *et al.*, 1993, 1994). The study to characterize the role of colloidal material on the up-take and transportation of radionuclides is proceeding (Vuorinen and Kumpulainen, 1993).

As groundwater flow is one of the principal factors affecting migration of radionuclides, considerable efforts have been focused on the location and characterization of modern flow routes at Palmottu (Kuivamäki *et al.*, 1991; Niini *et al.*, 1993; Paananen *et al.*, 1994). The target is to establish a robust model of the present hydrogeological pattern around the uranium deposit. This model could serve as basis for a future coupled transport analogue study. The present state of art is summarized in the report of the preliminary hydrogeological model of Palmottu (Paananen and Blomqvist, 1994). The hydrogeochemistry of the site that is based on the information of some 30 boreholes, and has proved to be a useful tool in predicting the present flow pattern (Blomqvist *et al.*, 1994b).

It is anticipated that the ongoing studies will lead to improved research methods applicable to nuclear waste disposal in crystalline bedrock. Due to the extensive number of drill holes available, the analogue study may also serve as a versatile reference area for authorities in their evaluation work of the actual disposal site studies (*e.g.* in fracture zone characterization, groundwater flow modelling, geometrical location of the various hydrogeochemical units etc.). Also, the results could be used to provide a reliable illustration for the general public of nuclear waste disposal and its consequences in bedrock. As a first step in this direction, a summary of the Palmottu studies was presented in a widely distributed brochure compiled by the Ministry of Trade and Industry in Finland (1992).

The planning of the next phase of the Palmottu Natural Analogue Project, scheduled to begin in 1996, is proceeding. As it is evident that the utilization of present results will benefit from a more extensive and versatile study approach, we in Finland are looking forward to starting an International Palmottu Analogue Project with several subtopics. The following topics are considered highly relevant:

- redox chemistry of uranium-rich groundwaters, including the role of uranium minerals and fracture mineralogy on solution Eh
- processes and mechanisms affecting groundwater evolution at Palmottu; approaches based on stable isotope studies and geochemical modelling
- the role of the various retardation processes (sorption, matrix diffusion, coprecipitation) in different hydrogeochemical regimes at Palmottu
- palaeohydrogeology: the role of glacial events on natural hydrogeological systems based on isotope studies of fluids and solids and U/Th dating

As it is evident that a satisfactory solution for the groundwater flow pattern can be achieved, various modelling approaches integrating groundwater flow with geochemistry and radionuclide retarding processes could prove a useful exercise to be performed by several different teams.

3. Palaeohydrogeological studies

Regional hydrogeological studies conducted in many study sites within the Central Baltic Shield show some groundwater bodies, based on $\delta^{18}O$ results, that have recharged at distinctly colder mean temperatures compared to the present day. Studies on the evolution of these groundwater bodies are still proceeding. Preliminary results point to recharge of glacial meltwater and subsequent mixing with other groundwater bodies (Blomqvist *et al.*, 1989; Ivanovich *et al.*, 1991; Blomqvist *et al.*, 1993).

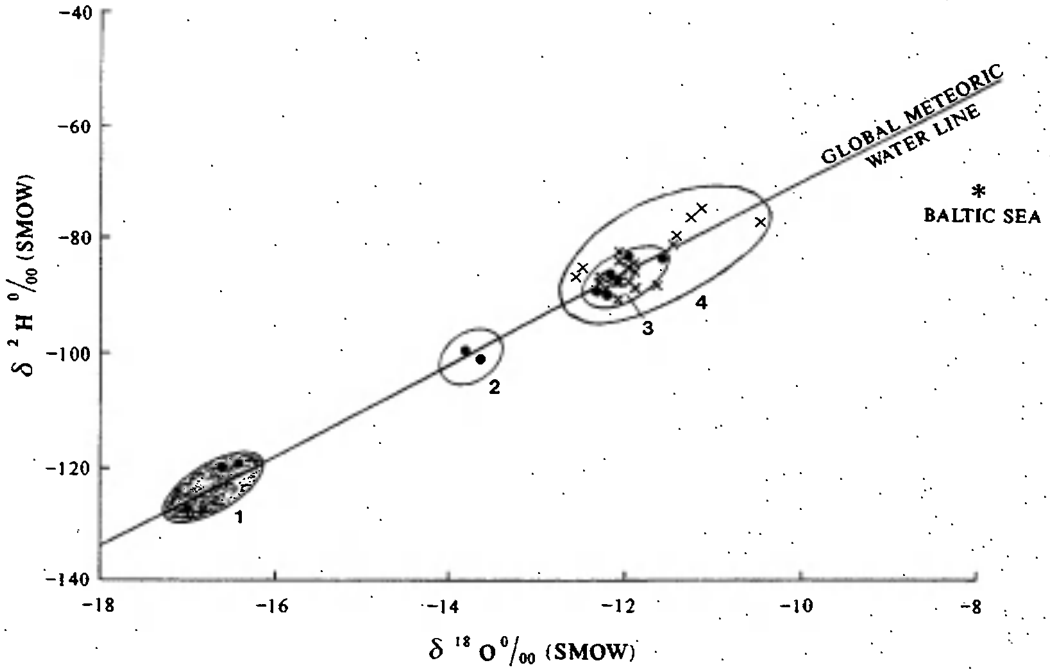

Fig. 1. ^2H vs. ^{18}O of various groundwater types at Palmottu. **1.** $Na\text{-}SO_4$, **2.** Na-Cl, **3.** $Ca\text{-}HCO_3$ — $Na\text{-}HCO_3$, **4.** Other sites in SW Finland (crosses).

At Palmottu preliminary $\delta^{18}O$ results of the different groundwater types indicate different recharge conditions for the various groundwaters (Fig. 1). The fresh bicarbonate waters have a $\delta^{18}O$ signature (-12 ‰) typical for present precipitation in Southern Finland. Compared to the bicarbonate groundwaters the sulphate waters possess a much lighter $\delta^{18}O$ signature (-17 ‰) indicative of a distinctly colder climatic conditions compared to the present day. In the event that this sulphate groundwater body proves to be a glacial meltwater or a mixture with a glacial meltwater, several interesting topics arise for further consideration: (1) the intrusion mechanism of this water to a depth of 120 — 200 m; (2) the geochemical evolution of the groundwater, especially the consumption of the oxygen of the meltwater, and (3) the potential for using this temporarily well-defined groundwater type in evaluating radionuclide migration results.

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THE EL BERROCAL PROJECT: AN EXAMPLE OF A NATURAL SYSTEM CHARACTERISATION EXERCISE

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ABSTRACT

After a brief discussion, regarding Natural Systems and Natural Analogues The El Berrocal Project is introduced as an example of a Natural System characterisation study which incorporates the concept of natural analogues. The Project is intended both to help to develop site characterisation methodologies and to provide actual data for models which will be used in future Performance Assessment of the Geosphere. El Berrocal lies in a granitic environment containing a hydrothermal uranium mineralization associated with a quartz vein, mined in the sixties, and lately restored for undertaking the current Project. The work began in 1987 and will continue to March 1995. The Project comprises a wide variety of characterisation techniques of mainly structural, geochemical and hydrogeological nature. Close to the end, The El Berrocal Project is about to provide valuable information concerning practical aspects of site characterisation in granitic rocks, having also served to create teams and to develop equipment within the site characterisation context. As regards information addressed to performance assessment the Project is creating a database that will provide information concerning far field processes; transport in solution, colloid transport, redox condition variability and their consequences in migration processes, microbiological effects in hydrochemical reactions, testing of thermodynamic databases and concerning retardation mechanisms, data on matrix diffusion and adsorption/precipitation.

1. Introduction

One of the main reasons for using Natural Systems as an aid to our understanding of the processes that may occur in a repository environment is the time dimension which they can provide. The expected long lifetimes of a repository are not reproducible under laboratory conditions but are, obviously, a component of natural systems. For a natural system to be considered a ´natural analogue´ it has to incorporate, in one way or another, either processes or materials, that will occur in the repository environment.

Natural analogues reproducing the totality of processes expected to occur in a repository do not exist. Therefore natural analogue examples are sought where one or more of those processes are likely to occur, in either the near or far fields. Accordingly a natural system such as El Berrocal enriched in, naturally occurring radionuclides has, in principle, the potential for being considered a natural analogue.

Natural analogues were originally used mainly for their illustrative role in providing understanding and qualitative conceptualization of natural system behaviour. However, they are being used and demanded increasingly as a source of quantitative data for input to Performance Assessment exercises

In general terms, studies performed on natural systems and,or, natural analogues are aimed at gaining information, either for developing techniques to be used in a site characterisation program or as a tool for developing model concepts and obtaining data that may eventually be integrated in a repository performance assessment. These two options are both discussed in this paper to show that far from being contradictory, these two aspects can not only be compatible, but even complementary.

2. Spanish National Program in Natural Analogues.

The following is a brief history of the use and integration of natural analogues within ENRESA´s disposal programme. ENRESA has an undertaking to characterise natural sites in order to locate suitable repository environments. Given the inherent problems in characterising fractured rocks, it was decided to seek an experimental station as a basis for a project to develop site characterisation methodologies. With the aim of optimizing the research potential of the site, it was also intended to chose a location where natural analogue studies may also be performed. Currently the project is at a mature stage, foreseen to be finished early next year, and other investigations at new localities are being planned which have the aim of continuing the building up a database that may be used in future Spanish performance assessment exercises.

The primary objectives of these investigations are mainly to create the foundations for the provision of data applicable to performance assessment and to provide information that can be used for illustrating to different audiences the feasibility and safety of radioactive waste management methods. A subsidiary objective is the continued development of teams, equipment and methodologies for site characterisation.

To fulfil each of these objectives entirely, several projects with different scales and scope are at the planning stage. On the one hand, small scale investigations are being designed to provide answers to specific questions concerning both near and far field processes in a clay environment using a series of small well-studied sedimentary uranium orebodies. As regards granitic environments further studies on the El Berrocal samples are envisaged but new sites will also be contemplated.

The process for defining the new research is preceded by a large effort to identify those design and performance assessment issues that need addressing or information that needs supplying. In this way, the field activities are focused on actual modelling requirements and it is hoped that the value of the data obtained will be this maximised.

For the undertaking of these activities ENRESA has established a Co-operation Agreement with CIEMAT, public research institute in energy and environment. As a result of this agreement, CIEMAT acts as the primary risponsable of accomplishing the projects.

3. The El Berrocal Project.

3.1 Introduction

In outline El Berrocal comprises a U and Th mineralised quartz vein formed by hydrothermal processes that occurred after a pervasive deuteric alteration event affecting the El Berrocal granite, a two-mica postectonic granite that is enriched in uranium in the form of primary uraninite. This uraninite is the source of all the uranium at El Berrocal, including that in the mineralised vein.

The site is located some 90 Km. SW of Madrid, Spain, in the mountainous region of the Southwestern part of the Sistema Central. The uranium orebody was mined and abandoned in the 1960s. A series of galleries and adits were excavated although most of the mine is now closed-off and inaccessible except for a 70 m long access gallery driven into the hillside that intersects the mineralised quartz vein.

Work at El Berrocal includes geological and structural mapping, detailed mineralogical lithogeochemical and hydrogeochemical analyses (stable and radiometric isotopes included), colloid studies, development of down-hole probes, hydrogeological characterisation with tracer tests and coupled flow and transport modelling. All of this work is done with the aim of understanding and modelling the past and present-day migration processes that control the distribution of naturally occurring radionuclides in a fractured granitic environment.

3.2 Objectives and scope

The main scientific objective of the project is the identification and characterisation of natural radionuclide (U, Th, and their decay products) migration processes in a fractured granitic environment and validation of models describing these processes.

Specific practical objectives include:

- the development of site characterisation methodology
- building up coordinated working teams, and
- development of equipment and instrumentation

The Project was preceded in 1988 by a Pre-study phase that was concerned mainly with determining the suitability of the site for the later, multidisciplinary study. The actual project was initiated in 1991 and planned as two two-year phases. It is intended to last up to March 1995.

3.3 Organizational aspects and participants

The project is managed and co-ordinated by ENRESA (Spain), with the technical assistance of Intera Environmental Division (United Kingdom). Participating organisations include CIEMAT (Spain), CIMNE (Spain), CEA/IPSN-Cadarache (France), AEA Technology (United Kingdom) and BGS (United Kingdom), in the second phase three more Spanish participants were incorporated; MBT, CSIC (Granada), and UC (La Coruña University). Partial funding is provided by the CEC-Brussels. JRC/CEC-Ispra laboratories co-operates with the project participants. CIEMAT has a major participation playing an important role in almost every activity and being risponsible of co-ordinating field work.

There are two associated projects also cofunded by CEC, namely:

(1) Rock Matrix diffusion as a Mechanism for Radionuclide Retardation: Natural Radioelement Migration in relation to the Microphractography and Petrophysics of Fractures Crystalline Rock. Main contractors: University of Exeter (UK) and University of Oviedo (Spain).

(2) Development of a Model for Radionuclide Transport by Colloids in the Geosphere. Main contractor: ARMINES (F)

Both these projects are connected with El Berrocal and receive samples for study as well as using the overall knowledge of El Berrocal as a foundation for their own modelling work.

3.4 Status of the El Berrocal Project

Abstracted highlights of the Project include the construction of a detailed geological frame for the El Berrocal batholith that has allowed the formulation of a complex three-dimensional structural Model, to which hydrogeological and geochemical features of the site can be related.

Geochemistry is in an advanced state of development for both solid and groundwater samples. An extensive study has been performed on the mineralogy and geochemistry of the rock matrix and fissure fillings with an accent on the uranium behaviour during each of the magmatic and alteration events that affected the El Berrocal granite. As part of the hydrogeochemical work more than 200 samples have already been taken and analyzed. The subsequent data have been used to classify the El Berrocal groundwaters into three main types. Samples from depths below 400 m. have only very recently been taken and they have not yet been incorporated in the interpretation. The data indicate that most of the waters are of a recent origin, nevertheless some of the analyzed waters indicate a more intense water-rock interaction and longer residence times.

Geochemical and hydrogeological data are being incorporated in a database specifically designed and constructed for the Project and most relevant data will be soon included in a three-dimensional model, with the aim of helping to develop an integrated interpretation of all the Project data.

Currently, an in situ cross-hole tracer test is being carried out which uses innovative downhole equipment both in sensors and transmitters. The tracer test has the aim of providing parameters for constraining groundwater flow models of the site.

4. The El Berrocal Project and Site Characterisation.

The El Berrocal Project was initially conceived as an experimental study site for the development and implementation of site characterisation methodologies. Accordingly, the whole set of activities is focused on site characterisation. Nevertheless, in some of the study areas there has been an important effort in gaining fundamental knowledge that is necessary as the basis for progressing to further work of a more specific nature and more relevant to site assessment.

The issues considered within the project that most clearly deal with site characterisation are methodological; mainly those points linked to practical work on site, such as timing of activities, prioritising and sequencing operations, minimising interference between activities and, in particular, practical aspects related to groundwater sampling operations.

Concerning the last point, balancing the requirement for representative groundwater samples against the risk of perturbing the natural system has been treated extensively at El Berrocal. A relevant set of data is being built up that includes pumping rates, flow volumes, and the corresponding variations of physico-chemical parameters; Eh, Ph, conductivity, and Fe, Zn and U concentrations. The variations are significant and apparently depend on the sampling site and the degree of physical connection between the sampling location and the main groundwater flow paths. The data already available are, as yet, limited and do not allow global conclusions to be established. More data are being obtained and a multivariate statistical analysis will be undertaken to provide a better understanding of the issue.

Further information concerning the quality of groundwater samples has been provided by the opportunity to contrast chemical analyses from samples from the same location but obtained by different means; first, conventional sampling after pumping and subsequent chemical analysis and, second from the downhole probes AUTOLAB and CHROMATOLAB which are able to provide chemical data *in situ* without pumping and, thus, without stressing or perturbing the system.

5. El Berrocal, natural analogues and performance assessment.

El Berrocal Project has been the first long term and large scope project within the R+D program of ENRESA, as regards geological studies of natural systems. It was envisaged as a natural system characterisation exercise that incorporates the concept of natural analogues.

The low temperature hydrothermal processes affecting the site, including the ones giving rise to the uraniferous mineralization itself, together with those of chemical weathering, can be considered as analogous geochemical processes, since they cause the release, retention and migration of U, Th, and REEs, in a similar fashion to some of the processes expected in a HLW repository.

As was mentioned earlier, some of the information that will be gained from the Project will be used in a performance assessment. At the present time, the development of performance assessment within ENRESA is in a preliminary state, it considers the major processes to be taken into account their links and interactions, and itemises the data actually required in a performance assessment. It is anticipated that some of the data could be provided by the El Berrocal Project.

In very broad terms, El Berrocal can be used to demonstrate that the underlying concept of geological disposal is sound because it can be shown easily that uranium mobility has been limited in the post hydrothermal geological history of the pluton. These simple comparisons between natural systems and the repository have no great quantitative value but they do provide a starting point for explaining to the public and lay audiences the disposal methodology. This is the first input of a natural analogue to performance assessment. This illustrative aspect of the El Berrocal Project is highlighted by the Project Brochure which compares the natural system at El Berrocal with a repository system as well as providing basic information on the site characterisation methods. Such illustrations are essential in supplying a coherent safety case because the mathematical performance assessment and its conclusions will not be readily assimilated by many concerned groups.

More specific and, in some cases, quantitative information is being provided by the Project. The planned formal performance assessment will have the option of using high-quality data concerning a *Spanish* fractured granitic environment rather than requiring imported data from other organisations programmes. Information from EL Berrocal will be used to construct and constrain the performance assessment models although the actual input from the project is, as yet, unclear because data acquisition and interpretation within the Project is still in progress. However it is envisaged that these data will include information concerned with, among other issues: radionuclide transport in solution; radionuclide transport on colloids; redox conditions and their influence on migration processes, microbiological influences on hydrochemical reactions, and matrix diffusion.

Detailed information concerning the studies in each of these areas will be presented in a series of Project Topical and Final Reports, which are listed at the end of this document. However, some broad conclusions can be presented here.

Radionuclide transport in solution and by colloids is being addressed and, although full quantitative interpretations are yet to be produced, it is apparent that transport by solution is the dominant process. The colloidal populations are relatively low and are associated with low concentration of adsorbed radionuclides.

Radionuclide retention mechanisms are being assessed by mineralogical and isotopic studies and it is found that radionuclide retention is enhanced by new mineral growth, with precipitation dominating over sorption in most cases.

Despite the relatively altered state of the granite and the high density of fractures, matrix diffusion has been found to be limited to a zone just a few centimetres deep, consistent with studies on other granites.

The time frame over which transport and retention mechanisms operate is a key feature of a natural system and one that needs to be quantified. This aspect of a natural analogue studies forms a large component of the Project through comprehensive and detailed isotopic studies.

Finally concerning contributions to performance assessment, a comprehensive blind predictive geochemical modelling exercise is being performed as part of the Project. This exercise is testing thermodynamic databases for many elements of relevance to repository safety, including U, Th, Ni, Sr and others. The later stages of this exercise will begin to test key concepts for the relationship between measured Eh values in the field and theoretical redox capacities of the system as well as coprecipitation and solid solution.

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El Berrocal Project: Six-monthly Progress Report series

First (It covers the period from March 1991 to August 1991)

Sixth (From September 1993 to February 114)

Topical Report Series

TR-1 Perez del Villar, L. and Pardillo, J. (CIEMAT)
Lithological map of El Berrocal Site.

TR-2 Marin, C (CIEMAT)
Structural and geological analysis of the El Berrocal experimental site

TR-3 J. Pardillo (CIEMAT)
Mineralogical and geochemical study of the reference granite intersected by borehole S-16 at the El Berrocal experimental site, Gredos, Spain

TR-4 M. Pelayo (CIEMAT)
Mineralogy of the fracture infill materials from boreholes S13 to S16 at the El Berrocal experimental site, S. Gredos, Spain

TR-5 P. Gómez (CIEMAT) & M. Ivanovich (AEA Technology)
Hydrochemical & isotopic characterisation of El Berrocal groundwaters

TR-6 P. Gómez and M.J. Turrero (CIEMAT), M. Ivanovich (AEA Technology) & J.M. Vinson (CEA/IPSN)
Sampling and characterisation of colloids in groundwaters from the El Berrocal site.

TR-7 M. D'Alessandro, F. Mousty (JRC-ISPRA), A. Yllera (CIEMAT), J. Guimerá (UPC/CIMNE)
In situ migration tests with conservative groundwater tracers at the El Berrocal Site, Spain.

TR-8 J.M. Vinson (VRS/IPSN)
Strategie d'étude et de qualification d'un site par mesure et experimentation in situ en forage.

TR-9 L. Pérez del Villar (CIEMAT)
An approach to the calculation of the mineralogical distribution of U and Th in the fresh granite from the El Berrocal site, Spain.

TR-10 L. Pérez del Villar (CIEMAT)
The clayey fissural fillings associated with N-100°-110°-E fractures at the El Berrocal Site, Spain: characterisation, genesis and retention capacity of radioactive and other elements.

TR-11 L. Pérez del Villar (CIEMAT)
Mineralogical and geochemical characterisation of the altered granite from the El Berrocal site, Spain.

TR-12 M. García (CIEMAT)
Distribution coefficient studies in separated mineral phases from the El Berrocal site, Spain.

TR-13 M. García (CIEMAT)
Experimental migration studies with granitic materials from the El Berrocal site, Spain: a first approach

TR-14 M. Ivanovich (AEA Technology)
Rock-water interaction using uranium series disequilibrium concepts at

the El Berrocal site, Spain.

TR-15 D. Holmes (BGS), J. Guimerá (CIMNE) & F. Recreo (CIEMAT
Hydrology, hydrogeological testing methodology, test equipment and results from boreholes at the El Berrocal site, Spain.

TR-16 J. Carrera (CIMNE)
Users guide for TRANSIN-II

TR-17 J. Carrera (CIMNE)
Users guide for TRANSIN III

TR-18 J. Carrera (CIMNE)
Inversion of nonlinear flow and solute transport

TR-19 J. Carrera (CIMNE)
Stochastic analysis of flow and transport in a single fissure

TR-20 W.M. Miller (INTERA). Technical Editor.
El Berrocal Project: Phase One Summary Report

TR-21 J. Bruno (INTERA)
Final Blind Predictive Modelling Report

TR-22 P. Gómez, M.J. Turrero (CIEMAT) & M. Ivanovich (AEA/Harwell).
Characterisation of colloids in groundwaters from El Berrocal site, Spain. (second report)

TR-23 M. García, A. Yllera, & A. Hernández (CIEMAT)
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TGR-1 R. Campos et al.
Structural Task Group Report

TGR-2 J. Guimerá et al.
Hydrogeology Task Group Report

TRG-3 L. Perez del Villar et al.
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TGR-4 P. Gómez et al.

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An Overview of the British Natural Analogue Programme

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1. Introduction

Investigations are being made by UK Nirex Limited for the proposed deep geological disposal of low- and intermediate-level (L/ILW) radioactive wastes at Sellafield in Cumbria, England. Owing to the temporal and spatial scales involved, performance assessment (PA) procedures rely heavily on computer-based models, including those which simulate groundwater movement, contaminant transport and a range of other geological processes. These models are supported by laboratory, site characterisation and natural analogue programmes.

Up to the end of 1992, Her Majesty's Inspectorate of Pollution (HMIP, the Regulator) funded a number of natural analogue studies in Britain and overseas. The British sites were focussed on a number of diverse shallow geochemical systems to increase our understanding and modelling of the transport mechanisms of natural U/Th decay series radionuclides and halide elements in sediments. The different studies were designed to boost our confidence in modelling uranium speciation and mass transport of different elements using PA-relevant computer codes (e.g. PHREEQE, CHEMTARD and NAMMU) and the CHEMVAL thermodynamic database [e.g. 1]. A brief summary of this past research at the British natural analogue sites, and the various implications for PA were described before [2]. In addition, HMIP, with Nagra and SKB, has co-funded a review of natural analogue studies and an important book has arisen from this work [3].

2. Current UK activities

Recently, there has been a number of UK contributions to international studies of natural analogue sites overseas, most notably at Maqarin in northern Jordan and at El Berrocal in central Spain. The analogue studies at these overseas sites are concerned with many geoscientific topics. Those of interest to the UK include natural hyperalkaline fluid-rock interactions, fracture flow, rock matrix diffusion, colloids and radionuclide migration. Studies of these topics have been actively supported by Nirex under the Maqarin Natural Analogue Project and the El Berrocal Project and brief descriptions of these studies form the main focus of this paper.

There is a number of other natural analogue studies in the Nirex programme [4] which includes studies of fluid flow and solute transport in rocks from the Reskajeage Quarry in Cornwall and investigations of the distributions of naturally occurring U-series radionuclides in Cumbria. However, these studies are not discussed further here.

3. Maqarin Natural Analogue Project, Jordan

3.1 Project participants from the UK

Since 1990 Nagra, Nirex and SKB (and, initially, Ontario Hydro) have funded a series of international collaborative studies under the Maqarin Natural Analogue Project. The UK teams have included scientists from AEA Technology, Harwell, the British Geological Survey (BGS), the University of Manchester and the Scottish Universities Research and Reactor Centre at East Kilbride These teams have interacted with groups in Clay Technology AB, Sweden, PSI, Switzerland, GSF, Munich, and the Universities of Berne, Jordan, Linköping and Ottawa. Other organisations involved in the project include MBT, Spain, Conterra, Sweden and the Geological Survey of Canada.

3.2 The Maqarin site

The Maqarin site in northern Jordan is an unusual area containing highly alkaline (pH 12-13) groundwaters occurring naturally within a limestone/marl environment. The hyperalkaline groundwaters are produced by the interaction of background bicarbonate-type groundwaters with zones of high temperature/low pressure metamorphic rock (wollastonite-larnite-spurrite-ellestadite-ferrite marbles) hosted within Upper Cretaceous and Tertiary pyritic organic-rich marls and limestones. The metamorphism has resulted from localised spontaneous combustion of the organic matter (probably triggered by exothermic pyrite oxidation) within the bituminous limestones and marl. This caused calcination of the sedimentary rocks. Retrograde hydration of these calcined rocks has produced a secondary mineralogy, similar to that encountered in hydrated portland cements, dominated by portlandite [$Ca(OH)_2$], calcium silicate hydrates (including afwillite, tobermorite, jennite and CSH gels), sulphates (including ettringite, thaumasite and gypsum) and carbonates (calcite, aragonite, vaterite). Continuing hydration and leaching processes are buffering the groundwaters to a high pH.

Phase I investigations at Maqarin were focussed on groundwater-rock interactions of natural Ca-OH-dominated groundwaters (pH 12.4-12.7) with the retrograde hydration of the metamorphosed marbles - the source of the high pH fluid - as an analogue of the near-field 'cement zone' [5]. Phase II work has concerned the marl host rock as an analogue of the interaction of a high pH plume within the repository disturbed zone. These investigations have principally been undertaken on readily accessible sites at Maqarin known collectively as the Eastern Springs. A Phase III is planned and will investigate the Western Springs nearby where the high pH groundwaters interact with colluvial deposits containing silicate-rich rocks.

3.3 PA relevance

In the proposed Sellafield L/ILW repository, the near-field will be dominated by cement-based materials with a significant proportion of the total volume of the proposed repository comprising cement and concrete in the form of construction materials, backfill, and immobilised waste-form materials. Therefore, the geochemistry of the near-field environment is expected to be dominated by cement-hydration reactions and the interaction of alkaline fluids, produced by these reactions, with the host formation. Such a repository concept has been developed to maximise radionuclide retardation in the near-field by taking advantage of the low solubility of most radionuclides in hyperalkaline groundwaters coupled with the high sorption capacity of the cement matrix.

Following repository closure, near-field conditions are expected to be highly alkaline (pH 13.5) , initially controlled by the leaching of KOH and NaOH from the cement. This will be followed by $Ca(OH)_2$-buffered leachates (pH 12.5) for at least 100 000 years [6]. These leachates will arise from the progressive dissolution of tobermorite-like calcium silicate hydrate (CSH) gels.

Migration of hyperalkaline porewaters into the far-field will lead to reaction with the host-rock minerals. The dissolution of primary host-rock minerals will increase porosity and permeability. In contrast, the precipitation of low-density secondary phases in fractures and pores will reduce porosity and permeability, and alter the sorption and ion-exchange characteristics of the disturbed zone. The evidence from the Maqarin analogue can be used to check that the observations from laboratory experiments can be extrapolated to long time-scales and that predictive modelling is effective.

3.4 Data for PA studies

Results from petrological and mineralogical studies at Maqarin by BGS and others have allowed reactions between cement porewaters and the geological disturbed zone to be investigated on a field-scale and over geological time-scales. Water-conducting fractures display significant evidence of rock-water interaction in the unmetamorphosed marls, with sealing of fractures by secondary minerals and enhanced wallrock porosity as a result of dissolution of calcite and dolomite in very narrow zones immediately adjacent to the fracture surfaces. Extensive calcite cementation along reaction fronts beyond the zones of porosity enhancement suggests that the potential for retardation by matrix diffusion may be limited. CSH compounds, ettringite and thaumasite were identified as the major alteration products. There is petrographic evidence that zeolites were also formed. For Ca-rich fluids, there is general agreement between field observations, laboratory results and modelling.

Trace element studies by laser-ablation ICP-MS and Fission Track Registration showed that uranium had been mobilised on a small scale. Uranium is observed in secondary CSH compounds, carbonates and zeolites but not in ettringite and thaumasite. This indicates that U had segregated to specific phases during mineral alteration processes.

Data have been used by AEA Technology and others to test thermodynamic databases of geochemical codes (HARPHRQ, PHREEQE and MINEQL). The main conclusion from the database study was that the predicted trace-element solubilities, based on the assumption that these were controlled by a pure end-member metal oxide or hydroxide, were typically 2-3 orders of magnitude higher than those measured in the field. Thus the predictions of the codes were 'conservative' for PA. Care was needed to ensure that the selected solubility-limiting phase was realistic for the geochemical conditions. Observations of trace-element distribution at Maqarin indicated that these elements were generally present as trace elements in major secondary minerals. The inability of the codes to account for the trace element co-precipitation in solid-solution phases was identified as a major difference between the model behaviour and the actual behaviour in the natural system [7].

Coupled geochemistry/transport codes (CHEQMATE and MARQUISS) have also been tested by AEA Technology at Harwell. The aim of this work was to use geochemical modelling programs to study the interaction between a $Ca(OH)_2$-saturated high pH water from Maqarin with a host marl and to compare the predictions with observations of samples from the site. The CHEQMATE and MARQUISS modelling was based on a one-dimensional section, perpendicular to the fracture plane, in the host marl. At time=0 in the model, the grid was assumed to be made up entirely of host marl, and a high pH groundwater of constant composition forming one boundary condition. As the groundwater flows through the fracture, hyperalkaline fluid diffuses into the rock, causing mineral dissolution and precipitation. This alteration process was modelled as a function of time, and the predicted extent and mineralogy of the alteration zone compared with what was observed in the field samples. The predicted scale of the alteration products was very similar to that in the samples. This gives confidence in our understanding of the type of mineral alteration reactions that may be observed around a cementitious repository.

BGS has supplied geomicrobiological data from Maqarin to test codes used to define the microbiological activity in a repository near-field [8].

4. El Berrocal Project, Spain

4.1 El Berrocal Project participants from the UK

Since 1991 the CEC (under contract FI2W0080) and Enresa have funded an international collaborative research programme under the El Berrocal Project. The project has many European participants who have the overall objective of characterising and validating natural radionuclide migration processes under real conditions in a fractured granitic environment. In the UK, Intera Information Technologies, Melton Mowbray, provides support for scientific management and acts as the Project Secretariat. The research side involves AEA Technology, Harwell, and BGS, both with support from Nirex. Under a separate CEC project (contract FI2W0082), the University of Exeter has been carrying out rock matrix diffusion experments on selected uraniferous samples from the El Berrocal site [9].

4.2 El Berrocal investigations by UK participants

El Berrocal is the site of a disused uranium mine where a mineralised quartz vein is hosted in granite [10,11]. The hydrogeological parameters of the fissured rock system have been investigated by BGS with assistance from CIEMAT using packered downhole hydraulic test systems. At the study site the groundwater flow regime is dominated by recharge with the vein exercising a large controlling influence. AEA Technology has been collaborating with CIEMAT and BGS in the isotopic characterisation of the groundwaters, concentrating in particular on the U disequilibrium series. On this basis 3 groundwater types have been distinguished with little evidence of any colloidal transport of the uranium. Fracture infill minerals are being examined for their natural radionuclide loadings and distributions as a means of modelling sorption processes.

Profiles of U and Th natural decay series radionuclide activity ratios have been obtained in rock cores using a six-phase sequential extraction procedure to distinguish the mobile from the primary components of the U/Th radionuclides. In one rock core profile, EB6, the fracture surface sample had a markedly different distribution of U between the phases from the rest of the profile samples, indicative of a more vigorous interaction with the contacting groundwater. Radionuclide mobility on the scale of centimetres is apparent in the EB6 profile demonstrating that rock matrix diffusion in the broadest sense occurs, although the detailed geochemistry remains to be resolved.

4.3 Relevance to PA studies

The research work from the El Berrocal Project continues to provide new field and laboratory data useful for hydrogeological and geochemical modelling studies in fractured crystalline rock. These may have some general value to studies of the far-field of the Sellafield site in the Borrowdale Volcanic Group rocks. The role of matrix diffusion in the Sellafield safety case is very important and the El Berrocal results are providing good evidence of this although some details remain to be resolved.

5. The future

Consideration should be given to research into a natural analogue at a UK location different from Sellafield but containing similar hydrogeological features i.e. high salinity groundwater in deep fractured crystalline rock. Deep tin mines such as South Crofty in Cornwall offer some good possibilities for far-field analogues of the hydrogeological and geochemical processes in the Borrowdale Volcanic Group rocks at Sellafield. In the light of the importance and success of the existing natural analogue investigations, there may be scope for the development of further natural analogue studies in other fields e.g. analogues of geomechanical effects.

Finally, ideas for using all sources of natural analogue information in PR could be developed further in the UK. A good example of a new PR product has been the recently produced video on natural analogues, which was managed by Nagra with co-funding from

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THE OKLO-NATURAL ANALOGUE PROJECT:

Recent outcomes and applications of phase I programme

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1. INTRODUCTION

In September 1972, researchers from the French Atomic Energy Commission (CEA) pointed out isotopic anomalies in the Oklo uranium ore deposit, in Gabon (Bodu *et.al.*,1972). From this starting point and subsequent additional work, it was possible to demonstrate the occurence of spontaneous fission chain reactions, two billions years ago within natural environment (IAEA, 1975).

The first scientific interest placed in this unique natural phenomena, was mainly devoted to the understanding of the nuclear reactor physics (see a synthesis by Naudet, 1991). Because the geochemical anomalies (depletion in ^{235}U and abnormal spectrum of REE) evidenced in the remaining reactor material were presenting analogies with what can be found in modern spent nuclear fuels, Oklo was thus included in nuclear waste disposal scientific research programmes.

Despite the fact that important quantities of fission products remained within a geological environment over a long period of time, Oklo was never considered as representative of a typical waste disposal site at the global scale. The analogy is rather considered for retention and migration mechanisms in the geosphere of non reprocessed spent fuel components (uraninite, fission products and actinide decay products). On the basis of this concept, the Commission of European Communities (CEC) launched an investigation programme, the Oklo-Natural Analogue project. The project, coordinated by the CEA, groups several research institutes of European Union (EU) member states and benefits from the collaboration of an international working group with institutes from non EU member states (von Maravich *et.al.*, 1992).

The different topics covered within the Oklo-Natural Analogue project have been developed in Chapuis and Blanc (1992) and summarized in Toulhoat *et.al* (1994). They are related to both ancient processes (synchron or post reaction time) and recent migration and are extensively developed in the project progress reports (last issue, Blanc Ed., 1993).

This paper aims to illustrate the type of geochemical studies developed within the project with some of recent outcomes of interest for nuclear waste disposal. To frame the geochemical mechanisms under investigation in their natural context, a synthesis of Oklo geological settings is first presented.

2. GEOLOGICAL CONTEXT

The Oklo mine is located on the territory of the Gabonese Republic, in the southeastern province of Haut-Ogooué. The project investigations are concentrated in two main areas, the Okélobondo mine, southern extension of the Oklo mine, near the city of Mounana, and the Bagombé site near the city of Moanda, 30 kilometers south of Mounana (Figure 1).

2.1. The Francevillien:

The Oklo region is situated in a sedimentary basin, the Franceville basin, filled by a 4000 meters thick sequence of detritic and volcano-sedimentary material from lower Proterozoic (2000 Ma). This sequence, called the Francevillien, is lying on uncomformity on a plutono-metamorphic basement from Archean age (2700Ma). The basin is limited North and South by Nord-Gabon and Chaillu basement massifs, West by the Ogooué mobile zone of and overlayed by Mesozoic continental formations in its oriental part (Figure 1).

The Francevillien stratigraphy is divided in five major units, indexed from FA to FE, and four paleogeographic regions, the Franceville basin being one of them (Weber, 1968).

The geodynamic history of the basin starts with its opening and its progressive subsidence along a major NW-SE fracture zone. The FA formation is deposited all along the subsidence event. It consists in a sequence of conglomerats and sandstones with a thickness varying from 500 to 1000 meters. The FA deposit stops with the collapse of the basin. It increases the basin depth and leads to a marine transgression. The FB formation is deposited at that time. It is mainly pelitic and it has been divided in two sub-units where two succesive sedimentary sequences have been evidenced: FB1 showing a progressive increase towards its top in organic matter, up to black-shale facies, and Mn-Fe carbonates as well as dolomite; FB2 labelled by occurence of thick sandstones. At the end of the FB deposit, the basin is filled up but dolomite formation at the top of the FB2 still shows marine conditions. The confinement of the Franceville basin ceases when a large subsidence cycle over all the Francevillien basins starts. It is associated to acidic volcanism and subsequent erosion of volcanic deposits. The FC to FE formations are deposited within this environment and uniformely cover the Francevillien area.

In total, the diagenetic history of the Franceville basin is 280 Ma long (2150 Ma to 1870 Ma). The uranium mineralizations result from the Francevillien diagenesis (Gauthier-Lafaye, 1986).

The Oklo-Okélobondo area is located at the border of the Franceville basin, in tectonic contact with the basement. The monoclinal series of FA-FB sediments dips towards the East with a deacresing pitch from the West (a NS bedrock vertical fault) to East (center of the basin). The Bagombé site is in the same structural position, along the same strike than the Oklo site.

2.2.The uranium ore and associated reactor zones:

Uranium mineralizations are found at the top of the FA sandstones in an horizon called the C1 layer. They result from the mixing of oxydizing solutions bearing uranium removed from placer deposits with hydrocarbon. The hydrocarbon are diagenetic products with the FA formation as a source rock and are now solidified. The deposits are located in hydrocarbon traps at the top of tectonic structure. Traps have been closed by FB pelitic sediments which are impervious with respect to underlying FA sandstones. Uranium ore deposits of the Franceville basin are all associated with the petroliferous history of the basin (Gauthier-Lafaye, 1986).

The uranium content of deposits is around 0.4%. In some deposit zones where tectonic was more active, oxydizing fluids have remobilised the uranium associated to the organic matter and have formed enriched oxydized deposits with uranium content up to 15%. In the parts of enriched deposits where the criticity was achieved (reactor zones), the thermal gradient created by nuclear reactions induced hydrothermalism resulted in an enrichement of the ore uranium content from 20 to 50%.

All reaction zones are characterized by two typical and associated facies, the "facies pile" and the "argile de pile". The "facies pile" represents the reactor core material. The uraninite is included within a desilicated clayey matrix. Core zones are the richest in uranium content with highest depletion in ^{235}U isotope content. The "argile de pile" corresponds to desilicated clay halo surrounding the "facies pile" and resulting from the sandstones hydrothermal alteration at the time of the reactions (Gauthier-Lafaye, 1978). Reaction zones are from lenticular form, metric to decametric long and decimetric thick.

Sixteen reaction zones have been discovered in the Oklo-Okélobondo deposit (Figure 2). Zones 1 to 9 were dug out from the Oklo open pit. Zone 10 and 13 were mined out and were partly preserved for scientific purposes. The OK84 depleted index was evidenced on drill-cores. One reactor zone was discovered in Bagombé ore zone, ten meters below the ground surface. The reactor zone has been only investigated on drill-cores.

3. THE NATURAL ANALOGUE PROJECT

Project interests are both in ancient and present processes and can be divided into three different fields. The first one corresponds to migration or retention processes which took place during or at the end of nuclear reactions. The second is related to hydrothermal events which could have lead to geochemical redistribution in beetween the end of the reaction time(2 Ga ago) and present time (Holocene). The last one is the modelisation of recent and present-day migration in hydrological systems interacting with fossil nuclear reactor.

3.1. NA studies associated to reaction time:

3.1.1.Mineral phases formed at reaction time

Previous studies devoted to repartition of end products and actinide decay products focused on occurence or absence of them in irradiated uraninite, in surrounding clay or elsewhere in the near field. The mobility of fission products based on a comparison of theoretical fission yields and whole rock samples analyses, was even estimated (Holliger,1992; english version, 1993a). The following step was to identify the mineral phases involved in fission products retention and to determine their selectivity with respect to element species. For instance, Holliger (1992) and Hidaka *et.al.*(1993) tracing the ^{99}Tc through its daugther product ^{99}Ru showed that most of it was concentrated into stable metallic aggregates at the uraninite grain boundaries. Same isotopes were used to evaluate the release rate of fission products from the host phase minerals (see Curtis, these proceedings).

The other possibility to implement mineral phases-fission products relashionship is to look in details into potentially existing or already reported mineral phases formed at reaction time. This approach is illustrated on two examples presented below:

- **Zircon**: Sère *et.al.*(1994) have demonstrated, for the first time, the occurence of zircon induced by nuclear reactions in reaction zones. In a core sample from zone 10, a newly formed zircon has crystallized around unherited core of detritical origin zircon. The newly formed part is relatively depleted in Si and Zr but enriched in fission products (Y, LREE, etc..) released during nuclear reactions. The incorporation of end products is a direct incorporation within the crystalline lattice itself. Moreover, small (5-10 μm) solid inclusions of galena have been observed. The nature of incorporated trace element species is a strong argument in favour of a crystallisation synchron to reaction time.
- **Apatite**: newly formed apatite at the time of nuclear reactions has been reported by Gauthier-Lafaye and Weber (1988). As for zircon, Carpéna and Sère (1994), describe an apatitic crystalline lattice which has chemicaly incorporated end products (Sr, L RRE, etc..). Recent investigations (TIMS analyses) gave for this apatitic matrix an ^{235}U/^{238}U isotopic ratio prooving the incorporation of ^{239}Pu (Beltritti *et.al.*, *in prep*). As well, the apatite has physically trapped fluid and solid inclusions of different nature and size: small (μm) and scarce glass drops, galena and large (100μm) uraninite inclusions enriched in end products. Here again, the nature of incorporated trace elements prooves their incorporation at reaction time and their confinement into the mineral phase untill now.

Relevance for radioctive waste managment: These case studies show the interest to investigate retention-migration mechanisms on separate mineral phases. But it illustrates as well, the capacity of some minerals to act as physical (traps) or chemical (incorporation into the crystalline lattice) barrier with respect to end products migration over a long period of time. These observations validate the approach we had in proposing some of these minerals for radwaste confinement (patents pending).

3.1.2.Mass balance of reactor zones

To build the mass transfer model of a reaction zone, several parameters and at least one boundary condition are needed. The boundary condition is the demonstration that the reactor zone is still representative of a nuclear reactor fuel repartition. Uranium isotopic measurements made on cross sections of several reactor zones demonstrated it (Holliger, 1993b). Necessary parameters are the total amount of ^{235}U consumed, the balance of fissiogenic isotopes (accessible through the ^{235}U consumed) and the energy liberated from fission reactions. The source term description and neutronic investigations carried out within the project are the basic work to assess these parameters. The data already obtained have permitted the first 3D reconstruction of ^{235}U-isodepleted volumes of reactor zone 10 and have led to an estimation of 90 kg of ^{235}U consumed during criticality (Holliger, 1993c).

Relevance for radioctive waste managment: this 3D geological modeling can act as the demonstration that reaction zones stayed in the same geological context since reactions ended. It can validate the use of Oklo as natural analogue for source term study disregarding from the disposal time and the far field environment.

3.2. Fossil migrations:

Fossil migrations may have occured in the Oklo context during eventual hydrothermal events. There are two prerequisites to study such migrations. The first is to separate what is due to recent migrations with respect to fossil migrations to avoid cumulative effects. The second is to control the fluid temperatures and the age of hydrothermal events. The first problem can be solved in considering the different mineral phases, as it is illustrated for nuclear reaction neo-crystallized minerals in section 3.1.1. The reconstruction of the Franceville basin paleothermometry using fission track method, fills the second requirement.

Part of the paleothermometry of the Oklo basin is already known from the doleritic intrusion study. The temperature environment of such volcanic intrusion is around 1000°C and Holliger (1993c) gives an age of 870±40Ma (Pb-Pb method).

Basement rocks below the Oklo basin have been sampled from drill cores. A detailled petrological study has been performed to precise P-T conditions which occured in the region. Thin sections have showed mineral assemblages from greenschist facies corresponding to a regional metamorphism around 350°C and at least 2 Kbar (Sère and Carpéna, *in prep*). This event has been dated by fission tracks method on apatite 160±16 Ma (plateau age and length measurements). This thermal event can be related to the Atlantic opening. This major tectonic phase has already been detected by the same method on samples from other African regions (e.g. in the Hoggar shield (Carpéna, 1982; Carpéna *et.al.*, 1988)). From length measurements of fission tracks in apatites from basements samples, it can be demeonstrated that a mild thermal event (temperature between 60 and 130°C) reopened the apatite clock. We can thus conclude that the Oklo basin cooled down below 60°C 5Ma ago and that this last thermal event was connected to the Red Sea rifting (Sère and Carpéna, *in prep*).

Relevance for radioctive waste managment: Further petrological and geochronological studies are in progress to accurate the Oklo basin thermal history. Then, future studies will focuss into investigations of near and far-field migrations related to the hydrothermal circulations, 160 Ma ago.

3.3. Recent migrations

This investigation is the far-field part of the Oklo project and the space scale considered is those of hydrological catchment basin. The purpose of the study as well as preliminary results have been reported by Toulhoat *et.al* (1994). Its relevance for performance assessment issues is analysed in these proceedings by Smellie (1994).

3.3.1.Hydrological framework

The present climate of the Oklo region is equatorial with a mean annual temperature of 25°C. Mean annual precipitation amount to 2200mm with a well marked dry season from mid-June to mid-September catching less than 10% of the annual precipitation.

The water infiltration rate was estimated to a mean of 900mm (30 $l.s^{-1}.km^{-2}$) but is probably less according to our on-going investigations.

Apart from the geological context, the FA-FB sequence with reactor zones at the top of the FA, the two systems under investigations are different (Figure 3):
The Bagombé one is a shallow groundwater system with simple tectonic and stratigraphic settings. Recharge and discharge areas are well defined, the fossil reaction zone being in the discharge zone. The ore body is located in the present weathering zone.

The Okélobondo one has a complex FB stratigraphy, litteraly called the "Complexe" sequence, a tectonic contact hydrologicaly active on one side of the system and two potential recharge region both discharging along the same valley, the Mitembé river valley. The reactor zone (OK84) is preserved from surface alteration but drainage due to mining activities has perturbated natural groundwater flow.

The difference is as well in samples representativity. An appropriate piezometers drilling programme was carried out in Bagombé. At the contrary, in Okélobondo, sampling points were existing investigation boreholes (Figure 4).

Conceptual hydrological modelling of the two sites, based on existing piezometric data, has guided the sampling strategy. The position of reaction zone within postulated flow paths led us to choose the $^{235}U/^{238}U$ ratio of dissolved uranium as tracer of present spent fuel leaching and transport.

3.3.2.Hydrogeochemical results

- **Okélobondo**: three types of groundwater circulations corresponding to different evolution transit time within the system can be described.

-The first type is low pH(<6), poorly buffered, high pCO_2 , low TDS, significant thermonuclear tritium content and water stable isotopes content equivalent to present recharge conditions. It corresponds to shallow waters.

-The second type has pH ranging from 6 to 7, alkalinities from 10^{-4} to 10^{-3} $moles.l^{-1}$, silica content reflecting intense leaching, increase of TDS with increasing pH. The samples are still bearing tritium and water stable isotopes content are depleted with respect to present recharge condition which is interprated in term of either recharge under cooler climatic conditions or mixing between present recharge and ancient recharge from the last glacial episode. This water which have a tendency to equilibrium with carbonates minerals are intermediate groundwater circulating into the "Complexe"formation (FB sequence).

-The last type are confined waters with high pH (>8), high alkalinities (>10^{-3} $moles.l^{-1}$), equilibrium with respect to carbonates and secondary alumino-silicates (kaolinite, low T° adularia and albite, chalcedony). They clearly show stable isotopes content reflecting ancient cool recharge conditions. They are tritium free (within a 2σ error). The transit time estimation, made by radiocarbon dating on one of these samples, gives a mean water transit time of 11200±1700 a. The estimation made from dissolved He accumulation on the same sample gives a coherent transit time (around 10000a). These waters are deep groundwaters from deep pelite horizons or penetrating the basement.

The chemical and isotopic groundwater partition is coherent with the conceptual model.

- **Bagombé**: The same classification in shallow and intermediate groundwater can be made . The last evolution stage (confined groundwater) is missing due to the shallower environment. However, the sample from the deepest piezometer is close to K-feldspar equilibrium. The water is tritium free and the radiocarbon dating gives a mean transit time of 6300±1700 a.

One sample from a pound in the discharge zone, exhibits stable isotopes comparable to Oklo deepest water and thus suggests the discharge of deep circulations around the reactor location. Again the hydrogeochemistry fits with the conceptual model

3.3.3.Comments on groundwater evolution

The confinement is the most important mechanism of groundwater evolution. In Okélobondo, reaction zone is only in contact with confined groundwaters which are not reducing. In Bagombé, the reaction zone is located in between almost confined water discharge and superficial water recharge.

No simple redox front can be evidenced. On both sites, the most reducing water are related to local control, organic-matter rich pelites at Okélobondo and organic-matter associated to reaction zone at Bagombé. This has important consequence on radioelement migration: creation of reducing traps along groundwater flow path in Okélobondo and relative preservation of reaction zone in Bagombé.

Colloid generation occurs during equilibration phase of confined groundwater.

3.3.4.Dissolved U tracing

Principle, analytical method and preliminary results of $^{235}U/^{238}U$ measurements are presented in Toulhoat *et.al.* (1994). Efforts were concentrated around Bagombé reactor as water sampling horizons are well defined: up-flow, below, within, upward and downflow reaction zone. results are showing a possible although low, present migration of isotopically depleted uranium from the reactor zone to upward shallow horizon.

Relevance for radioctive waste managment: The site characterisation has given boundary conditions and aquifer parameters needed for the coupled mass transport modelling. The U tracing gives us an unique opportunity to incorporate spent fuel dissolution and migration in a regional hydrologic modelling (Gurban *et. al.*, *in prep*).

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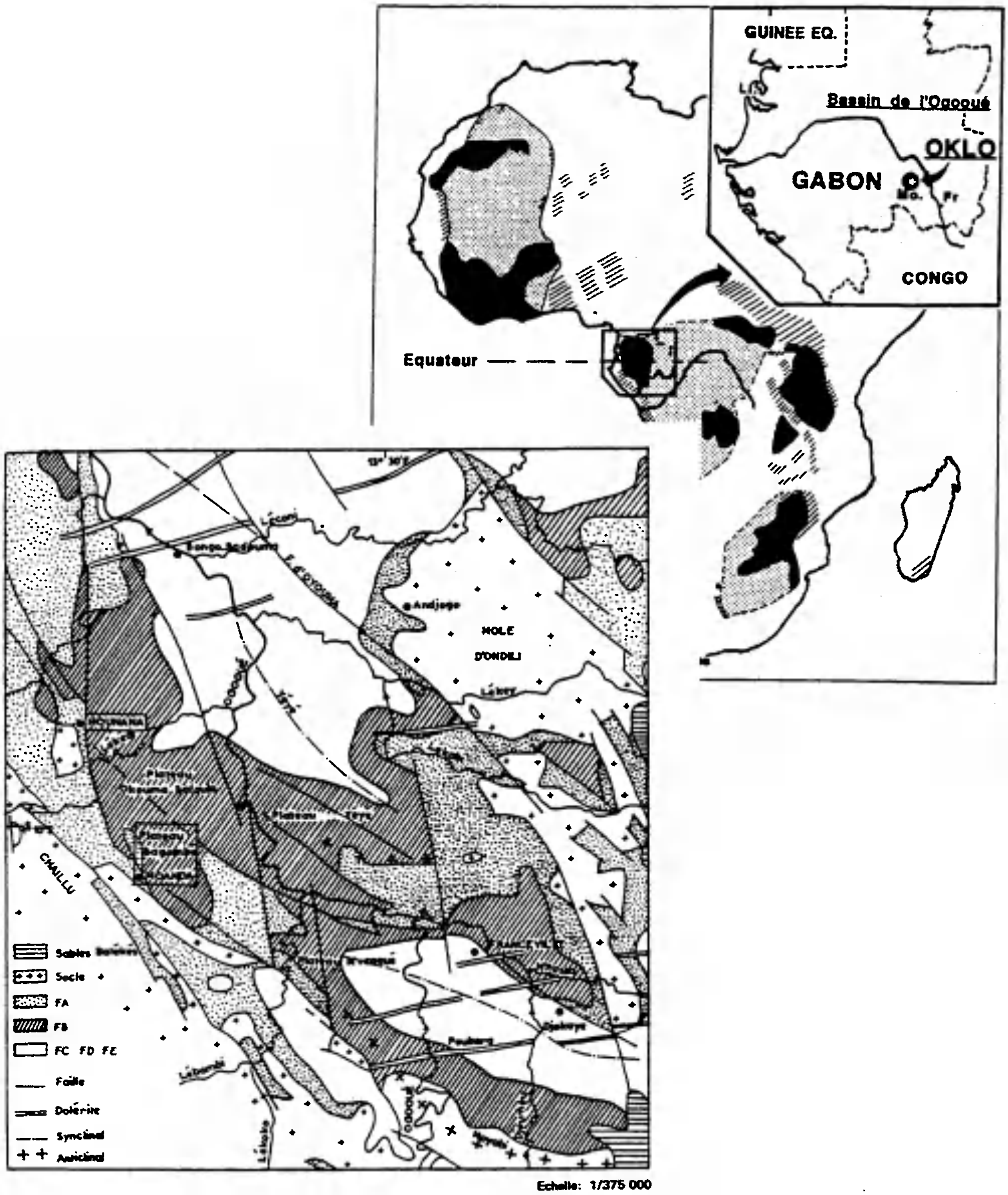
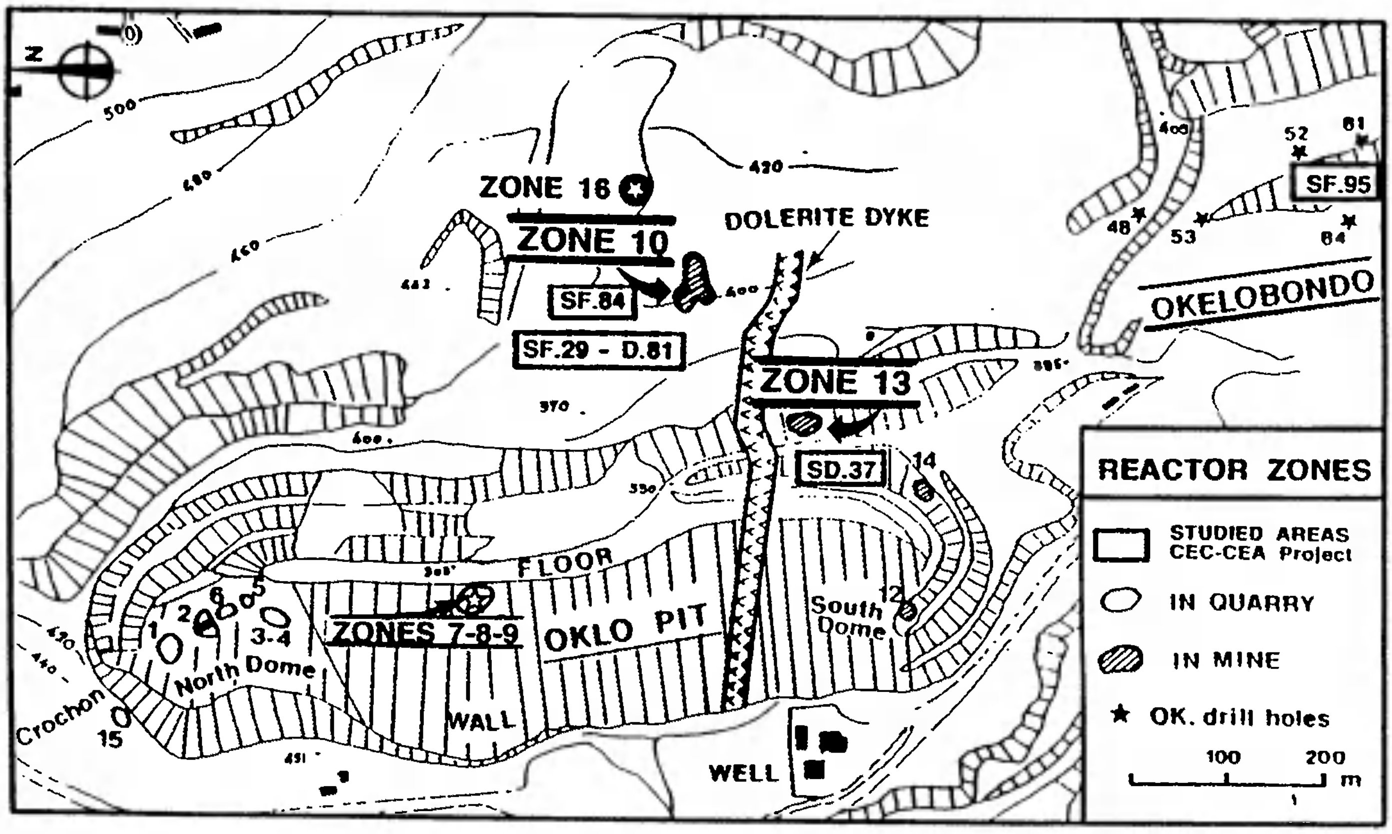
FIGURE 1



Carte géologique du Bassin de Franceville (d'après levés BRGM-CEA-COMUF).

FIGURE 2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ZONE 16
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SD.37
14
12
South Dome
OKELOBONDO
SF.95
52
81
48
53
84
FLOOR
ZONES 7-8-9
OKLO PIT
WALL
1
2
6
5
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North Dome
Crochon
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WELL
REACTOR ZONES
STUDIED AREAS CEC-CEA Project
IN QUARRY
IN MINE
OK. drill holes
100
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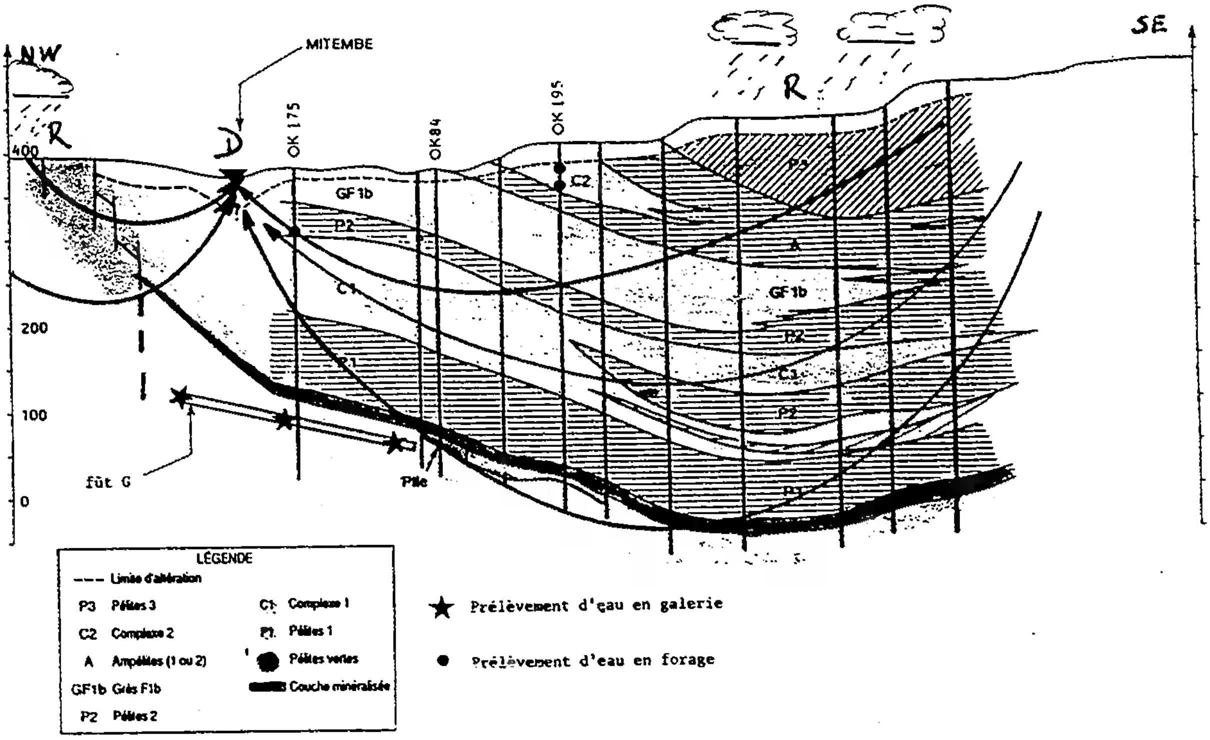
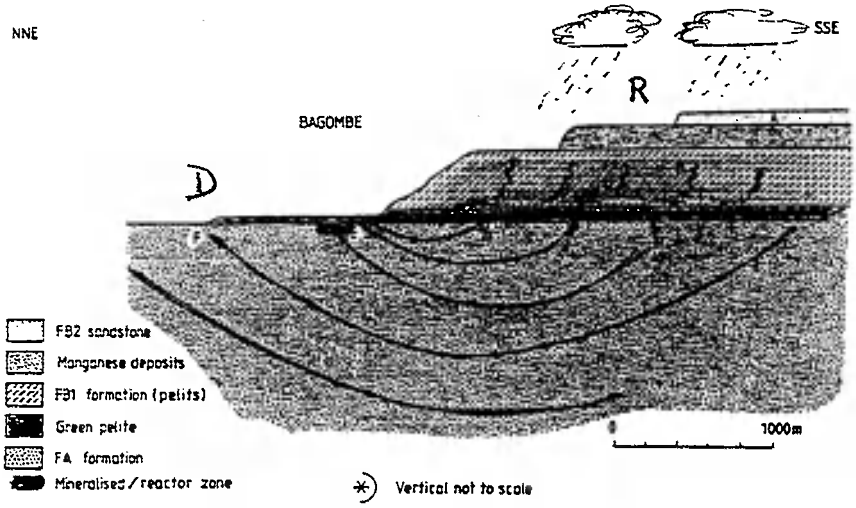
FIGURE 3



OKELOBONDO

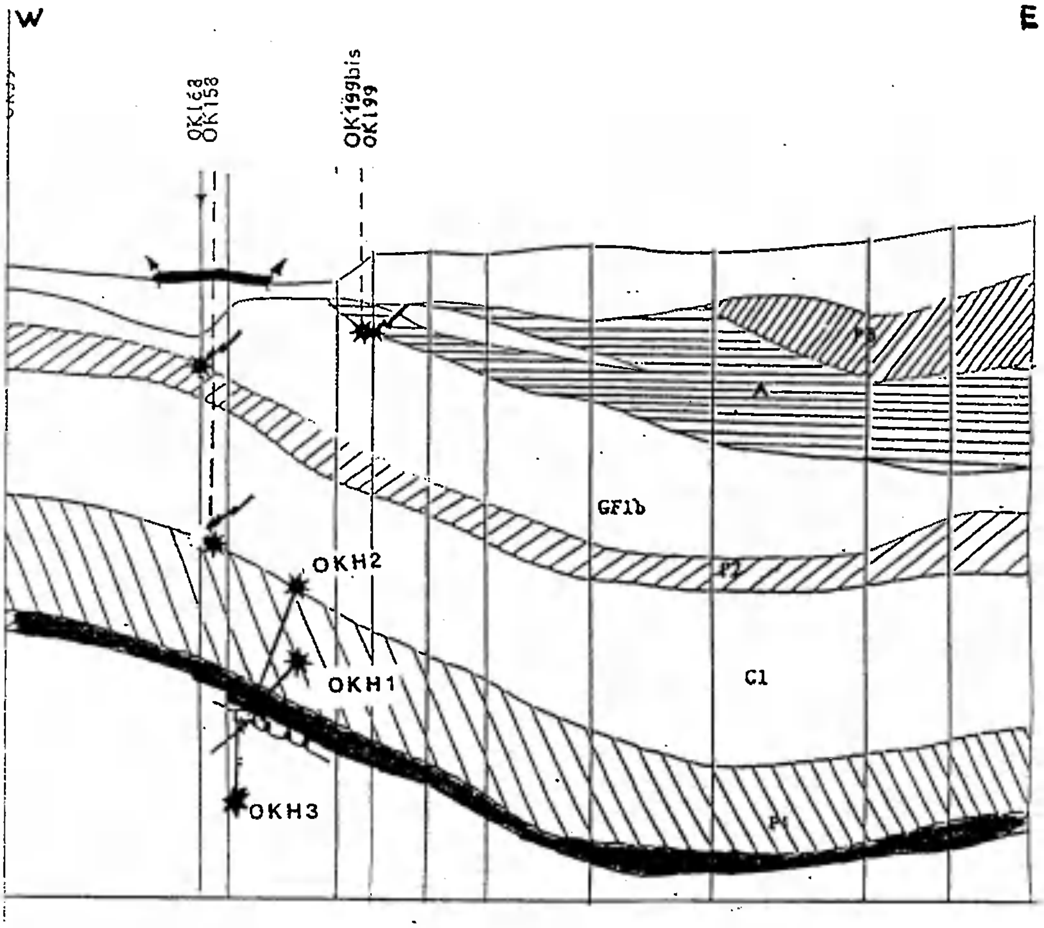
- complex stratigraphy
- simple tectonic
- complex hydrodynamic
- constraint sampling



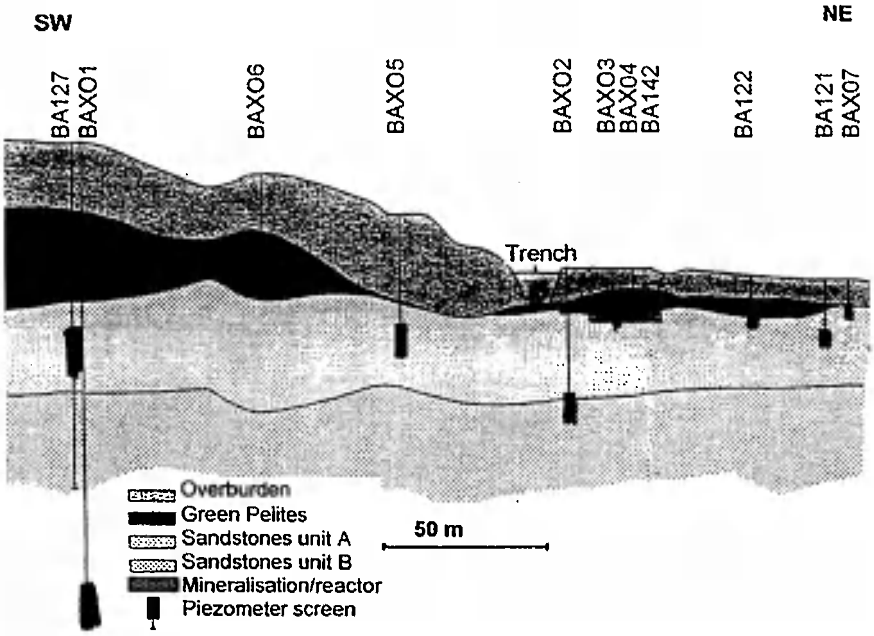
BAGOMBE

- simple stratigraphy
- simple teconic
- shallow groundwater system
- defined sampling

FIGURE 4



OKELOBONDO



BAGOMBE

THE DUNAROBBA FOREST AS NATURAL ANALOGUE:

ANALYSIS OF THE GEOENVIRONMENTAL FACTORS CONTROLLING THE WOOD PRESERVATION

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Introduction

Organic rich clay layers are often been found in the Tiber Valley (Central Italy). In these layers both well preserved and altered tree trunks are present. In particular, in the Dunarobba and in the Cava Toppetti quarry's tree trunks, still in physiological position, have been excavated in Plio-Pleistocenic clayey sequences. The hydrogen, oxygen and carbon ratios of the wood samples, collected at Dunarobba, are similar to those of the present day plants. This indicates that the alteration process of organic matter in these samples has not taken place while altered organic matter exists in the same clayey sequence just beside Dunarobba quarry, as shown by the presence of a lignite mine that was active until recently. All of this can be due to several factors such as: characteristics and properties of the impervious clay as an aquiclude; redox conditions of the sedimentary environment; type and abundance of the organic matter; etc.

To understand the geological, hydrogeological and geochemical processes that allowed the preservation of the organic substances and to assess the reliability of the Dunarobba clayey deposits as natural barrier a multidisciplinary study is in progress since August 1992 in the framework of the MIRAGE project, a research programme funded by the Commission of the European Community. The study is co-ordinated by the Department of Earth Sciences of Rome University (Italy) with the participation of other organisations including Perugia University (Italy), Exeter University (United Kingdom), Turin University (Italy), Naple University (Italy) and Ancona University (Italy).

Research line for the acquisition of geological data

In the study of a natural analogue geological investigations may provide the leading parameters for the knowledge of physico-chemical factors controlling, at far field scale, those processes that may occur around a repository. Therefore, for the assessment of the geo-environmental factors which controlled the wood preservation in the Dunarobba Forest, the following set of investigations has been planned (Figure 1):

- geological, structural and morphological surveys, together with deep gravimetric, geoelectrical and, locally, geomechanical investigations, have been carried out in order to understand the evolution and the geometry of the Dunarobba Basin;
- as the age of the tree trunks of Dunarobba Forest is still matter of debate, a detailed reconstruction of the host clayey sequences by means of palaeontological and palynological studies have been attempted;

- mineralogical and technical characterisations of rock samples with particular regard to hydraulic conductivity of clayey layers have been performed. Further, strontium, uranium and thorium isotopes have been used as tracers of fluid migration in clay samples;
- hydrogeological, geochemical and geophysical (geoelectrical) surveys have been carried out to understand the groundwater circulation, the water-rock interactions and the hydraulic conductivity of the sandy-clayey sequence as whole. Further, to assess the effectiveness of the Fosso Bianco Unit (host rock of the unaltered wood) as natural barrier to gas migration, soil gas surveys and gas injection tests have been performed.

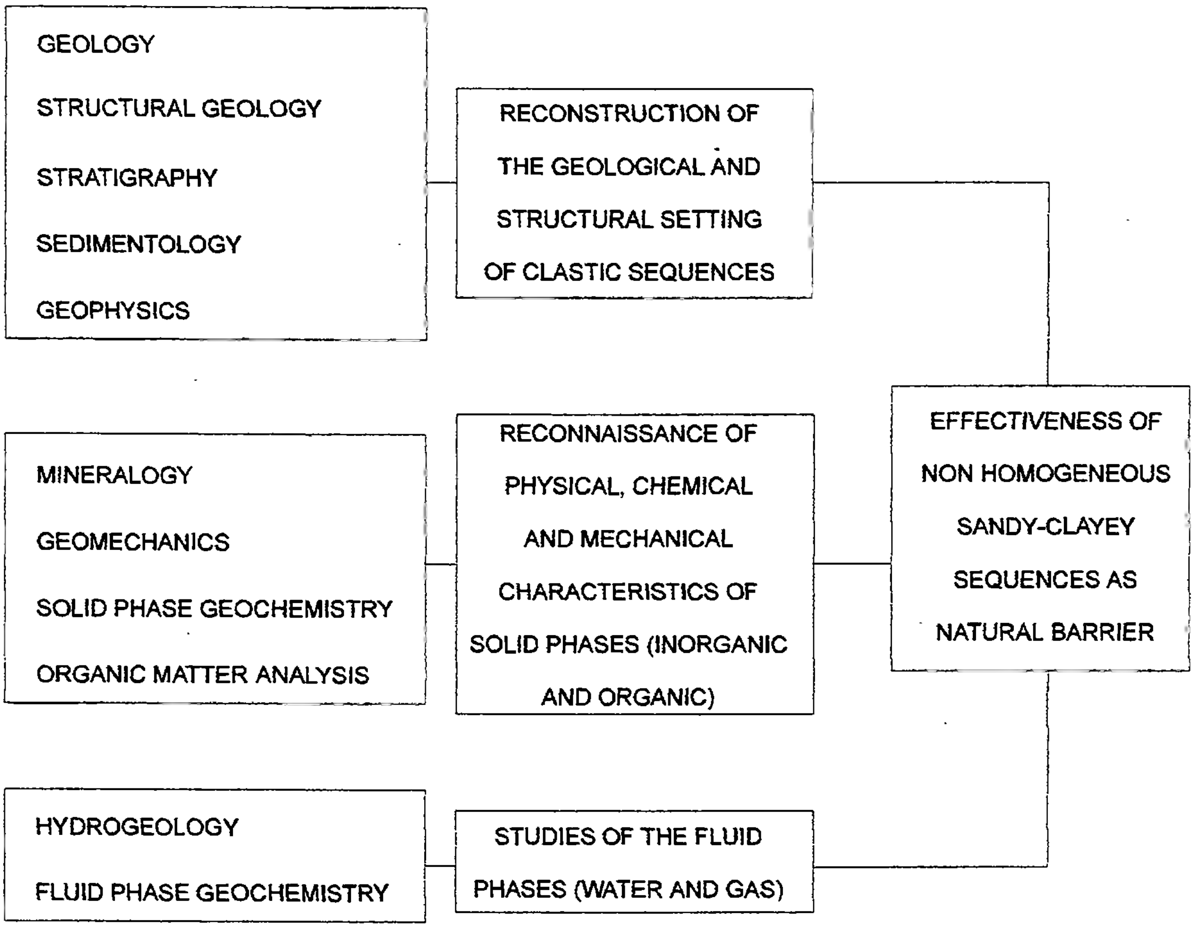

Figure 1 - In this figure the studies performed and the main objectives of the research have been summarized.

Preliminary results

All the studies mentioned above are still in progress; at this stage of the research only very preliminary results can be given.

The Dunarobba basin (Figure 2) is a sector of a wider one, the Tiber Valley. It has been interested by tectonics (probably still active) related to those of the Apennines; locally, normal faults and major joints show NW-SE, NE-SW trends. The basin underwent to several episodes of submersion and emersion; therefore, sedimentation (at quite high rate) and erosion phases alternated in the area. The sedimentological and paleontological analyses of the clayey-sandy sequences show that a lacustrine environment was present in this sector of the Tiber Valley since the lower Pliocene. The site of the Fossil Forest of Dunarobba (FFD) show in very close areas the outcrops of:

- silty clay and closely laminate carbonate deposits. The presence of a rich fresh water fauna and leaves indicates sedimentation in shallow waters (lacustrine sediments);
- silty clay interbedded with lenticular sandy strata showing structures formed by traction currents due to sheet flood (sandy deposits) inside shallow waters (laminated silty clay). The depositional environment of these sediments should correspond mainly to swamp and hydromorphic soil.

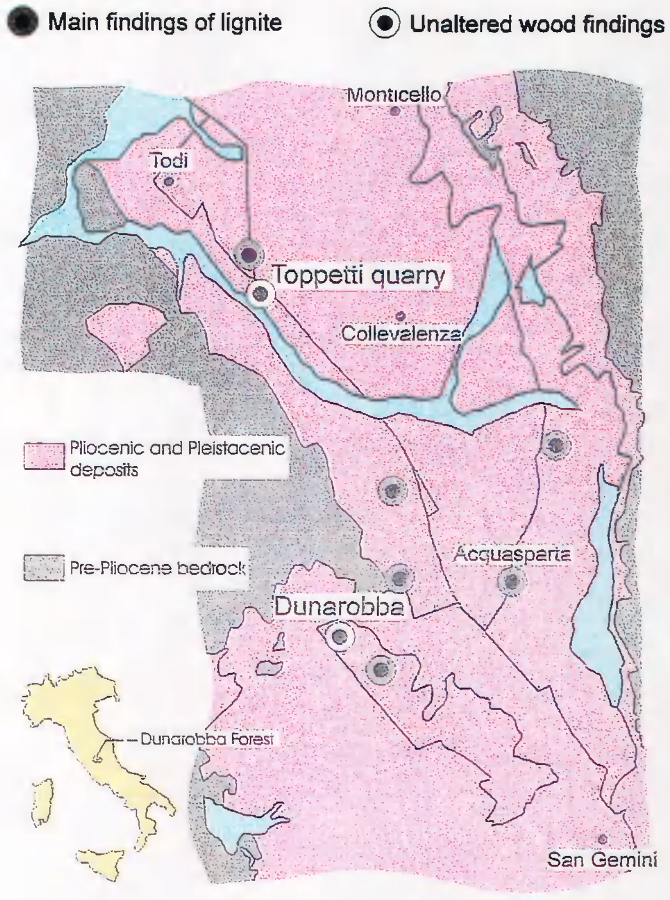

Figure 2 - South-west branch of the Dunarobba basin: main findings of lignite and unaltered wood.

The tree trunk (monospecific) have been identified as *Taxodioxylon gypsaceum* (Goppert) Krausel; this species became extinct during the Pliocene. Their anatomical characteristics are similar to the extant *Sequoia sempervirens* (Lamb) Endl. According to the results, the Fossil Forest host rocks (Fosso Bianco Unit - FBU), thus the fossil forest, can be referred to the Upper Pliocene. In this case, the fossil trunks are older than expected (more than 2My).

The FBU has been studied in different quarries in the Tiber Valley and in boreholes at Dunarobba site. It has been formed mainly by blue clay and silty clay interbedded by frequent sandy layers (usually 1 m thick). The clay and silty clay thickness as well as the frequency and the thickness of the sandy layers are different according to the depositional environments (deep lacustrine, prodeltaic and deltaic). The reconstruction of the sedimentary environments is shown in Figure 3.

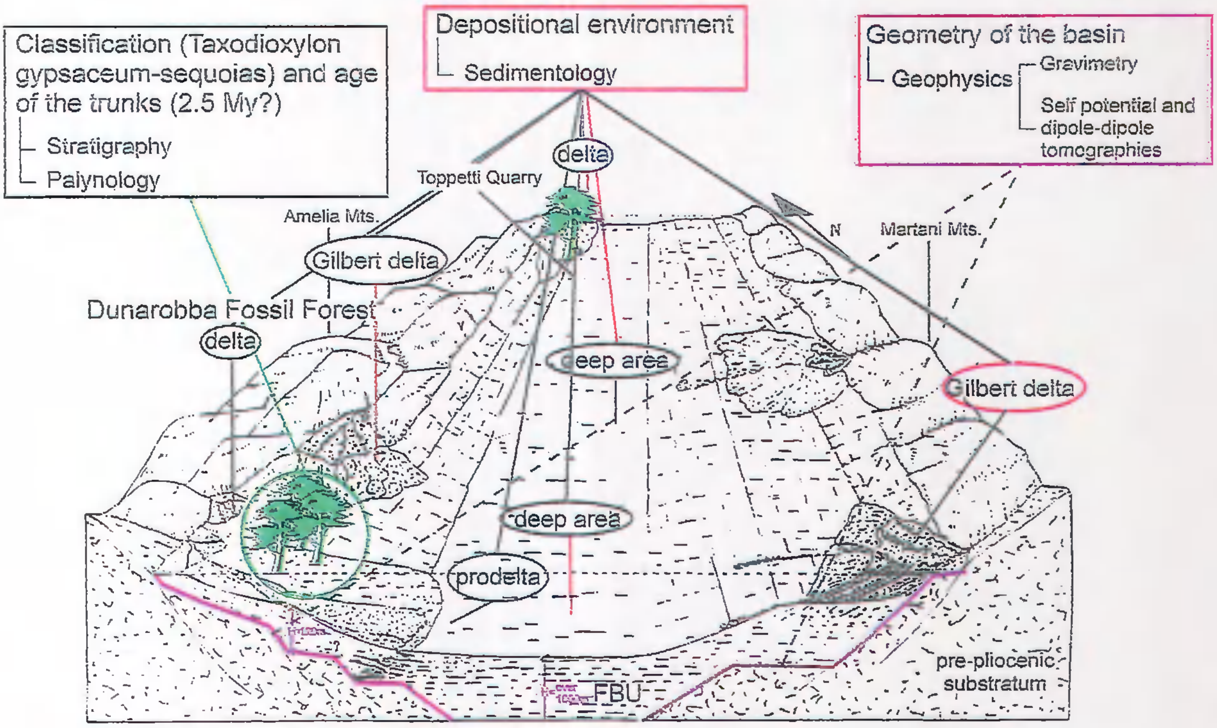

Figure 3 - Reconstruction of the depositional environment in the Tiberine Basin (modified from Basilici, 1993).

The hydraulic conductivity of the clay and silty-clay formations range from $2*10^{-13}$ to $2*10^{-10}$ m/s while the hydraulic conductivity (estimated) of the interbedded sand is $\sim 10^{-4}$ m/s. In the solid phase, a geochemical survey as been carried out and $^{87}Sr/^{86}Sr$ and the abundances and isotopic ratios of U and Th were measured in the whole rock as well as in the carbonatic and in the pelitic phases (Figure 4 a, b). The strontium isotope ratio values, different from sample to sample, seem to indicate that each pelitic layer behaves as a closed geochemical system. This is in agreement with the U, Th and Ra values. These radionuclides in the Dunarobba clay are characterised by a very low geochemical mobility as shown by the diffusive distances reached by each of them. All these results suggest that no meaningful advective fluid flow occur (or occurred) in the Dunarobba clay formations at least at microscale.

The fluid phase (water and gas) studies suggest that:

- two different groundwater systems are present in the Dunarobba area. The first, shallower, is linked to local meteoric waters circulating in the sandy and gravel layers in the upper part of the Fosso Bianco sequence; the second, deeper, is controlled by morphotectonic structures and has as recharge area in the surrounding carbonate massifs. The mixing of the two different water systems occurs through the main fault systems associated with Apennine tectonics still active.
- Flows of deep origin gases are evident in the whole Dunarobba basin. This has been pointed out by the presence in soil air of high contents of deep seated gases such as ^{4}He, ^{222}Rn and CO_2, which comes from hydrothermal alteration of the underlying limestones. These gases migrate through faults whose occurrence is confirmed by geological, geophysical and geochemical studies.

In the whole area, no evidence of mixing processes between shallow and deep fluids (water and gas) are recognised far away from the tectonics. This is in agreement with the results of the ^{87}Sr isotope study and can be explained as follows: water circulation occurs horizontally only in the sandy layers while vertical movement could take place in association with faults.

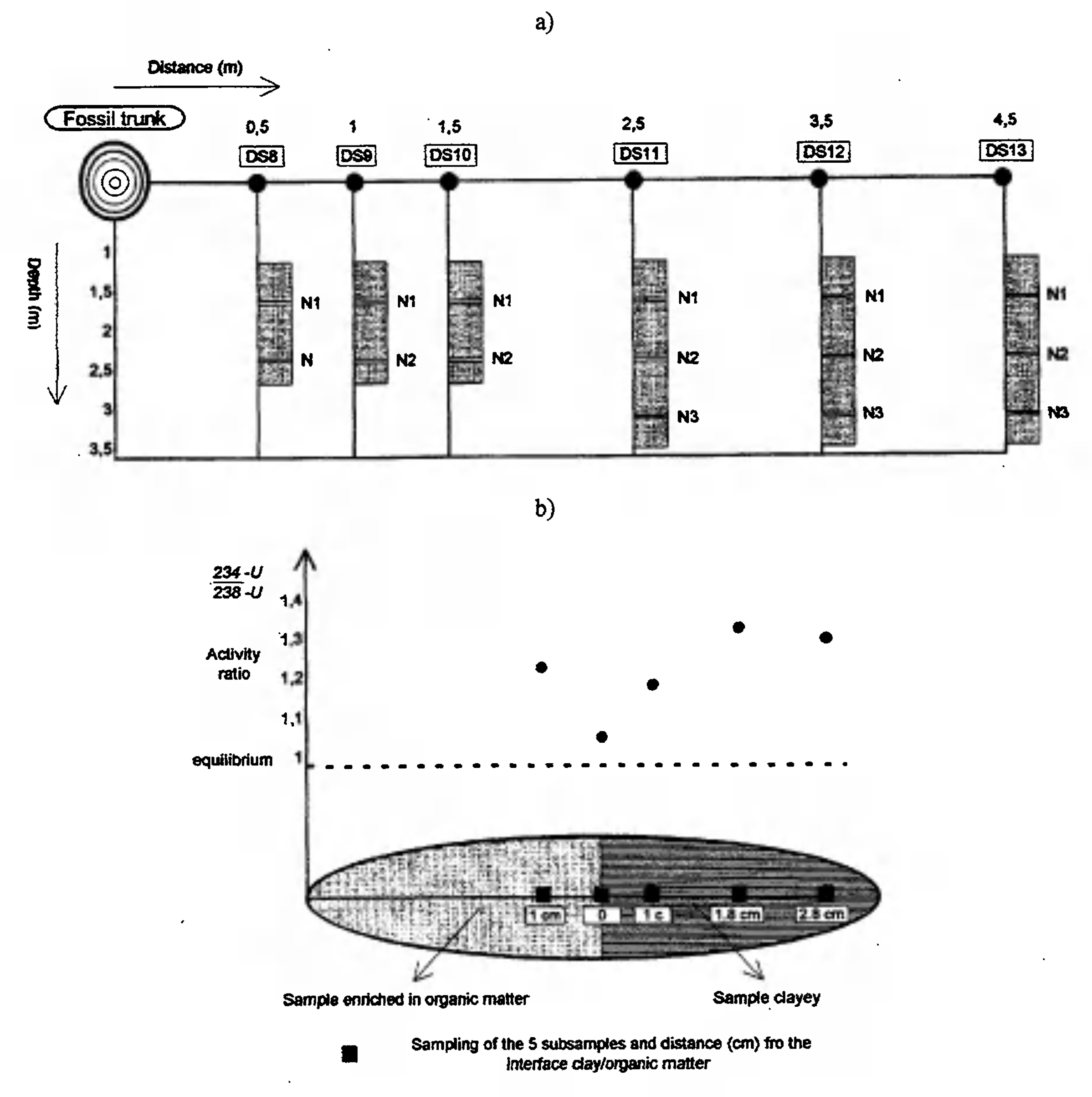

Figure 4 - U, Th isotopes were analyzed in samples collected at different depth and distances from the trunk; a) at metric scale; b) at centimetric scale. Results suggest that radionuclides have a vary low geochemical mobility and have not been involved in advective processes (from Barbieri in Ambrosettti *et alii*, 1994).

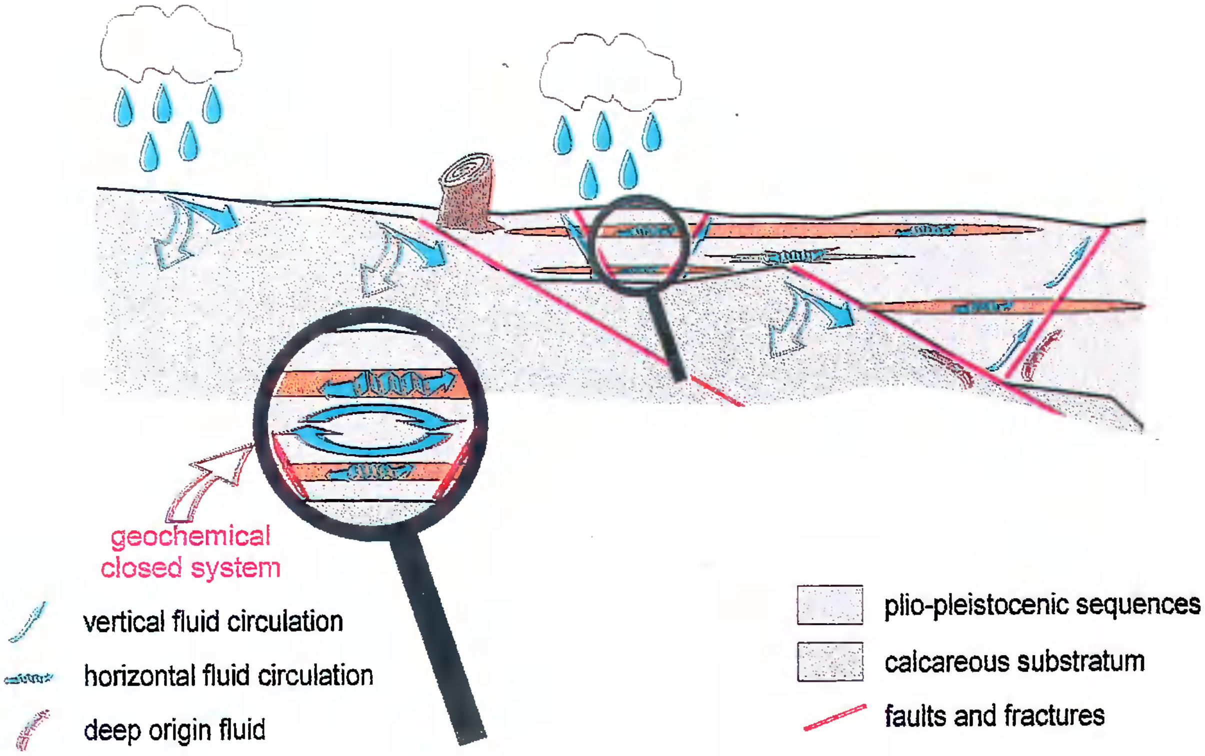

Figure 5 - Preliminary interpretative model of the obtained data.

Preliminary conclusions

These first results suggest that the Dunarobba clay formation can be considered as barrier for terrestrial fluids only at local scale and far from fractured zone; but as a whole this formation behaves as brittle and gas bearing media (Figure 5). It is worth of note that such results show the capability of clay to act as geological barrier against fluid and radionuclide migration (at least at local scale) even in areas affected by unsuitable geological conditions, such as active tectonics, uplift, intense erosive processes, groundwater circulation, etc.. Further studies should be carried out for a better definition of all the chemical and physical parameters which may play a role in the wood preservation, and for a modelling of radionuclide migration in sandy-clayey sequences. This can be achieved by more detailed studies including a comparison with the geo-environmental parameters occurring in correspondence with the lignite outcrops in the Dunarobba area.

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NATURAL ANALOGUES FOR A REPOSITORY IN ROCK SALT - THE GERMAN APPROACH

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Ladies and gentlemen,

maybe you are a little bit surprised about the fact, that a German participates in your meeting, especially since in Germany R&D-work in the field of natural analogues was till now, if at all, carried out on a relatively small scale. Therefore I'm very thankful to Dave Curtis and Henning von Maravic for giving me the opportunity to report about the German ideas, how natural analogues can be used in future German R&D-work concerning geological disposal of hazardous waste.

German scientists, who work in the field of geological disposal, are increasingly convinced that natural analogue studies are an indispensable part in evaluating the performance assessment of a repository. But not only a repository for radioactive waste has to be considered but also a repository for chemical and toxic waste. If you imagine that in Germany the annual total amount of this sort of waste is about 11 - 13 mio. tons, with the radioactive waste adding only .02 %, and the potential hazard is similar, long-term safety predictions are necessary, too. So, natural analogue studies may also be useful for this type of repository.

Especially modellers and long-term safety analysts are increasingly of the opinion, that natural analogues are a valuable and an important contribution to their work because they can be used to evaluate the completeness of the essential processes of a conceptual model, and to check the plausibility and proximity to reality of the model assumptions. Furthermore they can make evident lack of knowledge with respect to processes and therefore help improve the models. Natural analogue studies are especially useful for processes with spatial and temporal dimensions, which cannot be investigated by field or laboratory experiments. All this underscores the necessity of implementing natural analogue studies in R&D-work concerning geologic disposal.

Alas, hitherto natural analogue studies had only marginal character in the R&D-program of the Federal Ministry of Research and Technology (BMFT). Similarly, efforts in research laboratories were also low key, only some work was implicitly connected to natural analogues. But a systematic and strategic approach to use natural analogues was missing. From todays point of view it surely was a negligence that no German scientist participated in the important NAWG, although German scientists are holding memberships in several international working groups that are dealing with performance assessment and/or validation.

Because of the importance of natural analogues the BMFT intends that in future German R&D efforts, dealing with natural analogues be increased and the international cooperation intensified.

Why the growing interest in the use of natural analogues in German R&D?

In future, BMFT will concentrate its work on more generic R&D. The emphasis will be in the field of safety, that means R&D-work which contributes to enhance safety of humans and the environment. Especially, R&D-work concerning the post-operational phase of a repository will be intensified. Main objectives are to get a more detailed and realistic modelling of physico chemical phenomena, transport mechanisms and boundary conditions, in order to reduce uncertainties and to replace conservative assumptions by more realistic ones. R&D in this field plays also an important role in building confidence in the safe disposal of hazardous waste. Furthermore, emphasis will be laid on verification and validation where appropriate strategies have to be developed. Natural analogue studies will be used to supplement laboratory and field experiments.

Because of this new R&D concept and the conviction that natural analogues are very useful, the Program Management Group of BMFT (PTE) organized a workshop concerning natural analogues for a repository in rock salt. The papers presented were dealing with the importance of natural analogues, the national and international state-of-the-art and an outlook on possible R&D-work. Because of the positive resonance and the insight into the importance of natural analogues also for a repository in rock salt, it was felt that Germany take up R&D in this field of research.

As a first consequence of this workshop an expert group was established. Experimenters, modelling experts and performance assessment analysts from various institutions are serving in this group. The initial task was to define the essential processes for a repository in rock salt and try to find analogues for these processes in order to make proposals for future systematic R&D-work which will be implemented in the R&D-program of the BMFT.

The discussion to define these essential processes and their corresponding analogues were based upon results of systems analysis studies carried out for different repository concepts for a repository in a salt dome (Fig. 1). Additionally several processes and parameters which play an important role were discussed (Fig. 2) . The preliminary result of the discussions is summarized in Fig. 3 - 6, which show the important processes and the possible corresponding analogues. Furthermore the expert group proposed topics which have highest priority. These topics deal with the near field (retardation of radionuclides by materials in the near field), the performance of the barrier salt rock and the far field (migration and retardation of radionuclides during transport within the overlying strata). These proposals are relatively concrete and are therefore a basis for R&D-work. At present, this summary may be still incomplete and can be completed through future discussions. But we think it surely is the first step to start R&D-work pertaining to natural analogues.

One point which remains to be discussed within the expert group is public relations work. You may know that in Germany there is a very ambiguous attitude against nuclear energy. Therefore, it is our obligation to inform the public in an adequate, that means understandable, way to give insight in our work and to build confidence. I think your video on natural analogues is a very important step and a good example for pr-work.

Some of you may be of the opinion that the work of the NAWG as a whole was successful, even without German participation. Surely, that is correct. But it is worth considering the advantages of a German participation in the NAWG.

One can imagine the exchange of information and data which can be of interest in your work. An extended braintrust could give new insights and impulses. The possibility for verification and model validation may exist. Access to information and data available in eastern Germany's research institutes and via scientific connections cooperation and data transfer with countries of the former Soviet Union could be possible. These are by far not all points which suggest a German participation in the NAWG. Further discussions about the modalities of cooperation, tasks, fields of research and interests would be necessary.

In my talk I tried to give a short view on ideas and plans to intensify and to systematize German R&D-work in the field of natural analogues. The importance of natural analogues concerning performance assessment is accepted. The first step which supports this opinion was to establish the expert group, the next step will be the implementation of natural analogue studies in the framework of the R&D-program of BMFT and finally the start of real work. But we think an essential step towards this goal would be a German membership in the NAWG.

Thank you very much for your attention.

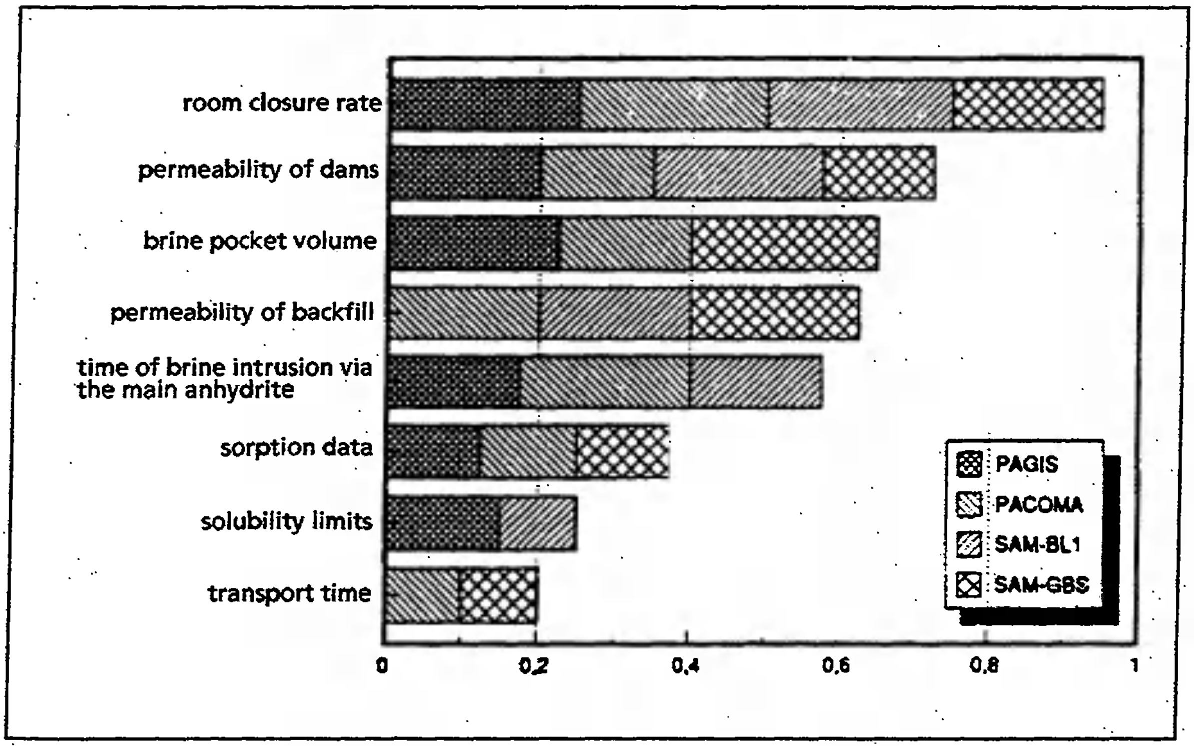

***Fig. 1:* Relevant Processes which Influence Radionuclide Transport (Results of Sensitivity Analysis Calculations, GSF)**

- Geologic and climatic changes
- Subrosion and rise of the salt dome
- Behavior of the barrier "salt rock" after thermal impact
- Corrosion of glass matrix and container material
- Mobilisation and retardation of radionuclides within the near field
- Radionuclide release into the overlying strata
- Migration and retardation of radionuclides during transport within the overlying strata
- Radionuclide migration within the biosphere

***Fig. 2:* Processes and Parameters which are Important for the Long-Time Isolation of Waste in a Repository in Rock Salt**

Corrosion of Waste Matrix and Container Materials

- HLW-glasses: corrosion of natural glasses in salt lakes, sea-water and salt rock
- UO_2-fuel: alteration of uranium ore in different deposits (oxidation/reduction)
- Container: rails and wire ropes in rock salt and salt solutions (salt mining)
- Cement: concrete stuctures in sea-water
- Bitumen: bituminous body in anhydrite

Retardation of Radionuclides by Materials in the Near field

- Corrosion products of waste matrix and container materials: distribution of trace elements in the presence of salt solutions materials, basaltic rock
- mineral backfill materials: distribution of trace elements in concrete materials in the presence of salt solutions
- salt rock: distribution of lanthanides and other trace elements in salt clay in interaction with salt solutions

Solubility Limits and Precipitation of Radionuclides

- Observation of solutions stored on the surfaces of fissures, cracks and other voids and analysis of trace element content

Creep Closure of Open Space in Salt Rock (with/without backfill, solutions, waste)

- time dependence: observations in old rock salt mines
- final state: genesis of salt rocks

Behavior of Geotechnical Barriers

- permeability development: condition and characteristics of old structures
- long term stability: condition and behavior of old structures in sea-water

Fig. 3: Natural Analogues for the Near Field

Performance of the Barrier Salt Rock

- macroscopic: size and flow mechanisms of solutions stored on the surfaces of fissures, cracks and other voids in salt rock
- microscopic: migration of fluid inclusions in the geologic past

Transport of Radionuclides on Pathways through the Salt Rock into the Overlying Rock

- composition of crack fillings and residue solutions, migration in salt clay and anhydrite, migration of trace elements

Mechanical/geochemical Behavior of Salt Rock after Thermal Impact

- basalt intrusions in the geologic past

Fig. 4: Natural Analogues for the Salt Dome

Migration/Retardation of Radionuclides during Transport within the Overlying Strata

- Sorption, colloid/humate transport and microbic influence: analysis of trace element distribution between groundwater and mineral surface as well as colloids and humates at a site; transport of U, Th and rare earth elements out of sedimental uranium deposits
- Dispersion: transport of non-sorbing materials out of spatially limited deposits

Fig. 5: Natural Analogues for the Far Field

- Integrity of the Salt dome after Thermal Impact and Seismic Processes: no NA found
- Subrosion of the Salt Dome, esp. after Ice Ages: no NA found
- Impacts of Climatic Changes (Ice Ages, Sea-Level Alterations) on the Stability of the Salt Dome and the Processes within the Overlying Strata: no NA found

Fig. 6: Natural Analogues for Future Geologic/Tectonic and Climatic Processes

SESSION 2: NEAR FIELD PROCESSES AND PERFORMANCE ASSESSMENT IMPLICATIONS

Chairpersons: F. Gera (I), W. Glassley (USA)

-	Radionuclide release rates from spent fuel for performance assessment modelling	D. Curtis (USA)
-	Long-term performance of canister embedment	R. Pusch (S)
-	Natural analogues for canister performance?	J. Vira (FIN)
-	Natural analogues for radiolytic processes	B. Hofmann (CH)
-	Testing geochemical models of radionuclide solubility and speciation in natural analogue studies	J. Bruno (E)

Radionuclide Release Rates from Spent Fuel For Performance Assessment Modeling

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Abstract: In a scenario of aqueous transport from a high-level radioactive waste repository, the concentration of radionuclides in water in contact with the waste constitutes the source term for transport models, and as such represents a fundamental component of all performance assessment models. Many laboratory experiments have been done to characterize release rates and understand processes influencing radionuclide release rates from irradiated nuclear fuel. Natural analogues of these waste forms have been studied to obtain information regarding the long-term stability of potential waste forms in complex natural systems. This information from diverse sources must be brought together to develop and defend methods used to define source terms for performance assessment models. In this manuscript examples of measures of radionuclide release rates from spent nuclear fuel or analogues of nuclear fuel are presented. Each example represents a very different approach to obtaining a numerical measure and each has its limitations. There is no way to obtain an unambiguous measure of this or any parameter used in performance assessment codes for evaluating the effects of processes operative over many millennia. The examples are intended to suggest by example that in the absence of the ability to evaluate accuracy and precision, consistency of a broadly based set of data can be used as circumstantial evidence to defend the choice of parameters used in performance assessments.

1. Introduction

In a scenario of aqueous transport from a high-level radioactive waste repository, the concentration of radionuclides in water in contact with the waste constitutes the source term for transport models, and as such represents a fundamental component of all performance assessment models. Under such a scenario, the aqueous concentration of radionuclides will be a function of either their solubility, or their release rate from the host phase. Simplistically, if the rate of release>rate of aqueous transport, then the solution will become saturated and radionuclide concentrations will be a constant function of element solubility. If the rate of release< rate of transport, then the concentration will be a function of the release rate. Processes influencing the solubility and release rate of many constituent radionuclides are poorly understood. This lack of understanding is an uncertainty in model source terms used to assess compliance with regulatory standards of geologic repositories for high-level radioactive waste.

Countries with a once-through nuclear fuel cycle plan to inter irradiated nuclear fuel directly in geologic repositories. As such, an understanding of processes controlling the rate of radionuclide release from *irradiated nuclear fuel* in such an environment is fundamental to the performance assessment process. In irradiated fuel, nuclear products are produced in such abundances that they are often in the host lattice in a state of "artificial supersaturation" (1). At the high temperatures produced during criticality, the resulting mix of elements rearrange to form phase assemblages presumably representing an approach to localized chemical equilibrium. These phase assemblages can generally be characterized as: 1) Metallic minerals and oxide inclusions, in the fuel matrix and at grain boundaries, containing non-volatile fission products. 2) Solid solutions in the UO_2 matrix including non-volatile nuclear products compatible with the fuel mineral structure. 3) Solid phases, in the cooler regions of the fuel rod, containing volatile products. 4) Gaseous bubbles reside within grains, at grain boundaries, in defects and in spaces between the fuel and fuel cladding. (1, 2, 3, 4, 5). The radionuclide source term in a performance assessment model of a spent fuel repository must manifest radionuclide release processes resulting from interaction between groundwater and these radionuclide bearing phases.

The overwhelming majority of long-lived radionuclides in spent fuel is contained in UO_2. This phase is sparingly soluble under chemically reducing conditions. It is generally thought that under such conditions UO_2 will maintain its integrity and thus represent an effective barrier to radionuclide dissemination. Once exposed to oxidizing conditions, UO_2 will accommodate oxygen atoms up to $UO_{2.33}$. Oxidation beyond this form induces major structural changes representing an increase in the molar volume, a physically destructive process in which the surface area of uranium bearing solid phases is increased, enhancing the rate of chemical reactions between solid and water (6). Accelerated tests on spent fuel (irradiated UO_2) show rapid oxidation up to $UO_{2.25}$ However, there is a decrease in the rate of oxidation from $UO_{2.25}$ to $UO_{2.33}$ representing a kinetic barrier to the onset of processes that destroy the physical integrity of irradiated UO_2 (7). There are a few reports of the formation of secondary solid phases from laboratory studies of the corrosion of spent fuel or spent fuel surrogates under oxidizing conditions. A phase produced during corrosion studies of spent fuel was identified as dehydrated schoepite (8). Dynamic leaching studies of pellets of unirradiated UO_2 with very small volumes of water over many years produced an assemblage of secondary uranyl oxide hydrates, and uranyl silicates (9). In nature the processes altering uraninite to $UO_{>2.33}$ are complex, variable functions of geochemical conditions. There are more than 160 natural uranium minerals. Most are products of uraninite alteration by oxidizing groundwater. In general the crystal structures, crystal chemistry, thermodynamic stabilities, and paragenesis of such secondary minerals are unknown (6). Currently the most comprehensive information regarding the alteration of uraninite in a large-scale, hydrologically complex system over long time-periods is likely to be obtained from the study of natural systems.

Many laboratory experiments have been done to characterize release rates and understand processes influencing radionuclide release rates from irradiated nuclear fuel. Natural analogues of these waste forms have been studied to obtain information regarding the long-term stability of potential waste forms in complex natural systems. This information from diverse sources must be brought together to develop and defend methods used to define source terms for performance assessment models. This manuscript will attempt to do this in a limited way to encourage a discussion of uncertainties in developing source terms, and experiments that might be done to address these uncertainties.

2. Radionuclide Release Rates in Spent Fuel Natural Analogues

2.1 High-Temperature Reducing Conditions - $^{99}Ru/^{101}Ru$ in Uranium Ore from the Oklo Natural Fission Reactors

Two billion years ago, pockets of rock containing very high uranium concentrations sustained nuclear criticality for several hundred thousand years. During this time copious quantities of nuclear products were formed within UO_2 minerals, the natural nuclear fuel. Under conditions resulting from sustained nuclear criticality, nuclear products were rearranged into phase assemblages presumably representing an approach to chemical equilibrium. New solid phases were formed from the non-volatile/sparingly soluble products. Volatile and soluble products were swept from the reactors and dispersed into the encompassing geologic media. The residual fossils of this unusual phenomenon contain insoluble fission-product-bearing metallic minerals and solid solutions formed by non-volatile nuclear products and the UO_2 fuel. The natural reactor fossils provide a unique opportunity to observe the long-term effects of natural processes on the stability of materials that are close natural analogues of spent fuel. Although conditions during the time of nuclear reaction cannot be defined in detail, the reactor materials interacted with fluids heated to several hundred degrees by the nuclear processes. The fluids were mobile, driven by thermal convection. Fluid compositions contained high concentrations of salts and were reducing. Anoxic conditions sustained for the entire geologic history of the reactor fossils are manifest by pyrite and well- crystallized uraninite.

Because of its half-life - short relative to the time that has passed since it was produced - copious quantities of ^{99}Tc no longer exist in the fossil reactors. However, the geochemical behavior of this fission product during criticality can be deduced from measurements of the isotopic abundance of its stable progeny, ^{99}Ru. A surprisingly constant proportion of the ^{99}Tc produced in the reactors was transported away from the natural reactors. Based upon a correlation in the relative abundances of selected fission products in an array of reactor samples, it was suggested that natural analogues of the anthropogenic fission-product-bearing metallic phases existed in the natural nuclear reactor wastes (10). Subsequent *in-situ* analyses of Oklo samples observed the previously hypothetical metallic aggregates of fission products (11). Thus it appears that, as in anthropogenic spent fuel, upon release from the UO_2 fuel matrix, ^{99}Tc was partitioned between a mobile phase and a stable one. A minimum of 33% of the fission product was removed from the reactor, the remaining proportion was retained in insoluble metallic phases.

The ^{99}Ru (fossil ^{99}Tc) deficiency can be used to calculate the rate of technetium/ruthenium fractionation. If we assume that fission produced ruthenium was quantitatively retained at the site of production and technetium was instantaneously and quantitatively removed upon release from its uraninite host, then the rate of ^{99}Tc removal was controlled by the latter process. Assuming that this loss was continuous at a constant rate for the duration of criticality, then the rate of ^{99}Tc loss can be calculated from the simple mass balance shown in equation (1):

$$\Delta=[\,(^{99}Ru/^{101}Ru)_{fp}-(^{99}Ru/^{101}Ru)_{m}/\,(^{99}Ru/^{101}Ru)_{fp}]/T_f \qquad (1)$$

Where $(^{99}Ru/^{101}Ru)_{fp}$ is the ratio produced by fission, $(^{99}Ru/^{101}Ru)_{m}$ is the measured ratio, and T_f is the duration of the criticality. Values of T_f (12) and ruthenium isotopic data (10) were obtained from the study of eight samples of Oklo reactor zone 9. Using these data, the rates of ^{99}Tc release in eight samples are shown in Table 1.

Table 1. ^{99}Tc Release Rates from Uranium Ore in the Oklo Natural Fission Reactors

Sample ID	T_f (10^5 yr)	Δ (yr^{-1})
5	0.64	1.3×10^{-6}
4	1.68	1.5×10^{-6}
35	1.90	1.9×10^{-6}
36	2.16	1.7×10^{-6}
15	5.56	0.6×10^{-6}
16	2.78	0.9×10^{-6}
30	1.81	1.6×10^{-6}
28	1.42	2.3×10^{-6}

The average of the results is $1.5 \pm 0.5 \times 10^{-6}$ yr^{-1}.

2.2 Low-Temperature Reducing Conditions - ^{99}Tc/U in Cigar Lake Uranium Ore

Cigar Lake is an ore body 450 m below surface at the contact between Middle Proterozoic (1.5×10^9 yr) sandstone and Lower Proterozoic/Archean metamorphic basement in the Athabasca Basin of northern Saskatchewan, Canada. Thick lenses of high-grade uranium occur in a clay-rich mineralized zone. Uraninite (UO_{2+x}), the principal uranium bearing mineral, occurs as two types, each distinguished by texture and composition. Much smaller quantities of uranium are contained in the silicate mineral coffinite. Petrographic properties show evidence of uranium mineral alteration in Cigar Lake ore. Alteration is probably the consequence of hydrothermal events of $>10^7$ yrs ago (13). However, coffinite petrogenesis is complicated, and it is possible that minor quantities of it may reflect low temperature uraninite alteration in the ore zone. Many properties of the ore body indicate that redox conditions have been reducing throughout its history.

The Cigar Lake mineralized zone, overlain by a highly permeable sandstone aquifer, has a characteristic low permeability so that groundwater flow is largely deflected over and around it. Any flow through the mineralized zone is fracture controlled. Water in the ore zone can be characterized as dilute, neutral to alkaline, and reducing (14). The aqueous composition is the result of interaction between sandstone formation water, and rocks in an overlying hydrothermal alteration halo and the ore body (14). Typical uranium concentrations in water from within the ore zone are 12 ppb and 4 ppb in the water from the surrounding sandstone. Geochemical and hydrological conditions in the Cigar Lake uranium deposit are such that the rate of mineral degradation is expected to be very slow.

In a uraniferous environment such as the Cigar Lake deposit, the rare natural radionuclide ^{99}Tc is produced in measurable quantities by natural fission processes in uranium minerals. Rates of natural ^{99}Tc release from uranium host phases can be inferred from measures of ^{99}Tc and uranium abundances, and an understanding of the systematics of the nuclear processes that produce the natural fission product (14). Such measures show large enrichments of ^{99}Tc in regions of the deposit with relatively low (<10%) uranium concentrations, and small to undiscernible ^{99}Tc deficiencies in samples containing extreme enrichments of uranium. The results are consistent with the loss or gain of sub-picograms of ^{99}Tc per g of uranium, concentrations that represent small relative deviations from undisturbed concentrations in rocks containing large quantities of uranium and larger deviations from equilibrium concentrations in rock containing smaller quantities of the actinide element.

Characteristics of ^{99}Tc in Cigar Lake samples are distinctly different from those in spent fuel. Information from the natural experiment is not directly relevant to the release rate of ^{99}Tc from spent fuel, where the fission product is largely contained in metallic phases. However, in nature ^{99}Tc is useful for studying the corrosion rate of its host phase, a natural analogue of UO_2 in spent fuel. The natural experiment involving the release of ^{99}Tc from Cigar Lake uraninite is analogous to the one described by Forsyth and Werme (8) in their spent fuel leaching experiments. " The release of ...uranium, is solubility-limited and hence measurements...[of its] concentration .....cannot yield quantitative measures of the ongoing dissolution process or processes.... it is useful to measure the release of ...fission products which are monitors of the corrosion rate of the ...matrix. This requires that fission product 'monitors' be homogeneously distributed throughout the fuel and that their solubilities in...[the aqueous phase] be sufficiently high so that solution saturation is not attained." In natural uranium minerals ^{99}Tc is produced *in-situ* by uranium fission and is thus distributed homogeneously throughout the mineral grains. Although technetium is sparingly soluble under some reducing conditions, the quantities in Cigar Lake samples are very small and we will assume for this purpose that contacting solutions are not saturated, and thus ^{99}Tc serves as a "monitor "of the long-term uranium mineral corrosion rate under the operative geochemical conditions.

A mathematical model may be constructed relating the state of radioactive disequilibrium between the daughter ^{99}Tc and the parent U to the radionuclide release rates (15,16):

$$\Delta = - \lambda_{^{99}Tc}(1-\alpha) / \alpha \qquad (2)$$

The construction of the model assumes that measured daughter/parent ratios reflect a state of dynamic equilibrium established by the nuclear processes *and* a continuous release of ^{99}Tc. The model describes the relationship between the fractional release rate (Δ), the radioactive decay constant for the daughter radionuclide ($\lambda_{^{99}Tc}$), and the ratio (α) of the measured (parent/daughter) to the (parent/daughter) at secular equilibrium. The assumption of a first order process exclusively involving daughter loss is reasonable if the quantity of released radionuclide is below the solubility limits of radionuclide bearing solid phases, if the radionuclide is not coprecipitated with secondary phases, and if it has no sorptive properties. Technetium-99 is likely to meet these criteria in many natural settings. Table 2. includes model dependent release rates calculated for all ^{99}Tc deficient samples from Cigar Lake.

Table 2. ^{99}Tc Release Rates from Cigar Lake Uranium Ore

Sample ID	Δ (yr^{-1})
CS-604	8.6×10^{-8}
CS-615	1.4×10^{-6}
CS-620B	1.8×10^{-6}
CS-627	1.5×10^{-7}
CS-235L	1.9×10^{-6}

Determined in this manner, an average fractional "corrosion rate" of uranium minerals in the Cigar Lake deposit is 1.1×10^{-6} yr^{-1}. A value remarkably similar to the one obtained from considerations of fission product Tc/Ru fractionation in the Oklo natural fission reactors.

2.3 Low-Temperature Reducing Conditions - ^{129}I/U in Cigar Lake Water

Like ^{99}Tc, measurable quantities of ^{129}I are produced in uranium ore at the Cigar Lake deposit. Measures of this rare radionuclide in water in contact with ore are unambiguous evidence of radionuclide release from the host minerals. We have a few measures of ^{129}I in groundwater extracted from the ore zone at Cigar Lake. The ^{129}I/I ratios in these water samples are orders of magnitude greater than produced in the atmosphere, and thus certainly contain quantities of the fissiogenic isotope released from the ore. The ^{129}I/U ratios are thousands of time greater than secular equilibrium values manifesting the preferential release of daughter relative to the parent. These measurements, along with a knowledge of ^{129}I concentration in the uranium ore in contact with the water, and the water residence time can be used to calculate the rate of ^{129}I release. Assuming that ^{129}I is a "monitor" element, this would be a measure of the host uraninite corrosion rate. The calculation can be made using equation (3):

$$\Delta = [([^{129}I]_{aq})(\rho)/([^{129}I/U]_{eq})(U_{ore})](T)^{-1} \qquad (3)$$

$[^{129}I]_{aq}$ concentrations of 6×10^{-18} M and 2×10^{-19} M have been measured in groundwater samples from two locations in the ore body (18); ρ, the porosity of uranium ore at Cigar Lake, is assumed to be 10% (14); $[129I/U]_{eq}$ is 4×10^{-12}, the calculated bulk ore equilibrium ratio(14); U_{ore} is 8%, the average Cigar Lake ore grade (14); and T, the water residence time in the ore body, is assumed to be 5×10^4 yr (14). Using these values, the calculated fractional release rate of ^{129}I in the two samples are shown in Table 3.

Table 3. ^{129}I Release Rates to Cigar Lake Groundwater

Sample ID	Λ (yr-1)
79-BL	9×10^{-9}
220-AL	3×10^{-10}

These results are two to four orders of magnitude less than the ^{99}Tc release rates from uranium ore. Because the disparate results are determined from samples of the same system, they cannot both be representative of uraninite corrosion rates in that system. For the desired purpose of bounding uraninite corrosion rates to be used in performance assessments, theses differences must be rationalized, and one of the calculated results discarded as erroneous. Calculations using $[^{129}I]_{aq}$ are extremely parameter dependent. It is likely that an extremely heterogeneous geologic environment such as an ore body, parameters describing the rock that the water has contacted cannot be accurately defined by a single value. The apparently low release rates may reflect dilution of ^{129}I concentrated solutions from the highly uraniferous rock with water containing little ^{129}I from the surrounding sandstone. Assuming the validity of such an argument, the results calculated directly from ^{129}I in water samples would be considered to be unrepresentative of uraninite corrosion rates under the conditions at Cigar Lake.

2.5 Oxidizing Conditions - Uranium oxidation in the Peña Blanca analogue

The Nopal I ore body in the Peña Blanca uranium district, Chihuahua Mexico is a large concentrated mass of uranium in a geologic and geochemical environment similar to the potential repository site at Yucca Mountain, Nevada. The Peña Blanca deposit resides in Tertiary silicic tuff near the surface, in a hydrologically unsaturated oxidizing zone one hundred meters above the water table. Exposure to oxidizing groundwater has altered most of the primary uraninite to a suite of uranyl silicate minerals (17).

Murphy & Pearcey (17) present arguments to suggest that the rate limiting step for uranium transport from samples is the solubility of the secondary phase assemblage. However, " ...dissolution of natural uraninite and/or partially oxidized spent fuel may control release of trace or minor elements that are not effectively incorporated in secondary solids." So for our purposes, the rate of dissolution/alteration of natural uraninite should be comparable to the rate of release of "monitor" radionuclides from spent fuel leaching studies. Murphy & Pearcey formulated the model of the rate of uraninite oxidation shown in equation (4):

$$R_0 = (U_e/t) + FC \qquad (4)$$

R_0 is the uranium oxidation rate, U_e is the mass of uranium currently in the ore body, t is the duration of oxidation, F is the water infiltration rate, and C is the uranium concentration in the groundwater leaving the system. Using field based data to evaluate these parameters, the authors conservatively estimate that the fractional oxidation rate at the Peña Blanca site has been 3.7×10^{-4} yr-1. This value would then be comparable to the fractional release rate for "monitor" elements. It is two orders of magnitude faster than the release rates calculated under anoxic conditions at Cigar Lake and Oklo. Although the methods of determining these values are distinctly different at the different sites, the results are consistent, in that the understanding of processes affecting release of monitor elements from uraninite anticipates that the processes will be more rapid under oxidizing conditions than under reducing ones.

3. Radionuclide Release Rates from Spent Fuel Laboratory Analogues

Traditionally radionuclide release rates used in model calculations are derived from laboratory based leaching studies. Such studies of spent fuel or spent fuel surrogates have been done since the 1970's. There have been more than 30 reports written on these tests. The works have investigated the kinetics of dissolution and the resulting release of fission products and actinides over a range of conditions. Recently reported results from different laboratories are used here to provide a perspective on release rates determined form laboratory studies. A more comprehensive survey of the literature on this subject would certainly provide additional insight. Forsyth and Werme (8) reported the results of leaching tests on spent fuels from the Swedish reactor program. These tests lasted for several years and were conducted under oxic and anoxic conditions at room temperatures. If ^{90}Sr is an effective monitor of the corrosion rate of the fuel matrix, the cumulative release rates are about 7×10^{-4} yr^{-1} under oxic conditions and about 2×10^{-4} yr^{-1}. under anoxic conditions. Release rates of ^{137}Cs and ^{99}Tc were faster, presumably because significant portions of these elements reside outside the fuel matrix where they were more accessible to the leaching solutions. Release rates inferred from actinides were less than those for ^{90}Sr reflecting solubility controls on the concentration of actinides in the leachates.

The release rates under oxidizing conditions are acceptably consistent with those determined for oxidizing conditions at the natural analogue at Peña Blanca. However, the rates measured in the laboratory under anoxic conditions are two orders of magnitude faster than we inferred from the data at Oklo and Cigar Lake. In the laboratory work, the measured effects are small, and the authors offer the possibility that the results do not reflect the release rates controlled by UO_2 dissolution, but rather are the result of "preferential corrosive attack at zones in the fuel enriched in ^{90}Sr". In this case the fraction of ^{90}Sr release would be dominated by processes other than spent fuel corrosion, and calculated rates of corrosion would be upper limits on the actual rates produced under the conditions established in the laboratory tests. This would explain the large discrepancy between results from the laboratory and those from analogous natural systems.

Stroes-Gascoyne (18) performed short-term leaching tests on spent CANDU fuel. These tests were done at temperatures of 100°-150° C for 30 days. A wide variety of leachates ranging from distilled water to brine, were used under both oxic and anoxic conditions. Total fractional release of the "monitor" element ^{90}Sr for the 30 day leach period ranged from 3.5×10^{-6} to 3.5×10^{-3}. The fastest of these rates were the result of leaching with high-salinity water. There was a general trend of greater release rates under oxic conditions than under anoxic ones. For purposes of comparison with previously discussed results, a simple extrapolation gives a range of fractional yearly release rates of 1.3×10^{-3} yr^{-1} to 1.3 yr^{-1}. These rates are quite high. The author of this work speculates that the short-term release rates do not reflect the cumulative corrosion rate of spent fuel matrix, but rather reflect the release of ^{90}Sr residing at grain boundaries produced by the decay of mobile radioactive precursors such as ^{90}Br, ^{90}Kr etc. In the Canadian program, these values are used to evaluate release rates for the instant-release source term.

4. Conclusions

Examples of measures of radionuclide release rates from spent nuclear fuel or analogues of nuclear fuel have been presented. Each example represents a very different approach to obtaining a numerical measure and each has its limitations: the result is model limited, or limited by uncertainties in key parameters, or conditions do not mimic those of a particular repository site, or the process duration is extremely different than that considered in the performance assessment, or the material is a poor analogue of spent fuel, etc. There is no way to obtain an unambiguous measure of this or any parameter used in performance assessment codes for evaluating the effects of processes operative over many millennia. The examples are not intended to be comprehensive, but rather to suggest by example that in the absence of the ability to evaluate accuracy and precision, consistency of a broadly based set of data can be used as circumstantial evidence to defend the choice of parameters used in performance assessments. As a matter of procedure, I suggest that all relevent information regarding radionuclide release rates be gathered into a data base. A very abbreviated version might look similar to that shown in Table 4.

Table 4 . Uranium Mineral Release Rates

Source	Type	Monitor	Parameters			Δ	Comments
			Solid	Redox	T (^{0}C)	(x10^6/yr)	
Oklo	Natural	^{99}Tc	Uraninite	Reducing	400^0	1.5	Model
Cigar Lake	Natural	^{99}Tc	Uraninite	Reducing	25^0	1.1	Model
Cigar Lake	Natural	^{129}I	Uraninite	Reducing	25^0	0.005	Model
Nopal	Natural	U	Uraninite	Oxidizing	25^0	370	Model
SKB	Lab	^{90}Sr	Spent Fuel	Oxic	Ambient	700	5 Year
SKB	Lab	^{90}Sr	Spent Fuel	Anoxic	Ambient	200	5 Year
AECL	Lab	^{90}Sr	Spent Fuel	Oxic	Ambient	1,300,000	30 Day
AECL	Lab	^{90}Sr	Spent Fuel	Anoxic	Ambient	1,300	30 Day

Such a data base would then be "scrubbed" seeking explanations for inconsistencies in the data. Editing this data would eliminate data from the AECL study as being inappropriate for the process of interest. The release rates determined from the ^{129}I monitor at Cigar Lake might be excluded because of the difficulty in obtaining meaningful model parameters. Laboratory data obtained under reducing conditions from SKB would have to bereconciled with release rates deduced under reducing conditions at Oklo and Cigar Lake. If the purpose was to ascertain release rates in an unsaturated tuff, perhaps experiments with ^{99}Tc similar those at Cigar Lake could be done at the Nopal deposit in Peña Blanca. Once the data was appropriately "scrubbed" and additional work completed, the performance assessor would have a data set that constituted a defendable basis for selecting radionuclide release rates used in the assessment.

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LONG-TERM PERFORMANCE OF CANISTER EMBEDMENT

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MECHANISMS OF DEGRADATION OF SMECTITE CLAY IN BENTONITIC MATERIAL

Smectite-rich clay embedment of HLW-canisters will be exposed to a temperature gradient and to electrolytes contained in the groundwater. The long-term chemical stability of smectite depends on temperature and groundwater composition in a very complex way but under commonly prevailing pH conditions the most probable alteration of smectite (S) is conversion to non-expanding hydrous mica ("illite", I), which has a crystal structure that is similar to that of montmorillonite but with a higher lattice charge due to partial replacement of tetrahedral silica by aluminum, and with the interlamellar space -defined in Figure 1 and visualized in Figure 2 - collapsed through replacement of the hydrated cations by non-hydrated potassium. Such conversion is assumed to take place in two ways: 1)

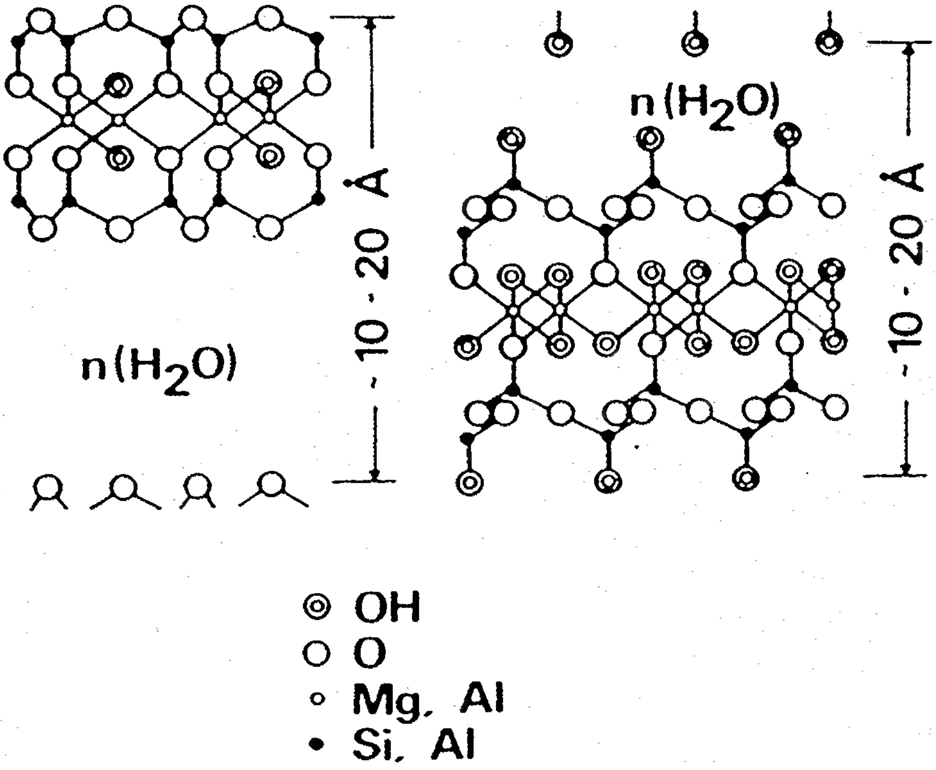

Figure 1 The montmorillonite lattice. Left: Common condition (Hofmann/Endell & Wilm). Right: Possible condition for Na or Li as adsorbed interlamellar cation and temperatures below about 150°C (Edelmann(Favejee)

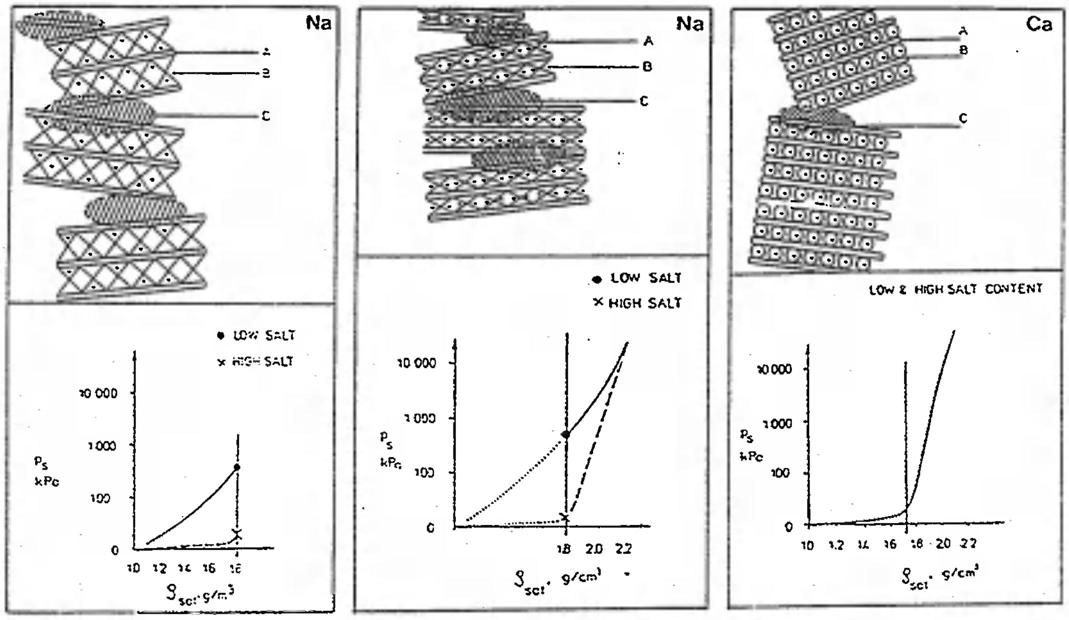

Figure 2 Schematic pictures of stack assemblages and influence of density (at water saturation) and salinity on the swelling pressure of Na and Ca montmorillonite clay. A) Flake, B) interlamellar space, C) Stack contact with interacting electrical double-layers. Left and central: Na clay, Right; Ca clay [5]

replacement of tetrahedral silica by aluminum and uptake of external potassium, leading to mixed-layer (I/S) minerals with successively dominating I, and 2) neoformation of hydrous mica in the voids of the smectite clay that supplies silica and aluminum or magnesium, while potassium enters from outside and triggers crystallization of hydrous mica as indicated in Figure 3 [1]. The I/S conversion, which is commonly assumed to take place stepwise yielding irregular or regular stratification, is believed to reach a final state with around 80-90% I and 10-20% S, as concluded from comprehensive field investigations particularly in the Mexican Gulf area. Neoformation of illite is expected to take place at suitable concentration of silica (H_4SiO_4), aluminum and potassium, yielding crystal nuclei in the form of laths. When precipitation takes place in the potassium concentration drops locally and the concentration gradient thus formed brings in more potassium by which the process continues. Geochemical codes tend to indicate that illite should be formed from smectites in a certain "window" of phase diagrams of silica, aluminum and potassium [2], but they do not seem to be able to indicate whether the conversion takes place via mixed-layer mineral stages or by dissolution/neoformation.

There is in fact a second conversion mechanism involved in the degradation of smectite, namely formation of chlorite [3, 4]. However, the similar behavior of illite and chlorite and the smaller amount of chlorite allows us to disregard from the latter mineral in this context.

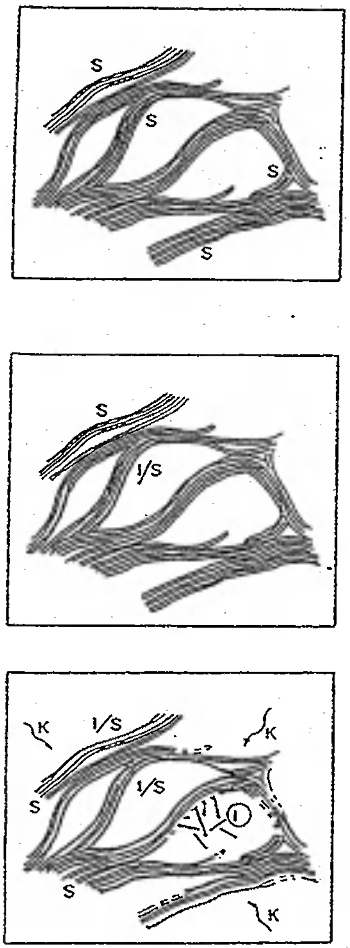

Figure 3 Schematic picture of conversion of smectite to illite via mixed-layer mineral formation or dissolution/neoformation

The smectite mineral formed by Si-to-Al substitution in tetrahedral positions is termed beidellite and it is the dominant mineral in certain natural smectite deposits, like in Spain. It is not suitable for use in repositories intended for long-term performance since the only requirement for conversion to illite is uptake of potassium, provided that the mixed-layer conversion model applies.

While neoformation of illite is an intelligible process that has also been documented in hydrothermal experiments [3], mixed-layer formation is not an easily imagined process because the smectite-to-illite conversion involves collapse of the stacks of flakes that requires either a high effective pressure and a temperature exceeding about 60°C, or drying. When heating only partly saturated clay, capillary forces may cause stack collapse and experience tells that cyclic wetting/drying yields permanent collapse and conversion of montmorillonite to non-expandable 10Å minerals which appear as illite but are not true minerals of hydrous mica type. While interlamellar dehydration of fully water saturated montmorillonite with calcium or potassium as exchangeable cations can be imagined as a successive loss of hydrates of these cations, the mechanism may be different in lithium and sodium montmorillonite. Thus, assuming that the hydrated montmorillonite crystal lattice is of the Edelmann/Favejee type one would expect that heating to a critically high temperature would invert the protruding tetrahedrons to the state they have in the Hofmann/Endell/Wilm structure. The interesting thing is that such inversion would be associated with an unstable state of the silica contained in the altered tetrahedrons, i.e. roughly ¼ of the total number of silicons, which would imply release of them and conversion to beidellite provided that aluminum enters the reformed tetrahedrons [4]. The released silica is expected to be precipitated at the periphery of the stacks forming cementing bonds since the porewater will already be largely saturated with silica.

There is, however, another factor that makes the mixed-layer conversion somewhat dubious and that is the required replacement of the initially present interlamellar cations by potassium. The fact is that the affinity for potassium is not much higher than that for sodium, which is present at much higher concentration than potassium in most groundwaters, and that the affinity for calcium is significantly higher than for potassium. Thus, it is hard to believe that potassium can enter and replace initially present interlamellar cations except, possibly, when potassium is present at much higher concentration in the porewater than sodium and calcium in electrolyte-rich groundwater. This seems to be a very rare condition.

Provided that transformation from montmorillonite to beidellite is related to a critical temperature it is expected that Ca-montmorillonite is more stable than Na-montmorillonite when this temperature is reached and this also seems to be the case [4]. This would naturally offer a possibility to accept temperatures of 150-200°C as would also the use of certain other smectite minerals like the magnesium-rich saponite and the iron-rich version nontronite, for which no heat-related transformation between different crystal forms has been proposed, but the risk of complete dehydration still suggests that the maximum temperature be kept below 100-110°C. The major reason for this recommendation is, however, the risk of cementation that may arise from the temperature gradient that prevails in deposition holes and tunnels. Thus, dissolution of the smectite minerals will yield more silicon and aluminum in the hot zone near the canister and less of these elements at the colder clay/rock contact, and the concentration gradient is expected to yield precipitation of cementing silica and aluminum compounds throughout the clay profile. Such effects have been noticed in field experiments with hot boundary temperatures of around 170°C and temperature gradients of about 10°C/cm, while they seem to be very moderate at temperatures below 130°C and gradients lower than 1-2°C/cm [5].

The lack of quantitative data for the cementation process calls for appropriate chemical modeling, which is underway in various countries. At present one can only make simple estimates, for which a general model for conversion of smectite to illite proposed by Pytte can be of some help as discussed below [5].

LONGEVITY OF MONTMORILLONITE-BASED BUFFERS AND BACKFILLS

The two major threats to the excellent barrier functions of smectite of any sort are 1) conversion to non-expanding 10Å minerals, and 2) cementation by precipitation of Si/Al compounds.

The rate of conversion of montmorillonite to hydrous mica in the heating period is assumed to be controlled by the access to potassium irrespective of the mechanism of conversion, if the temperature is high enough to provide the clay-water system with silica and aluminum at a sufficiently high rate. Assuming that smectite-to-illite conversion takes place through reorganization of the smectite crystal lattice, this rate is determined by the required activation energy, which is on the order of 20-30 kcal/mole, and applying a model proposed by Pytte for such conversion, the rate of illitization can be estimated for any given K^+/Na^+ [6]. An example referring to a relatively high potassium concentration in the porewater and the activation energy 27 kcal/mole is illustrated by the diagram in Figure 4. The model suggests that insignificant alteration and release of silica will take place in a 2000 years long period with temperatures of up to 90°C, while a 1000 year period with heating at 150°C will convert 50% of the smectite to illite and release significant amounts of cementing silica.

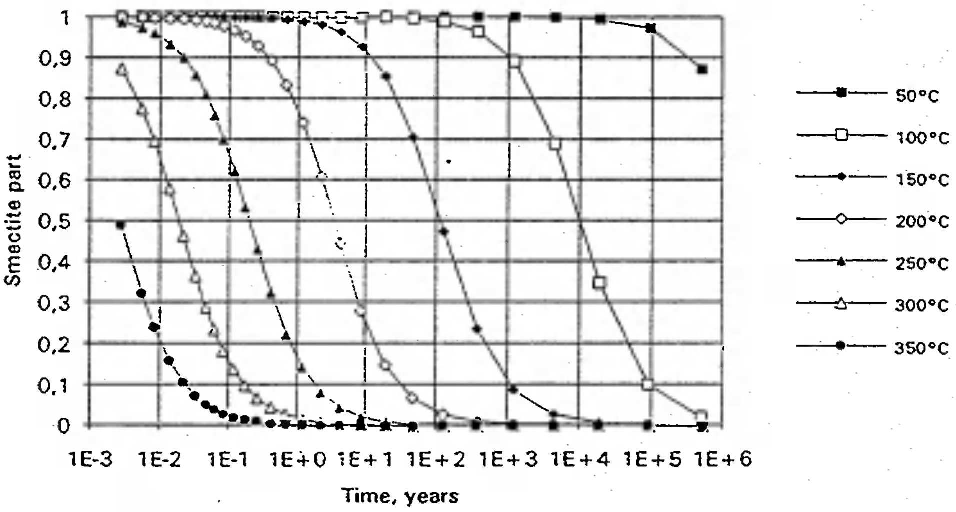

Figure 4 Rate of conversion of smectite to illite using Pytte's model applying an activation energy of lattice reorganization of 27 kcal/mole and appropriate literature-derived constants [cf. 6]. The initial content of smectite is assumed to be 100% (smectite part=1), and it drops to 0 depending on temperature and time

Nature provides several geological examples of smectite-to-illite conversion that are in reasonable agreement with this model but there are indications that the conversion is considerably slower in certain cases. This can be explained by limited access to potassium, which successively becomes the rate-controlling factor when the temperature increases beyond about 60°C as mentioned above. The matter of potassium supply is thus of primary importance and needs to be investigated for predicting the performance of smectite-based buffers and backfills.

A classic approach is to regard accessory potassium-bearing minerals in the smectite clay and also such minerals in the rock hosting the clay as the primary source of potassium for conversion of smectite but this does not seem to be entirely true. Instead, the potassium content of the groundwater may be the major supply of this element, at least at temperatures below 100°C at which potassium-bearing minerals like feldspars and micas are relatively stable. This would imply that the groundwater motion along deposition holes in repositories is of major importance. Thus, under stagnant conditions, migration of potassium takes place by diffusion, which delays the conversion very much, while moving groundwater will bring in potassium at a rate that may keep up the concentration at a level that produces quick conversion. Hence, in addition to the K^+-content of the groundwater, the hydraulic conductivity and gradients are determinants of the conversion rate in practice.

KBS3

Confining ourselves to discuss KBS3 deposition holes one finds, by using relevant hydraulic data and taking the hydraulic gradients as $2x10^{-2}$, that around 10-1000 litres pass along the central and lower parts of a deposition hole per year, which may make 0.4 to 40 g of potassium available for conversion to illite per year. Applying the crude criterion concerning the required amount of potassium for complete transformation from montmorillonite to hydrous mica that potassium must make up 5-10% of the solid mass, it is clear that complete alteration of the 15-20 t of montmorillonite in each hole will take hundreds of thousands of years. Insignificant changes in physical behavior are expected in the heating period.

In the period when temperature gradients prevail in the buffers and backfills, silica will also migrate from the hot part of the clay to colder parts where it is expected to precipitate in the form of cristobalite or amorphous silica, causing cementation. There are no physico/chemical models that describe this process but a rough estimate can be made by application of Pytte's model of smectite-to-illite conversion. This model suggests that 10% of the montmorillonite mass is converted in 100 000 years at 70°C, while less than 1% will convert in the heating period. Since 100% conversion will take place only through beidellitization, the ultimate amount of silicous cementing precipitates will not exceed 1% of the bentonite clay mass in the deposition holes, which is totally negligible in the few thousand years long heating period. However, this is under isothermal conditions and since the temperature gradient that prevails in the first few hundred years cause migration of released silica and aluminum from the hot zone near the canisters to the colder clay/rock boundary, some additional cementation is expected. Also, enrichment of cementing substances of low solubility at higher temperatures, like sulphates, will take place in the hot zone as long as temperature gradients prevail.

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NATURAL ANALOGUES FOR CANISTER PERFORMANCE?

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ABSTRACT

Corrosion behaviour of waste canisters seems to be one of the few areas where natural analogues have been directly applied in performance analysis. Studies of archaeological objects and native existence of canister materials have been used to support models and estimates. None of the studied cases are truly representative of the conditions in the planned repositories, but they do confirm that important processes are understood. In general, the uncertainties as to canister performance seem to be small in relation to uncertainties in the safety analysis of final disposal as a whole, but noting the emphasis placed on the canister in some planned disposal systems, additional evidence would probably not be overlooked, in particular, if it came from conditions sufficiently similar to those at disposal.

1. Introduction

Present nuclear waste management practices for high-level waste (HLW) aim at complete isolation of radioactive substances from the living environment. Although it is technically impossible to guarantee such perfect isolation for good, protection objectives usually span periods that sound eternal from the perspective of human life. Depending on whether the spent fuel is reprocessed or not it will take thousands or hundreds of thousands of years until the radiotoxicity of the waste has decreased to the level of the original natural uranium. If the comparison is based on the levels of radioactivity alone, it will take millions of years for unreprocessed spent fuel to reach the level of the original uranium ore. These are the time periods that one often comes across in the discussion of protection criteria for final disposal.

There is some international consensus on the fundamental safety principles of HLW disposal. For individual protection the dose or risk criteria suggested in various countries are fairly similar – or consistent – but there are important differences as regards the period of concern. In Switzerland the regulations provide no time limit, whereas in U.S. and Canada it suffices to prove the safety for the first 10,000 years. In the Nordic proposal for criteria 10,000 years is considered reasonable for individual dose calculations, but one million years is suggested as the ultimate limit of concern. The length of the period of concern is likely to have implications for the design of the multibarrier system.

Another factor affecting the barrier design is the waste form. The cases of Switzerland – where the waste form is high-level reprocessing waste – and the U.S. – where the waste form is spent fuel elements – suggest that there is no direct correlation between the regulatory period of concern and the waste form. However, together they largely determine the requirements for the buffer and canister designs.

In U.S. the regulations require that the disposal package must maintain "substantially complete containment" for a period of 300 to 1,000 years [Bullen 1993]. The Nordic criteria proposal states:" A minimum requirement for the canister lifetime is that it should, at least, prevent the release of the most active radionuclides which decay to an insignificant level within some hundreds of years. In the case of spent fuel disposal, it may be prudent to design for substantially longer periods of initial isolation as the activities of many transuranics decrease significantly within a period of about 100,000 years" [Anon. 1993a]. The present Swiss criteria seem to be on a general level, but they state that "during [the initial phase of around 1,000 years] complete containment of the radionuclides within the repository should be aimed at" [Anon. 1993b].

This is the context where the natural analogues should make their contribution. If the period of concern for the canister performance is some hundreds or thousands of years it may be rewarding to look at historical or archaeological evidence. If we insist on performance substantially longer we may also want to look for geologic analogues. Analogues of both types have been studied and they seem to support existing laboratory and theoretical data. Reviews of these studies have been lately published by both Nagra [Miller et al 1994] and SKB together with TVO [Brandberg et al 1993], and it is hard to add very much to the discussion already presented in these reports. In this paper the focus is on if and how natural analogues have been used in recent performance analyses of waste canisters and what more one could perhaps do.

2. Quest for an ideal canister

The principal purpose of the canister is to facilitate handling and to provide isolation of the waste for an initial period which may be directly set in safety regulations or is defined on the basis of safety analysis considerations. It follows that the canister must provide strength and corrosion resistance in the anticipated repository conditions in a provable manner. Predictability of the canister behaviour is essential for a successful safety case.

Both ceramic and metallic canister materials have been studied but at present only metallic materials (steel, copper and copper alloys, titanium) are being seriously studied. In early stages of the planning ceramic materials like alumina were considered promising [Ahlström

1980] but it turned out hard to predict their long-term behaviour reliably enough.

In Sweden a long-life canister has played a central role in the development of the KBS system for direct disposal of spent fuel. For the dominant granitic rock environment copper has been a natural choice. The KBS-3 design consists of a relatively thick-walled copper canister backfilled with lead. In Finland the conceivable difficulties with casting of molten lead gave rise to development of a composite canister design where the corrosion resistance is, similarly to KBS-3, provided by an outer hull of copper, but inside the copper container there is now another container of steel [Raiko & Salo 1992]. Since the steel gives the canister the desired mechanical strength, lead casting is avoided. SKB has recently decided to adopt a similar design [SKB 1992a].

The Canadians have studied a number of different canister designs. Their present safety analysis is based on a relatively thin-walled titanium container [AECL 1994]. As in Sweden and Finland, the Canadians plan to dispose of the spent fuel directly, without reprocessing, and also in Canada the material was chosen because of its corrosion resistance, but the life-time expectations attached to the canister are fairly modest in comparison with the Swedish and Finnish plans. The same holds for US, where also a fairly short canister life-time has been deemed sufficient. The present performance analyses for Yucca Mountain are based on steel canisters [Sandia 1994]. However, other materials like copper and copper alloys have also been considered [Peters & Kundig 1991].

Steel is the usual choice of canister material in the countries where the spent fuel is going to be reprocessed and the waste form is vitrified HLW. In Switzerland and in Japan a massive 25 cm thick steel container has been considered; thinner walls have been deemed sufficient in several other countries [Pagis 1989].

3. Recent assessments of canister performance

3.1 Copper canisters

SKB's recent safety analysis "SKB 91" pays limited attention to engineered barriers as the main purpose has been to assess the role of geosphere for the safety of disposal [SKB 1992b]. It mainly refers to the earlier assessment of the KBS-3 concept [SKBF 1983a] and states that despite comprehensive research nothing new has appeared that would call for re-evaluation of the KBS-3 assessment. The expected life-time of the canister is estimated to be well over one million years, which is the practical limit for the period of concern suggested in the Nordic proposal for safety criteria.

The SKB 91 life-time estimate is based on one revision to the assumptions of the 1983 analysis. In 1983 it was assumed that the pitting factor for copper corrosion could in the worst case be as high as 25 – although 5 was considered the more plausible upper limit. In the 1991 analysis the high value of 25 is considered unrealistic while 2 is proposed as the most likely value. According to Miller et al [1994] this is one of the few direct applications of natural analogues in performance assessments.

A pitting factor of 25 was considered very conservative already in the 1983 analysis. Such high value was based on a study of copper corrosion in soil during a 14-year period of exposure. However, the 1983 analysis also made use of natural analogues: three studies had looked into the pitting corrosion on (1) archaeological artefacts of copper, (2) a piece of native copper from Lake Michigan area and (3) three earth electrodes for lightning conductors.

The archaeological artefacts consisted of bronze objects and copper coins [Bresle et al. 1983]. Their age could be estimated rather precisely (300 to 3,000 years) but the information about the ambient conditions during the corrosion period was vague. The bronze objects had been found from various soils, the copper coins were from a wreck at the depth of 20 metres, covered by a thin layer of mud. For general corrosion the researchers suggest a value of about 0.2 mm per 1,000 years. This is based both on their own measurements and on an older study by Johnson and Francis [1980] where 40 archaeological objects of ages between 300 and 8,000 years had been studied.

For the bronze objects the pitting factor measured was about 3 while for copper coins they could observe no pitting at all. However, for the piece of native copper the same research team obtained a value lying between 2 and 6. The specimen consisted of a 37 gram piece of copper (purity about 98 %) found from soil with some 60 cm of sand and gravel above it (pH about 8.5). A total of 18 pits in this copper piece were measured for their dimensions, but it was not possible to obtain any value for the mean corrosion. On the basis of information about other comparable objects the authors estimate the mean corrosion to be at least 0.08 to 0.3 mm per 8,000 years. Consequently, the authors warn about the large uncertainty as regards pitting in this natural analogue specimen, and, all in all, the authors suggest that only the information about the bronze artefacts may be representative of true pitting corrosion.

The study of the lightning conductors suggested a maximum value of 5 for pitting factor [SKBF 1983b]. The conductors (copper plates) had been at the depth of 1 to 3 metres in soil (silt or clay) for 50 to 80 years. In this case the find sites could be rather well characterised for their chemistry but there were some uncertainties as to the exposure periods, and the excavations may have caused some disturbances.

Largely based on the natural analogue studies mentioned, the 1985 safety analysis concluded that the probable upper limit for pitting factor was 5, but at that time the analysts could not discard the value of 25, yet. The 1991 analysis does it. Partly this is said to be because of generally less pessimistic tone of the analysis, partly because of

Canadian studies based on extreme value statistics. No new analogue information has been introduced as evidence.

The "Project-90" of the Swedish regulatory authority SKI relies on KBS-3 studies of the copper canister, but the SKI has also made some supplementary calculations [SKI 1991]. SKI agrees with SKB on the expected longevity of the copper canister, but emphasises the stochastic nature of the canister lifetime in the repository conditions.

The "TVO-92" safety analysis makes reference to same studies as SKB 91 and Project-90 and only gives a very succinct discussion of copper corrosion [Vieno et al 1992]. Nevertheless, it lists some further analogue evidence albeit it is used only in a qualitative manner. First, the authors mention the work of Marcos [1989] about occurrence of native copper. In that report a number of natural copper deposits such as the Keweenaw Peninsula in Northern Michigan is described. As Miller et al [1994] note, none of the examples mentioned by Marcos is truly representative of the repository conditions in granite rock, but they may be taken as examples on the fact that copper can survive in quite many kinds of conditions, and at least such evidence rules out the layman's opinion that "nothing is eternal". In the same context Vieno et al. [1992] refer to the very high purity copper chisel of about 4,000 years of age that was found from a lake shore in Finland. It has not been studied in any analogue sense, but as such it certainly gives credibility to beliefs on longevity of copper materials.

Vieno et al. [1992] also mention the Swedish study of a bronze cannon. It sunk with the man-of-war "Kronan" in 1676, stayed for 310 years in the bottom clay sediments of the Baltic sea and then became a subject of a natural analogue study [Hallberg et al 1988]. The cannon has a high content of copper (> 96%) with some tin, zinc and iron alloyed. It was buried in a vertical position and for the most part it was covered by sand and clay materials (illite, montmorillonite and kaolinate). Before the cannon was recovered, a series of samples of the surrounding clay was taken and as it appears that the Eh is decreasing with depth of the clay cover there seemed to be a possibility for comparison of the corrosion behaviour in varying chemical conditions. However, the corrosion products have the same appearance all over the cannon and show no tendency to diminish with depth of the clay cover. It is suggested that oxygen plays no big role in the corrosion process here, although the conditions are generally oxidising.

The identified major corrosion products were cuprite and malachite. After comparison of different corrosion model hypotheses the authors conclude that the dominant source of the copper in corrosion products must be the slag product CuO, which was found to occur as inclusions in the copper matrix. This would explain how the corrosion had reached to as deep as 0.8 mm in the cannon metal. The amount of copper leached from the bronze matrix itself was estimated to be 4 mg/cm^2. This would correspond to a mean corrosion rate of 0.015 µm/year in a pure copper material in oxidising conditions.

The TVO-92 estimate of the canister longevity is based on the availability of sulphide. It is noted that corrodants emerging from the tunnel and from the fissures intersecting the deposition hole may be distributed unevenly on the surface of the canister causing localised corrosion. In estimating the corrosion lifetime of the canister this is taken into account by using a factor of five for uneven corrosion. With overall conservative assumptions Vieno et al [1992] calculate that in conditions roughly similar to those prevailing today at the deposition depth it would take 18 million years for the corrosion to break through the 60 mm copper wall of the ACP canister. Thus, in the most likely scenario corrosion is not a threat for the canister integrity in the period of concern (one million years). Consequently, most of the discussion of TVO-92 is devoted to various exceptional or disruptive evolution cases where the canister was either defective initially or lost its integrity because of some external cause other than corrosion. A complicating factor in the analysis is the double-wall structure of the canister.

3.2 Titanium canister

The Canadian AECL is just completing its extensive safety assessment of its spent disposal concept [AECL 1994]. An important part of the analysis is the performance study of the 6 mm grade-2 titanium canister which they have taken as reference. Crevice corrosion is judged to be the critical factor for canister longevity. However, the lifetime of the canister is estimated to well exceed the 300 – 1,000 year minimum required in the regulations. No explicit reference is made to natural analogue studies in the AECL canister performance assessment; the potential of finding useful analogues may be small as well. Petit [1992] mentions the studies at Cigar Lake where some consideration has been given to longevity of TiO_2 in natural conditions.

3.3 Steel canisters

Natural analogues were not directly used in the 1985 Swiss "Project Gewähr" performance assessment, but archaeological data (from Johnson and Francis 1980) were discussed in the context of the analysis [Nagra 1985; Chapman et al 1984]. If samples from oxidising marine environments are excluded, the archaeological data for iron and iron alloys support the estimate that a service life substantially longer than 1,000 years could be expected for the 25 cm thick steel canister. The Kristallin-I analysis gives further evidence on the conservatism of the canister lifetime estimate but does not bring forth new natural analogue evidence.

It is assumed that the corrosion behaviour of steel is rather sensitive to the ambient chemical conditions and also to the composition of the steel. The latter fact may rule out the study of meteorites as natural analogues of the present steels. However, it is significant that iron artefacts and samples of native iron have sometime survived for long periods even in oxidising environments [Miller et al 1994; Hellmuth 1991]. The reason may be the limited mass transport or, interestingly, the scavenging effect of the ferrous iron in the surrounding media. A famous example of the latter is the Inchtuthil nail pit [see, e.g., Miller et al 1994]. There over a million nails were buried nearly 2,000 years ago; those in the midst of the hoard show only very limited corrosion. The building of protective layer of corrosion products, magnetite in particular, may render the service life of steel canisters in repository conditions much longer than assumed on the basis of uniform corrosion rates.

Steel is used as material in the reference canister designs of the performance assessments made by Sandia [1994]. Both a thin 0.95 cm wall canister and a "robust" double-walled canister (simulating the multi-purpose canister suggested) have been considered, but neither of these is suggested to play a long-term barrier role, as the present assessment models predict a rather rapid corrosion due to the elevated temperatures after emplacement. No direct references to natural analogue information appear to have been made. However, discussion is going on – partly in the context of which kind of criteria should be applied to disposal – if more attention should be paid to canister as a release barrier. Particular interest in being devoted to various copper and aluminium bronze containers and in this context attention has also been brought to natural analogues as evidence of longevity of copper in various natural conditions [Peters et al 1993]. Furthermore, Peters et al [1993] suggest employing an engineered analogue in the repository: using copper container with material from the Keweenaw deposit as a backfill.

4. Further scope for natural analogues?

The conclusion of the TVO-92 safety analysis is that in the most likely case there will never be any significant releases from the spent fuel repository. The strong conclusion is mainly based on the expected high performance of the ACP copper-steel canister. In SKB 91 small leaks due to initial defects in a couple of copper canisters are considered to be statistically possible but they should lead to no significant dose consequences – even if rather weak assumptions are held on the geosphere performance. Thus both analyses attach a major barrier function to the canister.

Similarly both SKB and TVO consider that the corrosion properties of copper have been well explored and there is little need for further studies in this area. The 1992 SKB research programme mentions stress-corrosion cracking and localised corrosion in mildly oxidising environment as possible subjects for corrosion studies, but the creep behaviour of different copper materials may still have the highest priority in canister materials research [SKB 1992a]. The TVO-92 study points out the importance of better understanding of the behaviour of the double canister system after the breech of the copper hull; the uncertainties here are mainly related to modelling the steel corrosion process and the associated hydrogen generation and transport [Vieno et al 1992].

Hence, there is a strong commitment to copper at both SKB and TVO, but there is also good confidence that the commitment is justified. No evidence has shown up which would severely compromise the assessments made. The Swedish and Finnish authorities seem to agree on the principal conclusions, but noting the importance given to the canister, they also call for further studies [SKI 1993, STUK 1994]. For instance, SKI suggests that the canister surface should be subjected to systematic studies. These would be relevant for supporting the conclusions on pitting behaviour, but, additionally, they would give the SKB "an opportunity to further analyse whether any aspect of corrosion exists which has so far not been taken into account (e.g. if any phase exists which has previously not been considered)" [SKI 1993]. Similarly, SKI recommends that SKB should compile a state-of-the art report concerning bacterially induced sulphate reduction and the local corrosion of copper.

The Swiss disposal concept gives less emphasis to the canister performance and its remaining uncertainties; on the other hand, the bentonite buffer is probably conceived as more important than in the SKB and TVO concepts. In the present U.S. performance analysis modelling the barrier effect of the canister is small, but it is recommended that both the modelling aspects – e.g., the temperature dependence of the corrosion processes – and the design issues should be given more attention in the future work [Sandia 1994].

Miller et al [1994] emphasise the need to determine the nature and reactivity of both copper and steel corrosion products. One would need to assess their possible effects if any on radionuclide release and transport processes, but such studies could also address the concerns mentioned by SKI. For steel the investigation of the reinforcing rods in old concrete could provide such data, but for copper good analogue sites may be hard to discover.

Brandberg et al [1993] suggest studying archaeological copper artefacts in wells or springs that have been used for long periods for domestic water supply. In such a case it might be possible to assess the initial and boundary conditions rather reliably. However, with the present knowledge about copper corrosion it seems more than desirable that possible future analogue studies be focused on sites where the conditions are sufficiently similar to those in the planned repositories. Such sites may be hard to find.

As it has been mentioned by Miller et al [1994] none of the copper analogue studies so far made is truly representative of the conditions expected in repositories in granitic rock. A study of a really analogical situation would, of course, make a valuable contribution to building confidence in safety assessments. It could possibly confirm that the meaningful processes – e.g. sulphide attack, bacterially assisted or not – are those predicted. However, the first thing then should be to slate a procedure by which such representative analogue site could be discovered.

Otherwise, other means are likely to be more effective. These other means could be laboratory studies, but it is also important to note that even in SKB and TVO concepts the emphasis is on the whole of the multibarrier system and there must be a reasonable balance in research priorities. It will always be possible to suggest that we may not know everything, but then it is probably much more efficient to concentrate on basic natural laws and well-known physical phenomena (e.g. mass and energy balances, mass transport) and make corresponding bounding calculations to assess the uncertainty than to start looking for what we do not know.

5. Final comment

Miller et al [1994] note that there are probably only two examples of applying natural analogues in performance assessments. They suggest that the reasons lie in the background of performance analysis modellers and their general resistance "to the prospect of pitting their models against a real natural system rather than a laboratory or field experiment, let alone to attempting rigorous validation tests". This may be true to the extent that there may be opportunities for more extensive application, but it may be questioned whether possibilities for rigorous validation by natural analogues of performance analysis models or concepts really abound. The problem may not necessarily be the resistance from the modellers' side but instead the fact that there are too many possible interpretations for the analogue with no means of "rigorously" choosing the correct one.

Good analogues continue to be welcome and their study can valuably contribute to confidence building in performance analysis models and results. How much money should be allocated to them depends on resources available, priorities in their use and alternative ways of providing the desired data or confidence.

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NATURAL ANALOGUES OF RADIOLYTIC PROCESSES

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ABSTRACT

Radiolysis of water results in kinetically active oxidizing (H_2O_2) and kinetically inactive reducing products (H_2), the net result being oxidizing conditions unless redox buffering by steel containers or by other reductants is important. Redox sensitive elements mobilized under oxidizing conditions will likely be retarded at redox fronts developing around waste containers in the near field. In nature, good examples of radiolytical processes are rare. At Oklo, high temperatures prevailed during criticality and the presence of organic carbon prevented development of oxidizing conditions. The Cigar Lake deposit is the currently best quantified natural radiolysis system, with products of radiolysis being present in groundwater and solids. The current low rate of radiolysis in natural systems and the difficulty to distinguish radiolytic effects from other geochemical processes makes natural analogue studies of radiolysis inherently difficult. Topics to be addressed by future studies include: determination of radiolysis rates in several independent systems; role of organics; production of mobility-enhancing species (chelators, volatile species); influence of salinity; influence of radionuclide redistribution. The complementary use of small-scale analogue systems is recommended.

1. Introduction

In concepts of long term disposal of highly radioactive waste and spent fuel (further commonly referred to as HLW) in geological formations, the effects of high dose rates of α-, β- and γ-radiation on the performance of engineered and geological barriers must be considered. Radiolysis, used here as a general term for radiation-induced chemical transformations, will primarily affect groundwater, but trace organics and gaseous H_2O may also be influenced. This paper reviews radiolytical processes involving mobile phases in the near field of a HLW repository and of respective natural analogues. An attempt is made to identify radiolysis-relevant natural analogues that may help to cover gaps in current knowledge. Data from radiolysis experiments in pure systems are abundant, but it is difficult to extrapolate these findings to long term effects in complex rock-groundwater systems. Studies of radiolytical processes in natural analogue situations and experiments using components of natural systems are therefore needed.

Previous reviews of radiolysis-analogues were presented by Chapman et al. (1984), Vovk (1987), Brandberg et al. (1993) and Miller et al. (1994). Vovk (1987) presented an extensive list of radiolytical effects in nature. Based on stringent guidelines, most of this evidence must be classified as uncertain, however, because natural processes other than radiolysis may well be responsible for many of the reported effects.

Radiolysis of water produces reactive radicals (e^-_{aq}, $H^\cdot$, $OH^\cdot$, $HO_2^\cdot$) and molecular products (H_2O_2, O_2, H_2). Radiolysis efficiency is highest for α-, intermediate for β- and lowest for γ-radiation. Molecular hydrogen is less reactive than the simultaneously generated oxidizing species and rapidly diffuses away from sites of generation. As a result of the different kinetics of oxidizing and reducing species, radiolysis of water produces net oxidizing conditions. The efficiency of water radiolysis (expressed as G value: number of species produced/destroyed by 100 eV absorbed energy) is strongly dependent on solutes and bonding of water to surfaces. $G_{(-H2O)}$ in pure water is close to 2.7 (Christensen and Bergbakke 1982), but values up to 15 were cited by Vovk (1987) for brines. The highest yields of radiolysis probably occur in microporous, highly saline water-rock systems where a large proportion of water molecules is present as hydration layers on ions and mineral surfaces (Vovk 1987). In such systems, background concentrations of U, Th and K may result in geochemically significant water radiolysis (Hofmann 1992). Radiolysis in U ores will be strongly dependent on grains size, porosity and water chemistry. Radiolytically produced species containing C, N and S may form as well and possibly influence the migration behaviour of redox sensitive and other elements. Solid, mobile and dissolved organic matter is very susceptible to radiolysis.

2. Effects of radiolysis in HLW repositories

Radioactive material must be in direct contact with water to cause significant radiolysis because radiolysis mainly results from α- and β- radiation. Such a situation will occur only after canisters are breached. The most significant consequence of radiolysis in the near field of a HLW repository is the creation of net oxidizing conditions (qualitatively defined by the presence of O_2, H_2O_2) in the absence of active or radiolytically activated reductants, such as organic matter. Oxidizing conditions are most likely to be created in close proximity to highly radioactive waste material and result in possible enhanced mobility of redox sensitive elements such as U, Ni, Se, Pd and Tc. Uranium oxide in spent fuel may be radiolytically oxidized (Sunder et al. 1989). Although the oxidation effect of radiolysis is expected to be largely buffered by steel containers (McKinley 1985), this effect may be diminished by the formation of oxide coatings on steel.

If radiolysis creates oxidizing conditions near containers, the development of a redox front in the surrounding bentonite (with trace organics and pyrite as reductants) is likely and retardation of radionuclides due to reduction, sorption and co-precipitation will be important. Sharp spatial changes in redox conditions both in porewater and solid phases are commonly observed in nature and referred to as redox fronts (e.g. roll-fronts uranium deposits). Redox fronts are sites of effective retardations of many redox sensitive elements such as U, V, Se, Mo, platinum group elements (e.g. Thomson et al. 1993) and can, due to sorption, coprecipitation or other side effects, also retard non redox sensitive elements such as Ni, Zn, Cd, REE. The development of redox fronts around a HLW repository will likely retard the migration of many potentially hazardous radionuclides.

Quantitative estimates of radiolysis (Christensen and Bjergbakke 1982) and radiolysis-related redox front movement (Romero et al. 1992) are strictly dependent on a number of parameters that are poorly known for actual systems (e.g. influence of salinity). Realistic estimates seem to indicate that the oxidation front is unlikely to extent out of the clay barrier (Romero et al. 1992).

The radiolytic generation of oxidants is a potentially important factor for microbial growth. According to McKinley and Hagenlocher (1993), radiolytically generated species (H_2O_2) are likely to represent only a minor fraction of available electron acceptors. More abundant electron acceptors (e.g. sulfate) are energetically less favourable making microbial interactions with radiolytically produced oxidants potentially important.

Radiolytically produced hydrogen: Due to its inertness, hydrogen will diffuse out from the zone directly adjacent to waste and will ultimately be lost to the country rock, leaving behind the net oxidized area. Hydrogen of radiolytical origin will migrate together with H_2 produced by container corrosion and is a potential carrier of tritium and volatile metallic compounds. Several critical waste elements (Se, Sn) can form volatile hydrides (Ridley et al. 1977, Donard and Weber 1988). The mechanical integrity of the bentonite backfill may be disrupted by the generation of a gas phase. The reducing capacity of H_2 may potentially be catalytically activated in the near field.

Factors influencing radiolysis: The geometry of the water-HLW interface and the accessibility of water will critically influence the efficiency of radiolysis (Neretnieks and Faghihi 1991). While these authors consider two effects reducing radiolysis (limited availability of H_2O at sites of radiolysis due to H_2 evolution, and reduction of porespace by alteration products), radiolysis efficiency may also be enhanced by small-scale redistribution of radionuclides resulting in a larger radioactive surface area causing radiolysis.

Radiolysis of organic compounds: Radiolysis of organics is of limited importance because of the likely limited availability in HLW repositories. Nevertheless, possible sources are mobile organics from host rocks (e.g. black shales), backfill bentonite and microbial biomass. Radiolytic polymerization of organic matter leads to highly aromatic, insoluble polymers with semigraphitic units (e.g. Landais 1993, Leventhal et al. 1986, Lewan and Buchardt 1989, Mossman et al. 1993, Nagy et al. 1991, 1993). Direct polymerization of mobile organic matter on waste material surfaces in a manner similar to that observed on radioactive trace minerals in oil reservoirs (Rasmussen et al. 1989, 1993) may form protective surface layers that may retard dissolution, an effect also reported from Oklo (Nagy et al. 1991). Besides insoluble polymers, radiolysis of organic matter will also produce H_2 (Dubessy et al. 1988). Radiolytic oxidation of organic matter and radiolysis of dissolved inorganic carbon species may lead to the formation of potential organic complexants, e.g. oxalate (Hasselstrom and Henry 1956, Hummel 1961).

Radiolytic alteration of mobile or immobile organic matter may induce strongly reducing porewater conditions. Oxidizing radicals are scavenged by organics, and radiolysis of organics will create reducing organic radicals. Such effects may be responsible for the reducing conditions prevailing in the Oklo reactors (Curtis and Gancarz 1983), confirmed by the absence of O_2 in fluid inclusions from Oklo (Dubessy et al. 1988). The redox buffering capacity of organic matter is further supported by the fact that hematite of probable radiolytic origin, usually common near radioactive minerals, does not occur in the presence of organic matter.

In HLW repositories, several partly competing effects of radiolysis are thus possible. They need to be more thorougly evaluated theoretically and tested in the laboratory and/or by natural analogue studies. Natural analogues of radiolysis are potentially useful for the:

- quantification of oxidizing effects of radiolysis under repository conditions
- study of element behaviour at redox fronts (this is probably most advanced)
- characterization of the fate of radiolytically produced H_2 (catalytic oxidation?)
- investigation of possible radiolytic formation of metastable species that may influence the mobility of critical elements due to complexation or volatilization
- study of the effects of radiolysis of organic matter (generation of reducing conditions, "sealing" of waste, production of organic complexants)

3. Radiolysis in nature: general aspects

Geochemical effects of natural radiolysis processes associated with anomalous concentrations of U, Th (K) are poorly known and not generally recognized by the geochemical community. Evidence of radiolytical processes has been found in a variety of natural environments characterized by very different radiation dose rates. The effects of water radiolysis over geological time periods can be detected by oxidation effects that are restricted to the proximity of U and Th minerals and which most commonly produce ferric iron oxides such as hematite (Fe_2O_3). Although hematite is commonly associated with radioactive minerals, the precipitation of this mineral may be unrelated to radiolysis.

Where hematite is secondary in origin and solely confined to the immediate proximity of radioactive minerals in otherwise reduced (in terms of Fe) rocks, an origin due to radiolytic oxidation of ferrous iron appears likely. An example is the common rimming of accessory uraninite by hematite and the hematite-staining near uranium-rich areas in hydrothermal veins.

4. Radiolysis in nature: specific sites

Oklo: A natural analogue study focusing on radiolysis was performed at Oklo by Curtis and Gancarz (1983). Contrary to predictions based on water radiolysis, they found evidence of iron reduction in the rector zones and used the amount of iron to calculate the minimum amout of H_2 produced. Other redox sensitive elements (U, Mo, Tc) were found to be partly mobilized, however. The precise mechanisms of concomittant Fe reduction and U, Mo, Tc oxidation remains unclear.

Radiolysis of water in the Oklo reactor zones 7-9 is indicated by the presence of H_2-bearing fluid inclusions in quartz as observed by raman spectroscopy (Dubessy et al. 1988, Savary et al. 1993). Radiolysis of water prior to trapping is assumed by these authors. In contrast to other high-grade uranium deposits, no oxygen was detected in the Oklo inclusions. This was attributed to the presence of organic matter (Dubessy et al. 1988). The fact that hydrogen may leak from fluid inclusions in quartz at elevated temperature (Mavrogenes and Bodnar 1994) casts some doubt on the proposition that H_2 and O_2 were enclosed during fluid inclusion trapping (Dubessy et al. 1988). This fluid inclusion study supports the conclusion of Curtis and Gancarz (1983) that reducing conditions prevailed in the reaction zones. Considering the important role played by organic matter in the genesis of the Oklo deposit (Gauthier-Lafaye and Weber 1993, Nagy 1993, Nagy et al. 1991, 1993), the most likely explanation for reducing conditions in the reaction zone is redox buffering by organic matter, probably aided by organic matter radiolysis.

Cigar Lake: The Proterozoic (1.3 Ga) Cigar Lake deposit in the Athabasca basin (Saskatchewan) is one of the richest uranium ore bodies known (275'000 m^3 averaging 12% U). This deposit is the most thorougly studied in terms of radiolysis (Karlsson et al. 1993, Liu et al. 1993, Christensen 1994). Radiolysis products were found in solids and groundwaters. In groundwater, terminal products of radiolysis were found to be H_2 and SO_4^{-2} (resulting from sulfide oxidation). Release rates (equal to production rate if steady state is assumed) of $2.3 \cdot 10^{-12}$ and $1.7 \cdot 10^{-12}$ equivalents$\cdot m^{-3} \cdot s^{-1}$, respectively, were determined (Liu et al. 1993). Considering that these results are based on analytical results from one borehole only and possible influences during drilling (steel and sulfide oxidation) and regional groundwater chemistries are not discussed, further confirmation of the Cigar Lake results is needed. Applying the radiolysis model of Hofmann (1992) for homogeneous systems to Cigar Lake, the H_2 production rate of $2.3 \cdot 10^{-12}$ $eq \cdot m^{-3} \cdot s^{-1}$ can be reproduced with the (reasonable) assumption that radiolysis efficiency is 1% of the theoretical maximum in a homogeneous microporous system.

In the solids, limited surface oxidation of uraninite and possibly the formation of hematite in the clay surrounding the deposit may be due to radiolysis (Christensen 1994). The limited extent of uraninite oxidation is probably due to the scavenging of oxidants by ferrous iron and sulfides.

Dubessy et al. (1988) reported the occurrence of fluid inclusions with free O_2 and H_2 from the Cluff Lake and Rabbit Lake unconformity deposits (closely related to Cigar Lake). The findings were interpreted as resulting from primary trapping of a fluid in the ore with high concentrations of free O_2 and H_2. These findings are not yet comparable with hydrogen levels observed in present day groundwaters (Liu et al. 1993). The coexistence over geological time periods of O_2 and H_2 in fluid inclusions demonstrates that molecular hydrogen and oxygen do not necessarily back-react at relatively low temperature and in the absence of catalysts.

Shinkolobwe (Zaïre), Menzenschwand (Germany) : The only known natural peroxides are the minerals studtite $UO_4 \cdot 4H_2O$ (or $UO_3 \cdot H_2O_2 \cdot 3H_2O$) and metastudtite $UO_4 \cdot 2H_2O$ (Walenta 1974, Finch and Ewing 1989). Studtite is identical to synthetic uranium(VI) peroxide (Sato 1961). An origin of the peroxide component in studtite as a result of water radiolysis seems probable, because studtite is found in high-grade U ore both at Shinkolobwe (Zaïre) and Menzenschwand (Germany). In both deposits, studtite is associated with primary pitchblende and secondary uranly silicates in near surface weathering environments (Walenta 1974). Radiolysis may only be responsible for peroxide formation, while uranium oxidation is most likely is due to atmospheric oxygen.

Organic matter in uranium deposits : In uranium mineralizations, radiolytical alteration of organic matter iss well documented and includes aromatization, dehydrogenization, polymerization and oxidation, resulting in an immobilization of liquid or soluble organic matter, a destruction of biomarkers and shifts in C-isotopic composition. Investigated deposit types include sandstone hosted U-V, unconformity-related U, uraniferous black shales and Precambrian uraninite placers (e.g. Dahl et al. 1988, Landais 1993, Leventhal et al. 1986, Lewan and Buchardt 1989, Meyer et al. 1991, Mossman et al. 1993, Nagy 1993, Nagy et al. 1991, 1993). The formation of surface films consisting of aromatic organic polymers on radioactive minerals has been described by Rasmussen et al. (1989, 1993) from Western Australia. Nagy et al (1991) proposed that this effect may lead to a sealing of radioactive waste in the presence of organics. Despite the good characterization of solid organics in these deposits, little is known about possible low molecular weight, mobile products of organic matter radiolysis in natural systems.

5. Uncertain evidence of radiolysis in nature

Some of the evidence of radiolytic effects cited by Vovk (1987) are ambigous and could be explained by non-radiolytic geochemical processes (formation of salt-rich brines in Precambrian shields, presence of H_2-rich gas, formation of unstable sulfur compounds in roll-front deposits, hematitization and argillization close to U-deposits, red bed bleaching near sandstone-type U-deposits), while other effects may well be worth a re-evaluation (oxalates in uranium ores, H_2 and hematite in K-rich salts, unusual stable isotope ratios of H, O, C, S).

The common occurrence of local reduction phenomana in red bed sediments that lack an evident source of reductants has been interpreted as a result of porewater radiolysis followed by catalyzed reduction of trace elements by H_2 at discrete sites (Hofmann 1992). The spatial arrangement of redox environments produced by radiolysis in a HLW repository is comparable to the model proposed for the origin of reduction spots in red beds: diffusive separation of H_2 from oxidizing species results in a net oxidizing area while activated H_2 can serve to immobilize redox sensitive mobile elements at spatially separated sites.

6. Summary of results from natural analogues involving radiolysis

It appears that analogue studies of radiolytical processes so far have yielded relatively little clear-cut information covering the needs listed under 2:

- The rate of radiolysis in complex mineral-water systems is still poorly known. Seemingly low rates (Curtis and Gancarz 1983) may be influenced by the presence of natural reductants. The best results come from the Cigar Lake study but still are based on few data. Influences of formation water salinity and of the geometry of the water-solid interface are poorly constrained.

--> Needs: Radiolysis rate estimates from several independent natural systems free of interfering reductants (organics) should be obtained, possibly including hematite haloes around accessory uraninite in granitic rocks. Systems with realistic salinities should be used.

- The effects of radiolysis of organic matter should be evaluated even for systems that appear organic-free. A general retardation of radionuclide migration in the presence of organics is likely, mainly due to redox buffering and possibly also to sealing. Radionuclide mobilization may result from the formation of complexants.

--> Needs: Evaluation of complexing abilities of mobile radiolysis products of organic matter (the most obvious detrimental aspect in the presence of C_{org}).

- The inclusion of catalysts facilitating H_2 oxidation may help to activate the reducing potential of radiolysis (as well as that of H_2 from container oxidation)
--> Needs: Search for H_2 oxidation catalysts in natural H_2-rich environments

- The study of natural redox fronts indicates that many elements (including U, REE, Ni, Se, Pd, Mo, Re) are effectively immobilized at redox fronts
--> Needs: Detailed multielement geochemical surveys of redox fronts (partly completed). Reductants potentially present in the near field should be tested for their ability and efficiency to reduce typical critical elements.

- Radiolysis may be coupled with a number of poorly constrained geochemical processes the possible importance of which should be evaluated (i.e. formation of volatile metal compounds; interactions with dissolved salts; radiolysis due to mobilized radionuclides, radiolytic formation of chelating compounds)
--> Theoretical evaluation of possible impact, experimental approach, analogues??

7. Type of analogue sites required

Natural analogue studies of radiolysis so far were concentrated on large scale accumulations of natural radioactive substances. Such systems invariably have suffered a larger number of often poorly constrained hydrous and/or thermal events. Small scale systems (e.g. accessory minerals in ordinary rocks, reduction spots) have the advantage that unirradiated reference material is available nearby which greatly reduces uncertainties. The relevance and acceptance of results from small scale systems relative to large scale systems should be discussed.

8. Conclusions

Few natural analogue studies of radiolysis have been performed so far. Although some promising results have appeared, there remain a number of questions to be resolved, the most important perhaps being an estimation of radiolysis efficiency in a number of different settings with highly variable groundwater chemistry. A closer interaction between academic research and the radwaste community is desirable.

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Testing Geochemical Models of Radionuclide Solubility and Speciation in Natural Analogue Studies.

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Introduction

Geochemical models are used in the safety assessment of high level nuclear waste repositories in several aspects. These are:

-To understand and rationalize the main geochemical processes that control the master variables critical for the chemical stability of the geosphere, i.e., pH, Eh and major ion concentrations.

-To model the chemical behaviour of the different components of the repository and how they affect and are affected by variations in the master chemical variables and major ion concentrations.

The first usage of geochemical models is now firmly rooted in the tradition of geochemical modelling and stems from the pioneering work of Garrels and Christ (1965) and Sillén (1967). There is a consensus regarding the processes that control major ion concentrations and pH, but there is still some controversy with respect to the processes that control the redox state of a natural system and the possibility of measuring a relevant Eh value.

The second specific application of geochemical models in the safety assessment of a repository is less well established and requires some careful attention with respect to the different areas in which this particular application of geochemical modelling is used. In this respect chemical modelling has been successfully used to describe the stability and solubility behaviour of the main components, of different waste matrices. In particular the models derived for glass dissolution by Grambow (1985). Equilibrium and kinetic models are now being widely utilized to describe the main component behaviour of spent nuclear fuel since the pioneering work of Bruno, Forsyth and Werme (1985).

Geochemical models are also being used and refined in describing the chemical behaviour of bentonite as buffer material, since the initial model developments by Wanner (1986). The use of chemical modelling to describe the behaviour of different canister materials, particularly their corrosion properties is now widespread. Recently, a box model approach, that combines both the hydraulic properties of the medium, together with the thermodynamic and kinetics of the system by using the Steadyql code has been used to study the long-term corrosion properties of the bentonite pyrite system and the copper canister (Wersin, Spahiu and Bruno, 1994)

Finally, there is an additional area where geochemical equilibrium models are being used in performance assessment exercises, which requires deeper attention. This is to derive solubility limits and speciation of the various radionuclides in the far field.

For all the applications of geochemical modelling the following sequence applies:

System data =>Conceptual model =>Thermodynamic/kinetic data bases
=>Computerized models =>Model data

In most of the applications of geochemical modelling for safety assessment that I have described the main problems arise normally in the quality and quantity of system and thermodynamic/kinetic data. In this respect both site characterization programs and data base development efforts are crucial to strengthen our confidence in the current models applied in performance assessment.

However, in the case of the modelling of radionuclide behaviour in a repository system we are faced with additional complications. These are that our conceptual models for trace element solubility are not able to describe the real behaviour of trace components in a natural system.

So far, trace element solubility limit models for performance assessment rely on the individual solubilities of trace element solid phases to describe their behaviour. This approximation which is in contradiction with common geochemical knowledge was initially accepted on the grounds of producing "conservative" (over)estimates of radionuclide solubilities under repository conditions.

Recently, several natural system studies have been used to test the validity of trace element solubility calculations in complex systems. We have been using the so called "blind predictive modelling" (BPM) exercise approach started in the Poços de Caldas Analogue Project (Bruno et al, 1989) and extended in various natural system studies like, Cigar Lake (Casas and Bruno, 1994), Maqarin (Linklater et al, 1994) and more recently in the El Berrocal project (Bruno et al, 1994a). The overall objective of these exercises has been to test our geochemical modelling capabilities to describe trace element behaviour in well-characterized geochemical systems. The methodology used is simple and attempts to simulate the actual predictive modelling situation to be faced in safety assessment exercises. The objectives of this paper are:

To present a summary of the findings of the different trace element predictive modelling exercises, which have been performed in conjunction with natural analogue studies.

To discuss the implications of these studies in establishing the real processes that control trace element/radionuclide solubilities in natural systems.

To propose additional tests in natural systems studies, in order to advance our understanding of the key processes for radionuclide solubility and speciation to be considered in the performance assessment of nuclear waste repositories.

The Blind Predictive Modelling methodology

The BPM methodology is as follows. The participants in the exercise are distributed information about major ion composition and master chemical variable values for carefully selected waters of the site. They are asked to calculate the total solubility, the solubility limiting phase and the predominant aqueous speciation of a series of trace elements, chosen according to the geochemical characteristics of the site. Afterwards, the model results on total concentration of the trace element, the solubility limiting phase and to a lesser extent the dominant aqueous speciation are compared to the actual observations in the field. The results are analyzed both in terms of the agreement between different modellers and the observations in the field.

I will attempt to summarize the outcome of the various BPM exercises performed in connection to Natural Analogue studies. This is presented in a series of Tables that show, for each trace element considered, the degree of agreement/disagreement between predictions and observations, as well as potential reasons for the disagreement. The BPM exercises considered so far are: Poços de Caldas (PdC), Cigar Lake (CL), Maqarin (Mq) and El Berrocal (EB).

Uranium

This is the first trace element to be considered and normally its occurrence has been one of the driving forces for the selection of a site for Natural Analogue studies.

Table 1. Degree of agreement/disagreement between the predicted and observed uranium concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	Total concentration	Solubility limiting phase	Aqueous speciation	Reasons for disagreement
PdC	Poor, overestimation	Fair, the predicted phase is identified associated with Fe(III) oxides	Fair	U/Fe association not properly considered
CL	Good	Good the predicted phase is observed	no field observations	
EB	Poor, overestimation in the oxic zone	Poor	no field observations	U/Fe association not properly considered/Thermodynamic data not available
Mq	Poor, overestimation	Poor	no field observations	U association with secondary phases not considered

Thorium

As a naturally occurring radionuclide and due to its association with uranium, thorium is present in all NA sites. In Poços de Caldas, the Morro de Ferro thorium mine constituted a unique opportunity to test our models.

Table 2. Degree of agreement/disagreement between the predicted and observed thorium concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	**Total concentration**	**Solubility limiting phase**	**Aqueous speciation**	**Reasons for disagreement**
PdC	Good	Good, predicted phase observed in amorphous form	Fair	
CL	Good	Poor	no field observations	ThO_2(am) not observed in the field
EB	Poor, underestimation	Poor	no field observations	Incorrect choice of phase, ThO_2(c)

Lead

For natural (decay) reasons this is an element that is ubiquitous in the uranium sites under study.

Table 3 Degree of agreement/disagreement between the predicted and observed lead concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	**Total concentration**	**Solubility limiting phase**	**Aqueous speciation**	**Reasons for disagreement**
PdC	Good	Poor	no field observations	Pb observed to be associated with phosphate in solids
CL	Fair/Poor overestimation in oxic zone	Good in most reducing zone	no field observations	Lack of field data
EB	Poor in general. Fair in the reduced zone.	Good in the reduced zone	no field observations	Thermodynamic data not available

Zinc

This element is present in trace amounts in both Poços de Caldas and Cigar Lake, and is quite abundant in the groundwaters from El Berrocal, where concentrations up to 50 ppb are reached in deep boreholes.

Table 4. Degree of agreement/disagreement between the predicted and observed zinc concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	**Total concentration**	**Solubility limiting phase**	**Aqueous speciation**	**Reasons for disagreement**
PdC	Poor, overestimation	No field observations	Fair	Zn/Fe association not properly considered
CL	Fair	no field observations	no field observations	In reducing conditions sphalerite gives too low concentrations
EB	Fair	Fair	no field observations	Zn/Fe association not properly considered

Nickel

This element is chosen because of its importance in the safety assessment of high level nuclear waste repositories. However, this element is present in very small amounts in the selected groundwaters and therefore, source term control cannot be overruled.

Table 5. Degree of agreement/disagreement between the predicted and observed nickel concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	**Total concentration**	**Solubility limiting phase**	**Aqueous speciation**	**Reasons for disagreement**
PdC	Poor, underestimation in the case of Ni-ferrites	Ni associated with Fe in the redox front	No field observations	Ni/Fe association not properly considered
CL	Fair/Poor Only two measurements, one is underestimated	Good agreement with observations of bravoite in the most reduced zone.	no field observations	Trevorite gives good agreement in one sample, but underestimates in the second one
EB	Poor, general underestimation	Poor	no field observations	Mineralogical data suggest Ni/P association. No thermodynamic data available.

Strontium

This element is generally selected because of its relevance for the safety assessment of nuclear waste repositories and it is normally present in any geochemical environment.

Table 6. Degree of agreement/disagreement between the predicted and observed strontium concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	Total concentration	Solubility limiting phase	Aqueous speciation	Reasons for disagreement
PdC	Poor, overestimation	No field observations	Fair	Lack of thermodynamic data. Goyazite, was identified at the site.
CL	Poor, overestimation	no field observations	no field observations	Association of Sr with $CaCO_3$ not taken into account.
EB	Fair	Fair	no field observations	Association of Sr with $CaCO_3$ not taken into account.

Barium

This element is normally selected because of its chemical analogy to Ra, of far more radiological interest to safety assessment.

Table 7. Degree of agreement/disagreement between the predicted and observed barium concentrations, solubility limiting phase and aqueous speciation in the various BPM exercises.

Analogue Site	Total concentration	Solubility limiting phase	Aqueous speciation	Reasons for disagreement
PdC	No calculations performed for this element.			
CL	Good	no field observations	no field observations	
EB	Fair, better predictions in saturated gw's	Fair	no field observations	

Discussion

A look into the information summarized in Tables 1-6 gives us a mixed view about our capabilities to predict radionuclide/trace element behaviour in well-characterized systems.

Our geochemical understanding of trace element behaviour indicates that the mobility of trace components from their initial sources (ore/waste form) is linked to the cycling of the main components of the natural waters : S, Fe, C, Si and P. A common trend in these studies is the association of trace elements with iron(II) sulphide/selenide mineral phases under reducing conditions, and with iron(III)-oxy-hydroxides under oxic conditions. Another, major force is the dissolution/precipitation of calcite as a response to pCO_2/pH variation in groundwaters. Several elements appear to be associated with Ca-carbonates in several of the sites investigated, i.e., Pb, Sr and Mn. Finally, depending on the relative Si/C/P ratios in the waters, both silicates and phosphates appear to play a key rôle in limiting trace element solubilities. However, these processes seem to be important in a longer time perspective. The linkage between trace element and main component geochemical behaviour should be incorporated in our models. Recently, we have developed within the Chemval2 CEC project an approach to handle U/Fe oxy-hydroxide coprecipitation in a thermodynamic way (Bruno et al, 1994b). This approach is now being extended to other trace metals of interest. Similar approaches have been recently proposed to model the behaviour of Ni(II) in natural water systems. (Savage, 1994)

The kinetic control of trace element solid phase precipitation seems to be critical to understand their behaviour in natural systems. Most trace elements appear to follow Ostwald's rule, and the least stable phase is normally the first one to precipitate. The general sequence observed is:

hydrous oxides>oxides>carbonates>phosphates>silicates.

This time constrains on solid phase precipitation should be include for both trace component and major components in the geochemical models.

Much less can be said about our capabilities to predict trace element aqueous speciation. This is because of the lack of field speciation data that would allow a contrast with the model predictions. This is very unfortunate, because the sorption properties of radionuclides in the geosphere, and consequently their mobility, is largely dependent on the charge and size of their aqueous complexes. So far, the BPM exercises performed give an encouraging view of consensus among the different modelling groups regarding the thermodynamic data bases they use. This is the result of efforts in different aspects of geochemical modelling use like the NEA-TDB, the Chemval2 projects, and to a lesser extent these BPM exercises. However, this consensus could be misleading unless the modelling predictions are checked against field speciation measurements.

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SESSION 3: FAR FIELD PROCESSES AND PERFORMANCE ASSESSMENT IMPLICATIONS

Chairpersons: D. Lever (UK), A. Simmons (USA)

- Natural analogue studies of the role of colloids, natural organics and microorganisms on radionuclide transport	J. McCarthy (USA)
- Matrix diffusion. How confident are we?	I. Neretnieks (S)
- In-situ distribution coefficients derived from uranium and thorium decay series isotopes in water-rock systems: promise and practice	W. Murphy (USA)
- Geochemical transport modelling	D. Nordstrom (USA)
- Conceptualisation of hydrogeochemical systems uncertainty, bias and subjectivity	D. Read (UK)

NATURAL ANALOGUE STUDIES OF THE ROLE OF COLLOIDS, NATURAL ORGANICS AND MICROORGANISMS ON RADIONUCLIDE TRANSPORT

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ABSTRACT

Colloids may be important as a geochemical transport mechanism for radionuclides at geological repositories if they are 1) present in the groundwater, 2) stable with respect to both colloidal and chemical stabilities, 3) capable of adsorbing radionuclides, especially if the sorption is irreversible, and 4) mobile in the subsurface. The available evidence from natural analogue and other field studies relevant to these issues is reviewed, as is the potential role of mobile microorganisms ("biocolloids") on radionuclide migration. Studies have demonstrated that colloids are ubiquitous in groundwater, although colloid concentrations in deep, geochemically stable systems may be too low to affect radionuclide transport. However, even low colloid populations cannot be dismissed as a potential concern because colloids appear to be stable, and many radionuclides that adsorb to colloids are not readily desorbed over long periods. Field studies offer somewhat equivocal evidence concerning colloid mobility and cannot prove or disprove the significance of colloid transport in the far-field environment. Additional research is needed at new sites to properly represent a repository far-field. Performance assessment would benefit from natural analogue studies to examine colloid behavior at sites encompassing a suite of probable groundwater chemistries and that mimic the types of formations selected for radioactive waste repositories.

INTRODUCTION

The major pathways and mechanisms of subsurface contaminant migration must be included in models of radionuclide fate and transport if attempts to assess repository performance are to succeed. This paper considers the role of natural analogue studies in evaluating the potential significance of colloidal-size (submicron) particles and natural organic matter (NOM) in radionuclide migration in the far-field outside the engineered barriers of the waste repository. Models of contaminant transport processes typically treat aquifers as a two-phase system with radionuclides partitioning between immobile solids and the mobile aqueous solution. However, evidence suggests that a third phase may exist in groundwater systems in the form of inorganic or organic colloidal material capable of adsorbing or complexing radionuclides and potentially altering the rate and extent of their transport (McCarthy and Zachara 1989; McCarthy and Degueldre 1993).

The term "colloid" is formally defined as suspended material in the size range of 1-μm to 1-nm and can include inorganic materials, including mineral fragments (layer silicates, oxides, and other weatherable mineral phases) and mineral precipitates (notably iron, aluminum, and manganese oxides, hydroxides, carbonates, silicates, and phosphates, but also including colloids produced by processes of nucleation and growth of radionuclide species); "biocolloids" (bacteria and viruses); as well as NOM and other organic compounds and degradation products associated with low- and intermediate-level waste (L/LIW) streams. The emphasis on size as a criteria for defining "colloids" is somewhat problematic since measurement of fine particles is difficult. Operationally-defined size limits based on filter cut-off sizes are often used as a basis of identifying colloidal material in groundwater. However, it may be appropriate to replace the focus on operational definitions of colloid size (as will be discussed, radionuclides can complex with NOM that passes through a 1-nm filter), with an emphasize on the more fundamental issue of the geochemical transport mechanism for radionuclides. The significance of a "third phase" capable of altering radionuclide transport is more properly defined in terms of the question: What is the physicochemical form of the radionuclide in groundwater? Is the radioelement present as an ionic species (the typical assumption for modeling), or is it either: (1) adsorbed to a inorganic colloid (or existing as a homogeneous radiocolloid); (2) adsorbed to a bacteria or virus suspended in groundwater; or (3) complexed with NOM? Any of the latter three examples of radionuclide association with a "third phase" involve geochemical transport mechanisms that would invalidate modeling of radionuclide mobility as solute transport.

Existing scientific information is not sufficient to allow long-term predictions of abundance and distribution of colloidal particles in groundwater, colloid formation or mobilization under conditions typical of natural aquifers or waste repository sites, or colloid mobility in subsurface systems. Therefore, field studies at natural analogue sites are critical to determine the potential significance of colloids in the far-field environment. The far-field is emphasized because it appears to be generally assumed that compacted bentonite and other engineered barriers will minimize colloid advection from the waste package. However, the cement in barriers, backfill and encapsulation used for most L/LIW (and some transuranic) repositories are expected to produce colloids as they degrade, and little is known about the mechanisms of generation or transport of these colloids, or their potential significance to repository performance. Figure 1 identifies some of the key issues that will dictate the potential significance of colloids on repository performance. Generally, if colloids are absent, immobile, or do not adsorb radionuclides, they will not be significant to repository performance. The existing data from natural analogue studies that address these key issues will be discussed below. Although most studies have focused on inorganic colloids and NOM, the potential role of microorganisms on radionuclide transport in groundwater will be discussed later in this paper. Finally, general conclusions and uncertainties will be identified. The interested reader is also referred to reviews of colloids in natural analogue studies presented in Ivanovich et al. (1992) and Miller et al. (1994).

NATURAL ANALOGUE STUDIES INVOLVING COLLOIDS AND NOM

Operational difficulties confound almost all studies of colloids in groundwater. For example, the act of sampling can affect the nature and amount of colloids and particles recovered, and changes in thermodynamic conditions during sample recovery (e.g., introduction of oxygen or degassing of carbon dioxide) can produce colloidal artifacts. A detailed description of colloid sampling and analysis techniques is given in McCarthy and Degueldre (1993). Despite these difficulties, a number of studies have sampled colloids with the goal of assessing their potential impact on radionuclide transport. Results will be discussed in terms of a hierarchy of questions such as that identified in Figure 1.

Are Colloids Present? -- The presence of colloids has been examined at a fairly large number of subsurface environments, especially in the last few years since the potential role of colloids has been highlighted and more reliable methods for colloid sampling and characterization have been devised. The data base of colloid studies has been tabulated in McCarthy and Degueldre (1993). A number of studies have focused on groundwater environments considered analogues for geological repositories, including granitic formations in Switzerland, Germany, Sweden and France (Degueldre et al. 1987, 1989a, 1989b, 1990; Schlotis et al. 1993; Brutsch and Degueldre 1991; Alexander et al. 1990; Billion et al. 1991; Laaksoharju and Degueldre 1994), rhyolitic tuffs in Nevada (Buddemeier and Hunt 1988; Buckholz ten Brink et al. 1992; Kingston 1989), sedimentary deposits in Germany (Kim et al. 1984), and natural ore deposits in Brazil, Australia and Canada (Miekeley et al. 1991, 1992; Short et al. 1988; Ivanovich et al. 1988; Vilks et al. 1993). Although it is not yet possible to reliably predict the nature and abundance of colloidal particles as a function of the chemical, hydrological and mineralogical properties in a range of subsurface environments, some general relationships are beginning to develop (McCarthy and Degueldre 1993).

- Colloids appear to be ubiquitous. Although concentrations are extremely low in some systems (as low as 1-25 $\mu g\ L^{-1}$), there is no study which demonstrates the absence of colloidal particles.
- Colloid concentrations appear to be lowest in deep, geochemically stable subsurface environments; shallow aquifer systems generally appear to have higher colloid concentrations even in the absence of geochemical instabilities.
- Regardless of the geology or depth of the geological system, higher levels of colloids are routinely associated with some hydrogeochemical perturbation. For example, in studies of a series of fractured granitic systems, colloid concentrations are 20 to 1000-fold higher in ground-water zones affected by inputs of surface water or in hydrothermal zones with large temperature and pressure gradients, compared to stable hydrogeochemical systems (Degueldre 1994). In fractured rhyolitic tuffs, colloid concentrations were several-fold higher in locations affected

by underground nuclear testing, compared to locations with similar geology but remote from the test site (Buddemeier and Hunt 1988; Buckholz ten Brink et al. 1992). Disturbances occurring on longer geological time scales can also affect colloids. A reducing ground water resulting from microbial metabolism of NOM beneath a swamp was associated with increased levels of colloids, compared to oxic zones in adjacent formations (Ryan and Gschwend 1990).

- In most cases, the composition of the colloids observed in different subsurface systems "makes sense" in terms of the geology of the formation and the nature of the geochemical perturbations. In fractured granitic systems, the observed silica and clay/mica colloids would be consistent with production of primary and secondary minerals from geochemical alteration of the parent rock, and colloids in volcanic tuffs appear to be constituents of the parent rock and alteration products. Particles in a sandstone/uranium ore formation are composed of fracture-filling minerals characteristic of the host rock.

The implications of these relationships to repository performance is significant. Assessment of the role of colloids in the dissemination of radionuclides cannot be limited to consideration of the "background" population of colloids existing prior to development of the repository. Performance evaluation needs to reflect the potential for generating new types or increased concentrations of colloids by alteration of geochemical conditions as a result of disturbances arising from the near-field environment. For example, the hyperalkaline front emerging from a degrading cementitious repository may produce colloids, as will the redox front moving away from a corroding steel canister in a high-level water repository. The redox front may pass through the bentonite into the bentonite/host rock interface as well. In addition to localized effects associated with the repository, global climatic changes could affect ionic strength and composition of recharge water, inputs of organic matter, and other factors controlling colloid formation, stability and transport.

Are Colloids Stable? -- This question encompasses two separate issues: *colloidal* stability (are the colloids suitably charged to avoid aggregation or attachment to aquifer surfaces), and *chemical* stability (colloid formation and dissolution). Studies measuring the electrophoretic mobility of colloids recovered from groundwater have found that they have fallen within a relatively small range of negative values. These data suggest that the colloids carry a large negative charge and would, therefore tend to be stable in groundwaters (Longworth et al. 1989a, 1898b; Longworth and Ivanovich 1989; Degueldre et al. 1989a, 1989b; Dearlove et al. 1990a, 1990b; Liang et al. 1993). These observations include colloids such as iron oxide, which at the groundwater pH would be expected to have a strong positive charge; the charge reversal has often been attributed to coatings of NOM on the oxide surface (Longworth et al. 1989a; Miekeley et al. 1990; 1992; Liang et al. 1993). It should be noted that even low concentrations of NOM can bring about reversal of surface charge, suggesting that concentrations of NOM in groundwater may be able to stabilize radiocolloids expected to be inherently unstable in groundwater. For example, stable suspensions of negatively-charged ferrihydrite were formed following introduction of oxygen into a shallow sandy aquifer. The groundwater had a neutral pH and contained concentrations of only 0.5 mg-C/L of NOM, all of which was <1-nm in size based on ultrafiltration (Liang et al. 1993). The frequent observation of iron hydr(oxide) colloids in groundwaters of pH below the expected ZPC of iron oxides, such as Alligator Rivers and Poços de Caldas, suggests that NOM or inorganic anions (such as silicate) may be important in promoting colloidal stability.

The chemical stability of colloids (i.e., considering colloid formation and dissolution) over long times is more difficult to assess directly. Erosion of fracture-lining mineral (formed by geochemical alteration of primary minerals along fractures or by mechanical crushing) is postulated as the source of colloids in many formations (McCarthy and Degueldre 1993; Vilks et al. 1991, 1993). It is reasonable to expect that colloids can form or disappear due to advection into zones with different geochemical conditions. For example, iron oxide particles recovered from groundwater at the Osamu Utsumi mine were thought to be generated at depth by the upflowing, reducing waters, and not by downward migration of material from the surface during rainfall (Miekeley et al. 1990, 1992). The presence of ferrous phosphate colloids downgradient from a sewage infiltration site is consistent with equilibrium solubility calculations suggesting supersaturation with respect to this product within a plume of phosphate (from detergents in the sewage) flowing through an iron-rich aquifer (Gschwend and Reynolds 1987). Similar processes were postulated at a natural analogue site. Uranium colloids were found at Alligator Rivers, yet dissolved uranium concentrations were far below saturation for any U(VI) species. It was suggested that U-colloids could only form by precipitation in pockets of supersaturation, which might only occur where groundwater is in contact with U-rich rock for extended periods. Colloids formed by such a process would be short-lived since they would become unstable as soon as the water pocket moved away from the rock and mixed with generally more oxidizing groundwater (Miller et al. 1994).

Do Colloids Take Up Radionuclides and Is Uptake Reversible? -- Two types of analogue studies address these issues: "traditional" analogue studies involving geological formations containing naturally-occurring radionuclides or their analogues, and "anthropogenic" analogue sites created by disposal of radionuclides or by nuclear detonations. The latter studies, while providing little information about the long-term geological behavior of radionuclides, do provide information on processes relevant to speciation and transport in physically and chemically heterogeneous natural systems over periods of 25- to 50 years. The results of both types of studies clearly indicate that radionuclides do associate with colloidal species. For example, in studies at Cigar River (Vilks et al. 1993), Whiteshell Research Area (Vilks et al. 1991), Alligator Rivers (Ivanovich et al. 1988; Short et al. 1988; Seo et al. 1992), Grimsel, Reskajeage and Drigg (Longworth et al. 1989a) and Poços de Caldas (Miekeley et al. 1990; 1992), both uranium and thorium were associated with the colloidal phase. As might be expected, of the total concentrations of these radionuclides in the groundwater, the colloids accounted for a much larger fraction of the less soluble thorium, compared to only a few percent of the uranium. Rare earth elements (REE) show an affinity for colloids that is intermediate between uranium and thorium (Miekeley et al. 1990, 1992). Cobalt, cerium and europium were associated with inorganic colloids outside a nuclear detonation cavity at the Nevada Test Site (Buddemeier and Hunt 1988). Plutonium and americium were adsorbed to colloids in an alluvial aquifer three kilometers downgradient from a liquid waste outfall at Los Alamos National Laboratory. Humic colloids in Gorleben contained large numbers of trace heavy metals that are natural homologues of actinides and some fission products, and association of americium with humics was demonstrated (Kim et al. 1984). Champ et al. (1984) concluded that a number of radionuclides (including Co, Ce, Cs, Eu, Sb, Zr, Fe, Ni, I, Pu and possibly Am) in waste plumes at Chalk River Nuclear Laboratories were associated with organic ligands. The exception to the common observation of radionuclide association with colloids was in the hyperalkaline groundwaters at the Maqarin area of Jordan, where it was shown that uranium was not associated with colloids (Alexander 1992).

Alpha-emitting radionuclides, probably americium and curium, in groundwater downgradient of disposal trenches at the Oak Ridge National Laboratory appear to be associated with low molecular weight components of NOM. All the NOM and alpha-radioactivity pass through a 1-nm (3000 mol. wt.) filter. Although this size fraction is generally considered "dissolved" rather than colloidal, the $<$1-nm groundwater NOM could be isolated by adsorption on DEAE-cellulose anion exchange media. Step input of base mobilized the NOM from the column. The radioactivity co-eluted with the NOM, suggesting that the radionuclides were complexed with the NOM in the groundwater. In laboratory studies, ^{241}Am in a solution free of NOM was input to the DEAE column; the radionuclide did not elute with base but could be eluted with acid (J. F. McCarthy and J. D. Marsh, Oak Ridge National Laboratory, unpublished data). These results suggest that 1-nm may not always be an appropriate size cut-off for defining "colloidally-bound" radionuclides, especially when complexation with organics is possible. For example, at Alligator Rivers, the ^{230}Th and ^{232}Th in the "dissolved" phase (operationally defined as $<$18-nm in that study) was two- to three orders of magnitude above the solubility limit, probably because of trace organic complexation (Short et al. 1988). Association of radionuclides with even low molecular weight NOM has the potential to invalidate thermodynamic modeling based on assumptions that radionuclides passing through certain filter sizes are truly ionic species.

Evidence of reversibility of binding of radionuclides to colloids is based largely on data from uranium-series disequilibrium studies. It should be noted, however, that interpretation of data concerning the reversibility of adsorption can be controversial since it is difficult to distinguish processes of adsorption versus precipitation. Furthermore, it is not clear to what extent the composition of the interior of a particle (which may not interact with the water) biases interpretation of adsorption phenomena at the particle-water interface. While underlying mechanisms may be difficult to distinguish, natural analogue studies can help evaluate the extent of exchange of radionculides between colloidal and aqueous phases in groundwater.

The $^{234}U/^{238}U$ activity ratios for solution and *inorganic* colloidal phases are generally very similar, indicating that uranium in the two phases is in equilibrium (Longworth et al. 1989a, 1989b; Longworth and Ivanovich 1989; Degueldre et al. 1989; Dearlove et al; 1990a, 1990b). In contrast, corresponding activity ratios for humic colloids at Gorleben are significantly different, suggesting that the U bound to the humic colloids do not interact significantly with the groundwater. In studies along flow paths from uranium ore deposits, the U activity ratios of the solution and colloidal phases are similar near the ore bodies and diverge downgradient with a significant rise only in solute activity ratios. Colloids having lower ratios than groundwater probably contain ^{238}U inherited from the rock matrix (Vilks et al. 1993; Short et al. 1988). Generally, $^{230}Th/^{234}U$ ratios in solution are very low because of the low solubility of Th. Colloidal $^{230}Th/^{234}U$ ratios are also generally well below 1.0, indicating that ^{234}U had not been sorbed onto particles long enough for ^{230}Th to come into secular equilibrium with its parent (Vilks et al. 1991, 1993; Short et al. 1988; Longworth et al. 1989a). Short et al. (1988) noted that in transects of wells at Alligator Rivers, the ^{232}Th levels were independent of ^{230}Th levels and locations. Since the ^{232}Th is ubiquitous and present before any radiogenic thorium is available for solution, this isotope dominates the trace equilibrium processes of adsorption/precipitation and complexation. These authors suggested that there was considerable hysteresis in the process of thorium adsorption on colloids. Additional evidence for limited desorption of strongly adsorbed radionuclides was presented by Penrose et al. (1990). Plutonium and about half of the americium associated with groundwater colloids did not undergo significant exchange over a period of several days after solutions were spiked with other isotopes of the same elements.

In summary, colloids appear to be capable of binding a large number of radioelements and sorption appears to be generally inversely related to solubility. Solution and colloidal phases appear to be in equilibrium for weakly adsorbing species such as uranium, suggesting its binding is readily reversible. There is evidence suggesting that more strongly adsorbed elements such as thorium, and possibly plutonium, are not in equilibrium with the solution phase and that the association of the radionuclide with colloids is not readily reversible.

Are Colloids Mobile? -- There is evidence both for and against the transport of colloids. Much of the data suggesting that colloids are mobile derive from observations of movement of radionuclides downgradient of an "anthropogenic" source. Coles and Ramspott (1982) found much more rapid migration of ruthenium in the field than expected from batch adsorption studies. A well 91 m from a nuclear detonation cavity at the Nevada Test Site was pumped to induce flow into the well from the cavity. No radioactivity was observed for 2 years, but, with further pumping, the concentration of both ^{3}H (a nonreactive tracer of water flow) and ^{106}Ru increased at the same rates, suggesting that both traveled at the same velocity from the detonation cavity. Laboratory measurements of the equilibrium sorption coefficient (K_d) for Ru with rock and water from the site predicted that the Ru should have traveled 30,000-fold slower than the ^{3}H-water (i.e., the Ru should have moved only 3 cm during the time the ^{3}H-water migrated 91 m) (Coles and Ramspott 1982). Although laboratory K_d's have proven to be poor predictors of field behavior, the unretarded transport of Ru contrasts with its expected behavior as a solute, suggesting that colloids may have been involved in its transport. Also at the Nevada Test Site, Buddemeier and Hunt (1988) demonstrate the presence of inorganic colloidal particles (3 to 50 nm) with sorbed transition metals (manganese and cobalt) and lanthanide (cerium, europium) radionuclides. The colloids were recovered from ground water inside a nuclear detonation cavity and also from a well in a permeable fractured lava and tuff formation 300 m from the cavity. Plutonium and americium were associated with siliceous colloids (25-450 nm) in a shallow alluvial aquifer at Los Alamos National Laboratory (Penrose et al. 1990). Filterable particles (>400 nm) containing radionuclides of Co, Zr, Ru, Cs, and Ce were recovered from contaminant plumes in ground water at the Chalk River Nuclear Laboratory (Champ et al. 1984).

Additional evidence of long-distance subsurface transport of natural colloids was obtained in a fractured formation at Menzenschwand in the Black Forest of Germany. The Mg:Ti ratio and REE signature of colloids recovered from the granite groundwater differed significantly from that of the host granite, but appeared to reflect that of a neighboring gneiss several kilometers upgradient (Alexander et al. 1990).

Other data suggest that colloid transport is quite limited. At the Cigar River uranium deposit site, U and Ra contents of colloids in the ore and surrounding clay zones are significantly higher than in colloids from the sandstone, suggesting the clay is an effective barrier to colloid migration (Vilks et al. 1993). Similar results at Alligator Rivers and Morro de Ferro also suggest that colloids have a limited capacity for migration since the concentrations of colloid-bound radionuclides outside the ore body are low (Miekeley et al. 1992; Ivanovich et al. 1988; Short et al. 1988).

Some cautions should be noted in interpreting any of these data. Nuclear detonations at the Nevada Test Site undoubtedly promoted fracturing of the formation, and the extensive transport at the Los Alamos site involved a permeable alluvial aquifer. The long distance transport at the Menzenschwand site should perhaps also not be over-emphasized as the flow system is unusual (relatively wide, coated fractures) and the presence of the mine induced fast groundwater flow. Conversely, the studies showing limited transport are also not perfect analogues for the far-field environment. The reduction in colloid migration by the clay halo around the Cigar Lake ore deposit suggest that engineered barriers of clay may be effective, but says less about the potential role of colloids for transport of radionuclides once they reach the far-field environment. Likewise, although the Morro de Ferro study concluded that colloids were not transported, the ore zone lies in the unsaturated zone, and this must obviously affect the degree of retention of colloids in the system. Unfortunately, the general conclusions of these studies must be that no conclusion concerning the movement of colloids is proven.

ROLE OF "BIOCOLLOIDS" (Bacteria and Viruses) ON RADIONUCLIDE TRANSPORT

Microbiota can be significant at geological repositories and concern about their effect on corrosion of the waste form and engineered barriers is real. However, this paper will address another microbial issue: concern that bacteria and viruses can adsorb radionuclides and potentially enhance radionuclide migration if the biocolloids are mobile in the far-field environment. Bacteria have been shown to biosorb metals and radionuclides, probably due at least in part to the presence of polysaccharides in cells walls that undergo ion exchange with metals in solution. Available evidence suggests that different species of bacteria can exhibit wide variations in biosorption capacity. However, for at least some microorganisms including common soil bacteria, biosorption capacity for thorium is comparable in magnitude to thorium sorption to groundwater colloids (Tsezos and Volesky 1981). Given the fact that autochthonous microbial populations exist in host formations and that repository construction is likely to introduce additional biomass, the potential role of microbes as vectors for radionuclide transport cannot be dismissed *a priori*.

Transport of microorganisms includes processes that govern transport of inorganic colloids (size, shape, surface charge), as well as additional biological processes. Secretion of exocellular polysaccharides can increase "stickiness" of bacteria and make detachment more difficult, while sloughing of daughter cells from attached bacteria can promote advection of bacterial biomass. Bacteria can alter their transport properties (changes in size or surface characteristics) in response to environmental conditions, further complicating predictions of the rate and extent of biocolloid migration.

Field data suggest that transport of biocolloids can occur very rapidly and over long distances, in at least some locations. The mechanism of transport in these cases may involve travel through highly transmissive zones of preferred flow. For example, bacteria injected into ground water have been reported to travel up to 920 m at rates of 200 to 350 m d^{-1}, and viruses injected into a well migrated 680 m downgradient at a rate estimated between 36-180 m d^{-1} (Keswick et al. 1982). Yeast cells injected into a well moved 7 m in a sand and gravel aquifer in less than 48 h, and moved faster than nonreactive tracers of ground-water flow such as iodide and bromide (Wood and Ehrlich 1978). Likewise, Harvey et al. (1989) observed that bacteria injected into a sandy aquifer eluted slightly ahead of the nonreactive tracer. Of perhaps greater relevance to repository environments, McKay et al. (1993) demonstrated that viruses (bacteriophage, 26- to 65-nm diameter) were transported rapidly in a low permeability clay-rich till (hydraulic conductivity of 10^{-10} to 10^{-6} m s^{-1}). In this trench-to-trench tracer migration study, phage were detected in seepage collectors in a downgradient trench 4-m from the source trench with 1-2 days. The large contrast in the transport velocity of the phage (2- to 5-m d^{-1}) and the bromide tracer (0.01- to 0.07-m d^{-1}) was attributed to extensive diffusion of the solute, but not the phage into the pore water of the clay matrix. Only a small fraction of the viruses were recovered, however. The attenuation was attributed to biological inactivation of the phage and, more importantly, to attachment to fracture walls and diffusion into larger pores.

These short-term field observations may be of limited significance to deep geological repositories. The U.S. Department of Energy's Subsurface Science Program is initiating a more relevant field study on microbial transport and microbial ecology in deep subsurface environments at the Cerro Negro site in the Rio Puerco area of New Mexico (USDOE 1994). The goals of the study are to determine the mechanisms and environmental conditions by which microorganisms are maintained in the subsurface for extended periods, as well as the mechanisms and conditions by which they are transported through the deep subsurface over long periods and distances. At the Cerro Negro site, a volcanic intrusion penetrated through a thick Cretaceous sequence of marine sediments that included low permeability shale with interbedded tongues of sandstone. The heat from the igneous intrusion 3.4 million years ago would have sterilized the rock near the intrusion and created a gradient along which there may have been differential survival of any microorganisms present. Once the sediments around the intrusion became saturated again, recolonization may have occurred if 1) suitable microbial inoculum and transport vectors existed, 2) physical parameters permit microbial transport, and 3) geochemical conditions in the altered zone support microbial populations. The purpose of the research is to determine if the sterilized sediments are still sterile or if microorganisms have been able to re-establish themselves in the last several million years. Results may be relevant to assessing microbial activity, survival and transport at nuclear repositories.

SUMMARY AND CONCLUSIONS

Thus far, natural analogue studies have demonstrated that many radioelements or their analogues do adsorb to organic and inorganic colloids present in groundwater. Field studies of groundwater colloids suggest that colloids are ubiquitous. However, colloid concentrations, especially in geochemically stable deep groundwaters, appear to be quite low and may be insufficient to affect radionuclide transport (Vilks et al. 1993; Smith 1993; Smith and Degueldre 1993). Even if colloid populations are low, they may have the potential to affect radionuclide transport if the colloids are stable (with respect to both colloidal and chemical stability), if adsorption onto them is irreversible, and if physical transport pathways exist in the formation surrounding the repository.

The very fact that colloids can always be found in every site sampled suggests that colloids are stable, with rates of colloid loss balanced by colloid generation. Of potentially greater concern is the effect of geochemical changes on colloid formation in the far-field environment. Several studies have documented significant increases in colloid abundance in both deep and shallow systems affected by altered geochemical conditions (McCarthy and Degueldre 1993). Such changes could result from advection across groundwater interfaces, or be induced either anthropogenically by the disturbances originated from the repository, or naturally due to unforeseeable geological or climatic changes.

Concern about the effect of colloids is not diminished by uranium-series disequilibrium studies that suggest the strongly adsorbing radionuclides such as thorium are not readily desorbed over long periods. Significant hysteresis in adsorption/desorption could significantly accelerate contaminant migration; the transport of the contaminant would then be strongly dependent on the extent of colloid–aquifer media interaction (Smith and Degueldre 1993).

Field studies to date have not been notably successful in proving or disproving the potential of colloids for transport. Examples of analogue sites where colloid mobility seems limited (e.g., Cigar Lake and Morro de Ferro) are balanced by other examples demonstrating transport in fractured formations (Menzenschwand) and a clay till (McKay et al. 1992).

Additional research is needed at new sites to properly represent a repository far-field. As noted by Miller et al. (1994), different basement groundwaters exist at many sites. In Swiss granites, water chemistry ranges from deep reducing NaCl-type water to shallower oxidizing Ca-HCO_3-type waters. Likewise, inhomogeneities in groundwater compositions exist at the UK Sellafield site and the Precambrian Fennoscandian Shield, and colloids crossing these boundaries may become unstable. Performance assessment would benefit from natural analogue studies to examine colloid behavior at sites encompassing a suite of probable groundwater chemistries and that mimic the types of formations selected for radioactive waste repositories.

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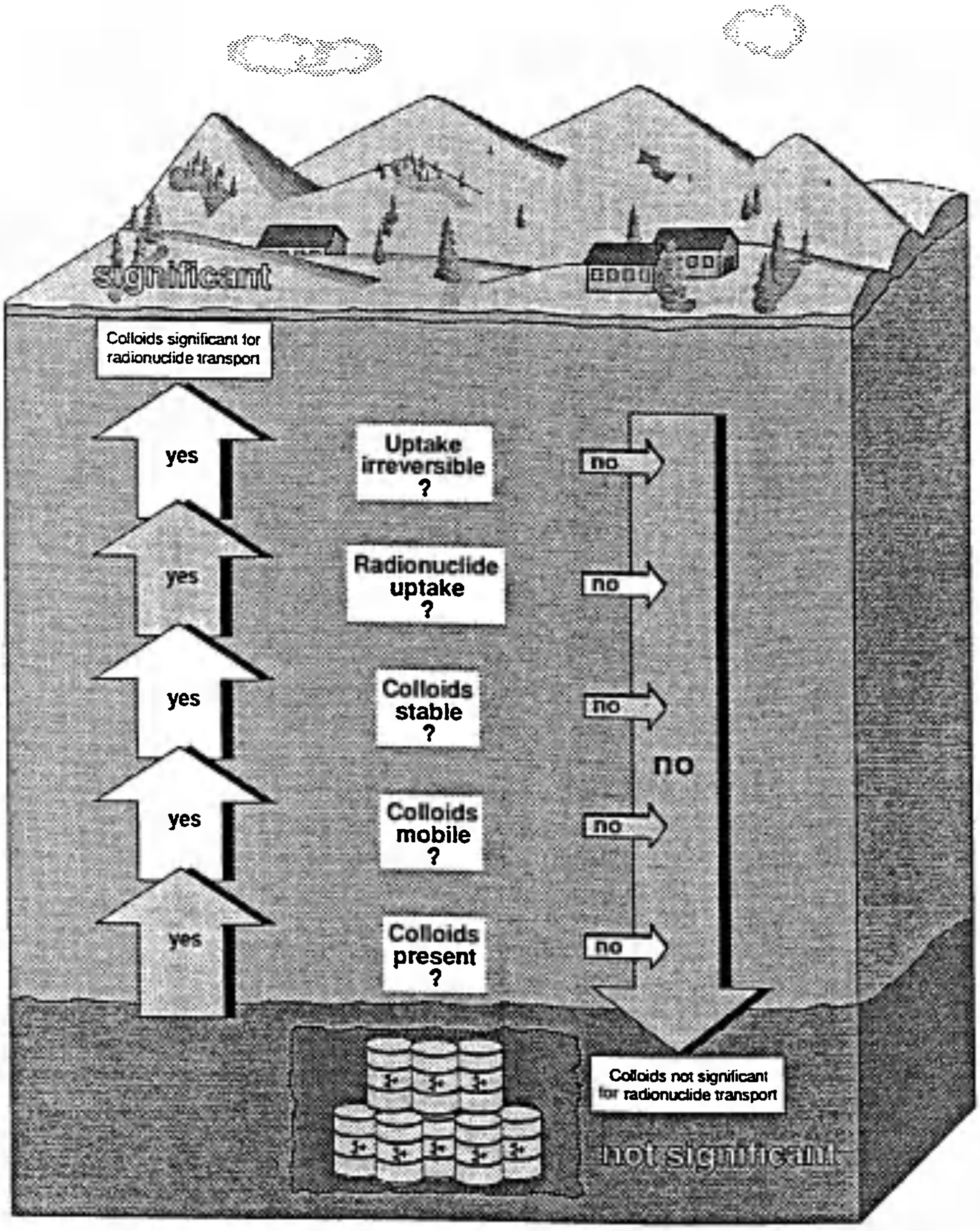

Figure 1. Diagram illustrating the general issues that need to be considered in assessing the significance of colloids to repository performance (Miller et al. 1994). The simplicity of the diagram makes it a useful didactic tool. However, it should be noted that the questions are inter-related and cannot be answered as simply as is suggested by the arrows. For example, irreversible uptake becomes less important when higher concentrations of colloids are present or if colloids have a large adsorption capacity. Similarly, colloid stability and mobility are interdependent since stability must be compared with the time required for colloids to transport radionuclides to the accessible biosphere.

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MATRIX DIFFUSION - HOW CONFIDENT ARE WE?

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ABSTRACT

Matrix diffusion and sorption in crystalline rock matrices is the most important retardation mechanism for nuclides potentially escaping from deep geologic repositories for nuclear waste. A review of the theory and studies of the phenomena is made covering laboratory and field experiments as well as natural analogues. The potentially very important mechanism of surface diffusion is discussed as well as the importance of the coupled mechanism of matrix diffusion and redox front formation. It is concluded that there is clear evidence that the pore systems are open even in undisturbed rock at repository depth stresses but that more evidence from observations of long time phenomena for penetration beyond 10 cm and of redox front formation would be of value.

1. Background and introduction

Radionuclides escaping from a deep geologic repository in saturated crystalline rocks such as granites or gneisses will be transported by the water seeping in the fractures. In several safety analyses (KBS-3 1983, Nagra 1985, SKB-91, 1992) it has been found that the most important mechanism for retarding the nuclides is the uptake into the porous rock matrix and sorption onto the micropore surfaces in the interior of the rock matrix. This potential retardation mechanism has been studied since the late 1970:s. Several investigations have since been performed to understand and quantify the processes which govern the uptake into the rock matrix. Another potentially important aspect of matrix diffusion is that oxygenated water either infiltrating from the surface or formed by radiolysis in and near the radioactive waste, may react with reducing minerals such as ferrous oxides, hydroxides or sulphides in the rock matrix. This would prevent the formation of oxidizing pathways where many of the important radionuclides have higher solubilities and lower sorption coefficients. The bulk of the rock matrix of granites and gneisses contains large amounts of reducing minerals that can be made available by diffusion.

The hydraulic conductivity of the rock matrix is very low and, over short distances at least, the transport is much faster by molecular diffusion than by flow. Most investigations have therefore been aimed at studying diffusion. Laboratory and field measurements of matrix diffusion have been performed using nonsorbing as well as sorbing species. Ion migration in electric fields which is a known technique to study ion diffusion, has been used to speed up the processes and to cover longer distances. Diffusion experiments in rock samples under stresses similar to those at repository depth have been made in the laboratory and in situ diffusion experiments at large depths to study the transport in rock under natural stress have also been made. Solutes of different sizes and with different chemical properties have been used.

Theories of diffusion and sorption in the rock matrix have been developed and tested experimentally and there seems to be an agreement on most of the basic processes of importance.

Nevertheless, because the man made experiments in the laboratory and in the field seldom have a duration of more than a few years, but the time of interest for the radionuclide retardation is in excess of ten thousand years, it is necessary to find evidence in the nature that these processes are active over much longer times and distances than man made experiments can cover. This paper gives an overview of experiments and theories and discusses some of the questions which are posed on their reliability and applicability to long term predictions. Observations from some natural analogue sites indicating matrix diffusion are discussed and areas where there is a need for more information are mentioned.

2. Questions posed

If laboratory data are to be used for predictions of transport over much larger time and space scales, a good understanding of the important processes is needed. Some key issues which to varying extent have been addressed in different investigations are the following.

1 Is the pore system connected over long distances

2 Will larger molecules be less mobile than small because of geometric constrictivity effects

3 Many mineral surfaces are negatively charged and electric repulsion may "constrict" the pores for an-ions

4 Are the sorbed cat-ions always immobilized or are they mobile even in the “sorbed"state

5 What influence does rock stress have on the porosity of the rock and diffusivity of the solutes

6 Have the de-stressed samples taken to the laboratory been irreversibly changed

7 Will fracture coating and filling material allow diffusing species to access the underlying matrix or can the pore system be clogged

8 Do the transport and sorption properties change over long times

9 Will nuclides in colloidal form have access to the inner pore system

10 Must the rock be hydrothermally altered to allow diffusion.

3. Concept of diffusional transport in a porous rock matrix

This section will describe some of the theoretical background and some of the mechanisms of importance for subsequently discussing the interpreting experiments and observations.

Crystalline rocks are made up of small crystals ranging in size typically from 0.1 mm to many mm:s. There are micro fractures in and between the crystals which make up a connected pore system. Some pores are dead ended. The surfaces of the crystals forming the pore walls are predominantly negatively charged in the range of pH values found in the deep groundwaters.

At steady state the transport will only take place in the connected pore system. During the non steady state phase the dead end pores will also contribute by acting as sinks and/sources. The dissolved solutes move by diffusion in the pore water. Some sorbed species may be bound by mechanisms which make them immobile in the sorbed state and they can only move if they first are desorbed. Other sorbed species may be mobile as e.g when they are attracted by diffuse electric forces which makes the water near the surface more concentrated in the "sorbed" species without actually binding the ion at a specific location.

At steady state the transport can be described by Fick's first law

$$N = - D_p \varepsilon_t \frac{\partial C}{\partial x} \qquad (1)$$

N is the flux, ε_t is the transport porosity, D_p is the diffusivity in the pore water which can be related to the diffusivity in unconfined water, D_w, by the often used relation

$$D_p = D_w \frac{\delta_D}{\tau^2} \qquad (2)$$

δ_D is the constrictivity and τ is the tortuosity, the group $\varepsilon_t.\delta_D/\tau^2$ is called the formation factor F_f and the effective diffusivity D_e is defined by $D_p\varepsilon_t = D_e$.

If all solutes were influenced in the same way by the pore system it would suffice to measure the formation factor for one solute. This is not always the case. A negatively charged ion will be repelled from the negatively charged pore walls and on the average seemingly utilize a smaller cross section area of the pore than a neutral species. On the other hand a positively charged ion will be attracted to the walls and have a higher average concentration than in the water far from the walls. This could be viewed as if the pore is larger from the transport point of view if the ion is ready mobile. The constrictivity δ_D and formation factor F_f can thus be different for different species and must be used with caution. F_f still can be a useful entity for comparison purposes.

When the transport is instationary and the solute accumulates, or is depleted from the pore system, Fick's second law and the law of conservation of mass is used to describe the transport and accumulation. Assuming at present (another transport mechanism will be discussed later) that transport takes place only in the water in the pores, i.e. sorbed ions are immobile, and the diffusion coefficient is constant and that the sorption is reversible, the following equation results

$$(\varepsilon + K)\frac{\partial C}{\partial t} = D_p \varepsilon_t \frac{\partial^2 C}{\partial x^2} \qquad (3)$$

ε is the total porosity including dead end pores and K is the volumetric sorption coefficient which may be concentration dependent.

The establishment of the concentration profile after a change in boundary conditions will thus take a much longer time if there is sorption because not only the pore water must be filled with the species, all the sorption sites in local contact with the water must also be equilibrated. This is called the retardation effect. A retardation factor R_d for diffusion in the porous matrix is sometimes defined as

$$R_d = \frac{(\varepsilon + K)}{\varepsilon_t} \qquad (4)$$

The retardation factor can have values ranging from about unity to five to seven orders of magnitude or possibly even larger. This makes it extremely difficult to measure diffusion of strongly sorbing species in crystalline rock samples. As an example consider a rock where the pore diffusivity $D_p = 3 \cdot 10^{-11}$ m^2/s, and which has a porosity of 0.003, typical values for Swedish gneisses and granites. The penetration depth by diffusion, η, can be estimated using the solution of Equation [3] for the appropriate initial and boundary conditions (Bird et al 1960) to be

$$\eta = 4\sqrt{\frac{D_p}{R_d}t} \qquad (5)$$

For a one year contact time η is slightly more than 10 cm for a non sorbing species. For a sorbing species with a K of 3000, a low value for actinides under reducing conditions, the retardation factor is 10^6 and the penetration depth 1000 times smaller than for the nonsorbing species. η = 0.1 mm. This distance is much smaller than the crystal sizes of most rocks and the performed analysis is not applicable. It may be concluded, however, that the often observed phenomenon that the sorbed actinides only can be found on the "surface" of the rock samples subjected to the tagged water does not contradict that matrix diffusion could be active over longer distances- given time. A ten thousand year contact time would give 1 cm penetration depth using the above theory. For natural processes that have been active for a million years penetration depths of up to tens of centimeters can be expected. This is also found for uranium series disequilibration as will be discussed later.

Ion mobility in an electrical field can be used to determine diffusivity of charged solutes and is used to determine the formation factor which is directly obtained from the ratio of electrical conductance of the solution filled sample to the conductance of the same solution. It has been observed that if the conductivity measurements are made with the natural waters or waters with low ionic strength, the conductivity of the water filled rock sample is much higher than can be expected if one only accounts for conduction in the pore water. In samples with pores filled with a brine (0.1-1 mol/l) of e.g. NaI, the conductivity agrees very well with what can be expected from diffusion measurements with neutral species. It has been suggested that at low concentrations the cat-ions which have a much higher concentration at the pore surfaces because these are negatively charged, contribute significantly to the electric conductivity. This will be discussed some more below because if at least part of the accumulated (sorbed) species are mobile then the retardation factor concept as discussed above is not valid.

There are experimental indications that some sorbed species may be mobile in the "sorbed" state (Skagius and Neretnieks 1988). Cesium and strontium were found to have penetrated much deeper into the rock tablets than expected if there was retardation. Similar effects were found by Lehikoinen (1992) with sodium.

This is sometimes called surface diffusion. The process is not well understood (Rasmuson and Neretnieks 1983). It can be thought of as the opposite to the ion exclusion process mentioned above where the cat ions concentrated at the surface are essentially as mobile as those further from the surface. These conditions can be expected when the "sorption" process is nonspecific and dominated by the diffuse forces.

In such cases there will be a gradually increasing concentration near the surface. For visualization purposes one can think of the water far from the surface as one region and the water near the surface as another region where there is a high concentration of the "sorbed" but mobile species. Then, parallel to the transport in the pore water there will be transport of the sorbed species. The rate of surface transport can be written

$$N_s = - D_s \varepsilon_s \frac{\partial C_s}{\partial x} \qquad (6)$$

C_S is the concentration of the sorbed substance in the hypothetical water film where the cat-ions are concentrated (sorbed). As sorption is fast, equilibrium is assumed to exist between C_S and C. ε_s is the hypothetical volume fraction of water at the pore surfaces where the "sorbed" ions are concentrated. It is only used for visualization purposes and need not be be known. The equilibrium relation is

$$\varepsilon_s C_s = K\, C \qquad (7)$$

The total transport rate under steady state conditions then is the sum of the transport by pore diffusion and by surface diffusion.

$$N = N_{pore} + N_s = - D_s \varepsilon_s \frac{\partial C_s}{\partial x} - D_p \varepsilon_t \frac{\partial C}{\partial x} \qquad (8)$$

For instationary transport the equivalent expression to Fick's second law is

$$\varepsilon \frac{\partial C}{\partial t} + \varepsilon_s \frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x}\left(D_s \varepsilon_s \frac{\partial C_s}{\partial x} + D_p \varepsilon_t \frac{\partial C}{\partial x}\right) \qquad (9)$$

It may be noted that if D_S is not concentration dependent and if C_S is in linear equilibrium with C then Equation (9) reduces to

$$\frac{\partial C}{\partial t}(\varepsilon + K) = \frac{\partial^2 C}{\partial x^2}(D_s K + D_p \varepsilon_t) \qquad (10)$$

If the diffusivity in the concentrated film is equal to that in the dilute solution, $D_p = D_S$, and if the total porosity and the transport porosity are equal then

$$\frac{\partial C}{\partial t} = D_p \frac{\partial^2 C}{\partial x^2} \qquad (11)$$

and there will be no retardation although the accumulation in the solid may be considerable. This will considerably speed up the uptake into the matrix and the withdrawal of species from the flowing water in the fractures. It is potentially a very important mechanism to "retard" the movement of cesium and strontium from water flow paths as these species have been found to diffuse by "surface" diffusion. Some experimental evidence of these processes is presented below.

4. Experimental techniques

Different experimental techniques are used to determine the transport properties. In the "through diffusion" experiment the rate of transport through a section of rock is monitored (Garrels et al 1974, Skagius and Neretnieks 1986a, Bradbury and Green 1985) as the solute moves from a vessel with high concentration to a receiving vessel with low concentration. The early instationary part of the experiment can be used to determine the capacity of the rock for holding the solute, ε+K. Different solutes, both charged and uncharged and of different molecular weight have been used in the diffusion experiments. Colloids have also been used to determine their possible blocking of the pore structure (Bradbury and Green 1986). Diffusion in fracture coating materials has been measured (Skagius and Neretnieks 1984, 1986a and Bradbury and Green 1986). Total porosity is often determined by weighing the sample wet and dry.

For large samples and for sorbing solutes the through diffusion method is very time consuming and strictly instationary methods have been applied. Immersion of tablets and larger pieces of rock samples in traced solutions has been used Skagius (1986). The decrease of the bath composition is then utilized to determine the transport properties and the final steady state to determine equilibrium sorption. Profiling of the samples was used by Skagius and Neretnieks (1988) to get profiles of cesium and strontium in granites and gneisses.

Electrical conductivity measurements of rock samples saturated with highly saline solutions have successfully been used to determine the formation factor (Skagius and Neretnieks 1986b). This technique has been used on samples of meter lengths (Atkinson and Titchell 1985).

Through diffusion and electrical conductivity measurements have been performed in pressure cells in the laboratory to determine the influence of stress on porosity and transport properties (Brace et al. 1968, Skagius and Neretnieks 1986b, Bradbury and Green 1986 and Gilling et al. 1987).

Diffusion experiments in undisturbed rock at depth under natural stress conditions have been performed in granite (Birgersson and Neretnieks 1987, 1990, Birgersson 1988) over times of more than 3 years. Attempts have also been made to measure concentration profiles of salt water intrusion in granite over time scales over 30 years in a large block immersed in salt water (Jeffries 1988) and salt water diffusion in rocks exposed to fresh water after glacial uplift (Lehikoinen 1992).

5. Results from laboratory experiments

Skagius and Neretnieks (1986a) made measurements in granites and gneisses from 8 different locations in Sweden. The samples were taken from depths down to more than 500 m. The diffusing substances used were Iodide, Cr-

EDTA and Uranin. The sample thickness was 10 mm. Several of the samples were taken adjacent to fractures and had fracture coating materials.

In Figure 1 the effective diffusivities of Iodide in the granites, gneisses and fissure coating materials are plotted versus the porosities determined by the leaching method. Results obtained by Bradbury et al (1982) for Iodide diffusion in different granites from the United Kingdom are also presented in the figure for comparison. The logarithmic mean values are marked in the figures. The effective diffusivity in the granites, logarithmic mean value = $22.0 \cdot 10^{-14}$ m^2/s and arithmetic mean value = $25.2 \cdot 10^{-14}$ m^2/s, is higher than in the gneisses, logarithmic mean value = $5.1 \cdot 10^{-14}$ m^2/s and arithmetic mean value = $9.2 \cdot 10^{-14}$ m^2/s. The mean values of the porosity determined by the leaching method are also higher for the granites, logarithmic = 0.24 % and arithmetic = 0.26 %, than for the gneisses, logarithmic = 0.13 % and arithmetic = 0.15 %.

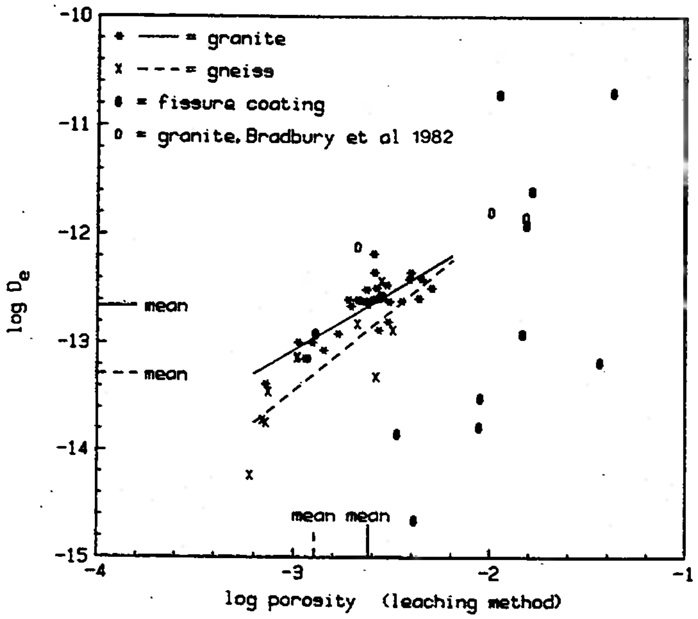

Figure 1 Effective diffusivity of Iodide in the rock materials versus the porosity.

Figure 1 also includes values for fissure coating materials. The effective diffusivity of Iodide in the fissure coating materials is of the same order of magnitude or higher than in the granites and the gneisses. Porosities are higher. There is no indication of pore clogging.

The effective diffusivities for Cr-EDTA and Uranin typically are an order of magnitude lower than those for Iodide. For iodide, values of the formation factors were mostly in the range $1\text{-}20 \cdot 10^{-5}$, with only a few outliers, and about a factor 5 lower for the other two solutes. Skagius and Neretnieks (1986b) also measured formation factors, using the electrical conductivity method. Potassium iodide was used as ionic conductor. Formation factors in the range $1\text{-}30 \cdot 10^{-5}$ were found with only a few outliers. Variations in porosity and diffusivity between samples taken at neighboring positions from the same core typically give values which differ by 2-3 times.

These results indicate that the electric measurement technique gives comparable results to the direct diffusivity measurements. Electric conductivity measurements can be and have been made over sample lengths of 0.3 to over 1 m and they show that the pore system is connected and has the same transport properties over these distances, Skagius (1986), Atkinson and Titchell (1985)

The large difference in formation factors for iodide on one hand and Cr-EDTA and Uranin on the other hand indicate that the latter two bulkier molecules are considerably more influenced by the pore structure.

Bradbury and Green (1985, 1986) measured diffusivities in 4 British and 1 Canadian granite using iodide as the diffusing substance. They found effective, or in their terminology intrinsic, diffusivity values ranging from $2 \cdot 10^{-14}$ to $130 \cdot 10^{-14}$ m^2/s. Formation factors were found to lie between $1.2\text{-}\ 80 \cdot 10^{-5}$. Porosities determined from the instationary part of the diffusion experiment were between 0.06 and 1.2 %.

Fracture coating materials and weathered surfaces, were found to have higher porosities and diffusivities than "good rock". The increases in diffusivity ranged from 20-200 times and the porosity from 10-100 times.

The change in transport properties with distance from the fracture surface has been measured by Skagius and Neretnieks (1986a) and Bradbury and Green (1986). In both investigations it was found that both porosity and diffusivity dropped off with increasing distance from the surface. The decrease with distance strongly depends on the degree of weathering.

5.1 Stress effects

To simulate the stress that may exist in the bedrock at large depths, diffusion experiments with iodide and electrical resistivity measurements in rock materials under mechanical stress have been performed by Skagius and Neretnieks (1986b) with stresses up to 35 MPa, and by Bradbury and Green (1986) up to 16 MPa. In the first mentioned experiment, which covered 6 different granites, the formation factor decreased 1.2 to 2 times for an increase in stress of 5 MPa and then decreased more gradually. At 30-35 MPa the formation factor has decreased by 1.6-4 times. Bradbury and Green(1986) found a faster initial decrease and a leveling off at already 5 MPa for one granite.

The formation factors calculated from the diffusion experiments under stress are in fair agreement with the formation factors from the resistivity measurements at higher pressures.

The results from Skagius and Neretnieks measurements are summarized in Figures 2 and 3. The results from the various methods are compared. Figure 2 shows the diffusivities of iodide determined in granites and Figure 3 the diffusivities of iodide determined in gneisses. The open bars represent the diffusivities in samples under stressed conditions and the filled bars the diffusivity in samples under atmospheric pressure.

The formation factor in samples at 30-35 MPa stress relative to the formation factor in the samples at atmospheric pressure obtained in the diffusion experiments are in fair agreement with those determined from the electrical resistivity measurements for the same rock materials. Electrical resistivity measurements can thus be used to give values of the diffusivity.

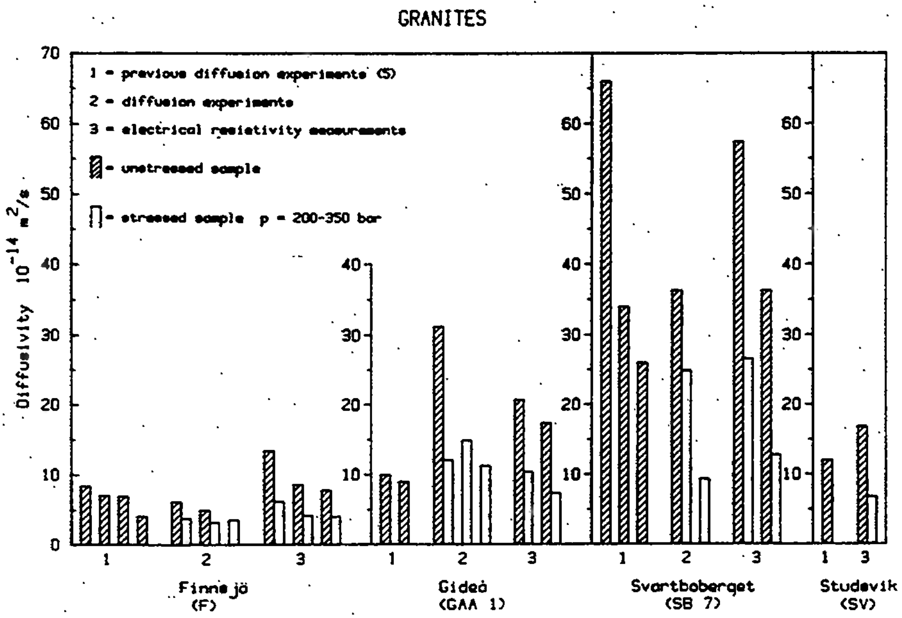

Figure 2 Effective diffusivities in granites.

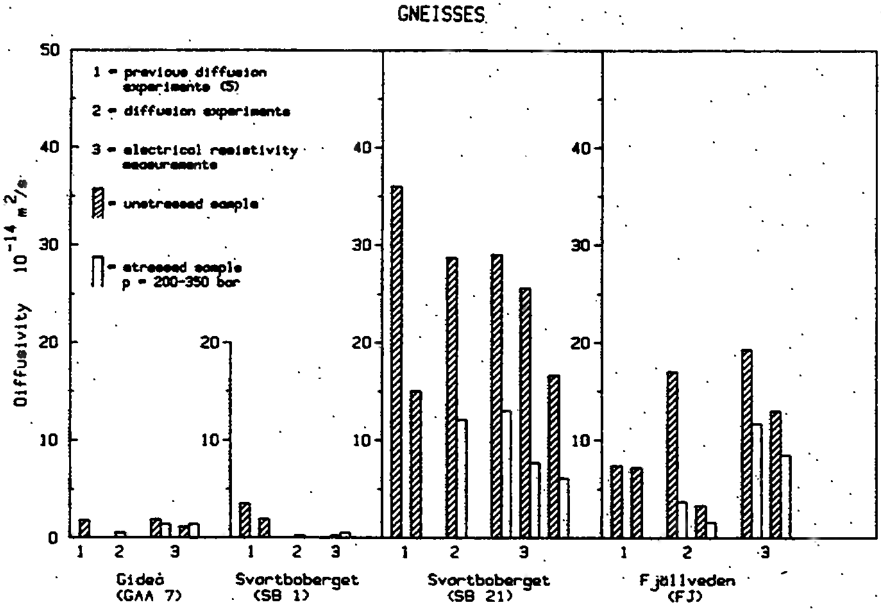

Figure 3 Effective diffusivities in gneisses.

The diffusivity and the formation factor in samples at 30-35 MPa was typically a factor 2 lower and in no case lower than about 1/5 of the value in unstressed samples.

5.2 Sorption and surface diffusion effects

Diffusion experiments using sorbing tracers have been made with different solutes. Skagius et al (1982) made sorption and diffusion measurements on two different granites. The technique used was in-diffusion into crushed particles with 6 different size fractions ranging from 0.1 to 5 mm. The sorption isotherm for strontium was found to be linear whereas that for cesium was slightly nonlinear with Freundlich exponent of about 0.6 for both granites. The experiment were run for more than 10 000 h. The sorption coefficient and the effective diffusivity are obtained simultaneously by fitting the concentration time curve to the solution of Equation [3].

The sorption capacity was found to be practically independent of the particle size if account was taken of the larger outer surface for the smaller particles.

Skagius (1986) made another set of batch in-diffusion experiments into 5 mm thick tablets on Finnsjön and Stripa granites. The sorption coefficients were up to three times lower in the machined tablets.

Skagius and Neretnieks (1988) made sorption and diffusion measurements on rock pieces by the in-diffusion as well as the through diffusion method using cesium and strontium. Biotite gneiss from Fjällveden was used. After contact times of up to 1.5 years the tablets were profiled by grinding off thin sections. Sorption and diffusion values were determined both from the concentration profiles in the samples and from the time lag of the break through curves. Sorption coefficients determined from measured uptake in the rock were about half those determined from the time lag of the breakthrough curve. This contrasts strongly with the large differences obtained by Bradbury and Stephen (1985), who found up to two orders of magnitude differences.

Attempts by Skagius and Neretnieks (1988) to evaluate the effective diffusivity assuming only pore diffusion and retardation failed because the "pore diffusivity" was much higher than can be explained by pore diffusion only. The pore diffusivity of cesium would have to be larger by at least a factor of two over the diffusivity in pure water. This is nearly hundred times more than expected from the formation factor measured with Iodide. By assuming that part of the transport at least is by surface diffusion a good fit could be obtained. Most of the transport must then be by surface diffusion and the transport by pore diffusion would be practically negligible. These results strongly support the notion of surface diffusion.

Figure 4 summarizes Skagius (1986) results in the form of formation factors obtained for different solutes. It is seen that the formation factor is very much higher for cesium and strontium than values obtained from electrical conductivity measurements and from Iodide measurements. This has been interpreted as indicating the presence of “surface” diffusion in addition to transport in pore water only.

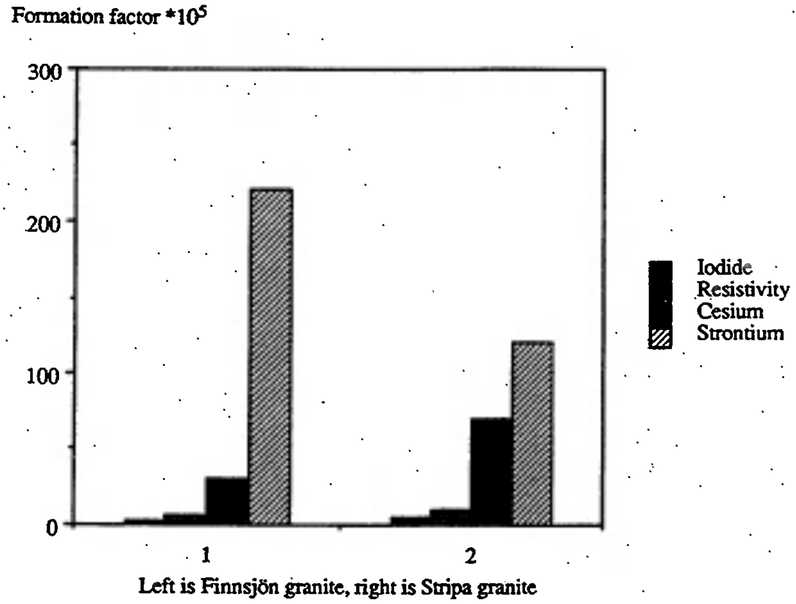

Figure 4 Formation factors for different solutes

Lehikoinen et al (1992) measured the rock capacity factor and effective diffusivity for Na and Cl in concentrations ranging from 0.001 to 1 M. The effective diffusivity for the anion Cl^- is expected to decrease with decreasing concentration, which it did by a factor of 2.0 over the concentration range. The rock capacity factor, ε+K, for the cat-ion Na^+ is equal to the sum of the volumetric sorption coefficient and the porosity, the latter being negligible, and is expected to decrease with increasing concentration which was very clearly found. The effective diffusivity D_e decreased by a factor of 12, and the apparent diffusivity D_a decreased by a factor 1.5. This means that there essentially is no retardation due to sorption and that the sorbed Na^+ must be mobile.

6. Field experiments

One question often posed is if the rock at large depths which has not been stress relieved has an open and connected pore system. It is argued that samples taken to the laboratory have been stress relieved and an irreversible connected pore system may have developed which may not close when the sample is re-stressed in the laboratory.

To test if the matrix of granites at large depths has a connected porosity, a set of three experiments were made by Birgersson and Neretnieks (1990). The experiments were carried out in "undisturbed" rock under its natural stress environment, at the 360 m level in the Stripa mine (Stripa, Sweden). The rock is subject to nearly the same conditions as the rock surrounding a nuclear waste repository as proposed in the Swedish KBS-3 concept.

A mixture of three nonsorbing (conservative) tracers, Uranin, Cr-EDTA, and I^-, were injected into the granitic rock matrix for three different time periods: 3 months, 6 months, and 3.5 years. The subsequent over-corings of the injection holes and surrounding rock showed that the tracers had in some cases migrated at least about 400 mm (measuring limit) into the rock matrix for the experiment with the longest injection time.

The cores from the excavation were sectioned and sample cores were drilled from the sections. The sample cores were leached and the tracer concentrations of the leachates were determined. About 1800 sampling cores were taken in the experiment with the longest duration. Concentration profiles could be obtained outward from the injection hole at various distances along the hole. It could also be seen that there were large differences in migration distance into the rock matrix for samples taken fairly close to each other.

The results from all three experiments showed that the three tracers had migrated through the disturbed zone close to the thin (20 mm) injection hole, in some places through the fissure coating material, and a distance into the "undisturbed" rock matrix. (Birgersson 1988).

The experiments were designed in such a way that the rock accessed by the tracers was not stress relieved during the experiment. This was ensured by injecting the tracer, using a slight over pressure, from a 20 mm diameter hole starting at at distances more 10 m from the drift where the drift has negligible influence on the stress.

The diffusivity D_p and hydraulic conductivity K_p were evaluated at the locations illustrated in Figures 5 and 6. The evaluation was made by fitting the obtained concentration profiles to the advection-diffusion equation for radially symmetric migration. It was not possible to follow the concentration profile as far out into the rock matrix as needed for the evaluation of D_p and K_p at the other locations. The difference in behavior between the tracers is also clearly illustrated. Iodide has diffusivity values that are one to two orders of magnitude larger than Cr-EDTA, while the diffusivity for Uranin is somewhere between these two tracers. The pore diffusivities vary between $2 \cdot 10^{-12}$ to $5 \cdot 10^{-10}$ m^2/s.

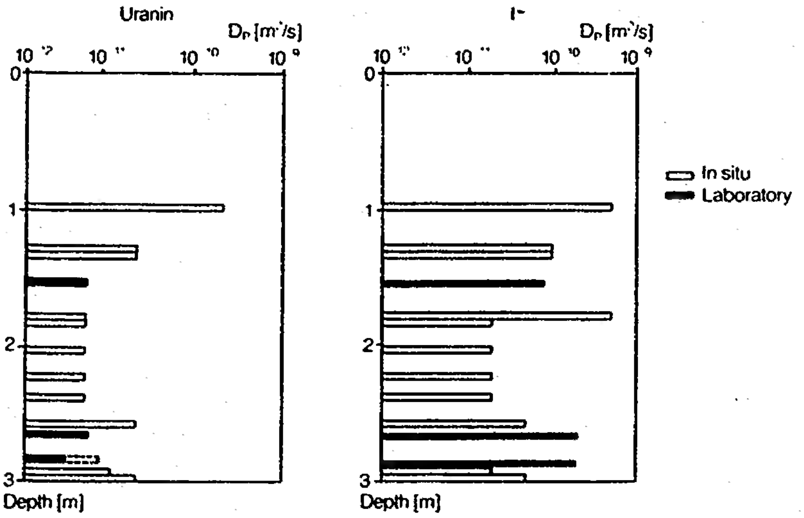

Figure 5 Comparison between diffusivities obtained in the laboratory and in situ.

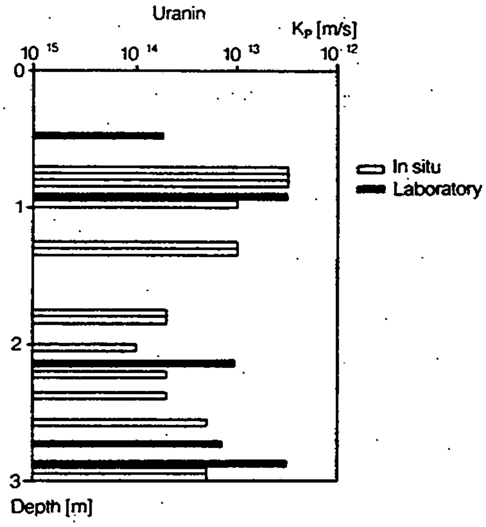

Figure 6 Hydraulic conductivity vs depth in core. From in situ conditions and laboratory experiments.

This difference between the tracers was also seen in the laboratory experiment. These values are of the same order of magnitude as those obtained in situ and are illustrated in Figure 5. The difference in stress levels between the laboratory and the in situ measurements are expected to make the laboratory data about a factor 2 higher (Skagius and Neretnieks 1986b).

The hydraulic conductivities obtained in situ and those obtained in the laboratory experiment are of the same order of magnitude
It was concluded from the investigations that the pore system in virgin undisturbed and unaltered rock is open and connected. This was found to be the case for at least 40 cm. Locally the diffusive and hydraulic properties vary by order to orders of magnitude even at close locations.

The changes in migration properties at different locations and in different directions could not be explained by the laboratory experiments performed concerning porosity, pore size distribution or direction of micro fissures.

The diffusivities and hydraulic conductivities obtained in situ compared well with those obtained in the laboratory experiments.

It may be argued that the tracer intrusion into the rock from the injection hole was not only by diffusion as there was a slight overpressure needed to compensate for the natural head difference between the beginning of the injection section and the bottom of the injection hole. The overpressure was a few percent of the natural pressure in the injection section. In the evaluation of the hydraulic conductivity from the measured concentration profiles, injection volume and overpressure, it was found that advective flow did take place but that it may have contributed to approximately half of the tracers found in the rock. This is not a serious objection, however, because the presence of the tracers shows that the rock has a connected pore system of up to 40 cm under natural stress conditions. Furthermore if a pore system is open to flow then it certainly is available to molecular diffusion.

7. Natural analogues

A number of other attempts have been made to find long time evidence of matrix diffusion. They cover times from a few tens of years on man made objects, salt water profiles caused by glaciation changes over thousands of years to geologic time events spanning millions of years.

7.1. Time span of decades to millennia

Jeffries (1988) has reported on the investigation of a salt water profile in a block of granite rock which was immersed in salt water 30 years ago. The block of granite was 1.5*1*0.6 m and was taken from the Carnmenellis pluton in Cornwall. It was used to construct a water break in Falmouth 1956. After 30 years of immersion in salt water it was retrieved and samples were taken by coring through the block in the shortest direction.

The core was sectioned and leached of its dissolved anions, Cl^-, Br^- SO_4^{2-}, and F^-. The concentration of the ions in the leachates were measured and concentration profiles were obtained. Cl^- and Br^- concentrations were 15 to 40 times higher than those in fresh granite samples obtained from the same quarry. The profiles were flat and only lower bounds of the diffusivities could be determined. The pore diffusivity was estimated to be larger than $9 \cdot 10^{-11}$ m^2/s. Measured values on samples of fresh unweathered rock were found to be at least 3 times lower.

The SO_4^{2-} and F^- profiles had sharp concentration peaks about 10 cm from the surface which were interpreted to be caused by weathering of the rock which contains minerals with these species. It was suggested that these species are slightly sorbed on the mineral surfaces and that the movement of these species is slightly retarded in relation to non-interacting species. Diffusivities and sorption coefficients could not be determined unequivocally from the data but the assessed apparent diffusivities were found not to be unreasonable, although some of the intrusion of the salt water may have been caused by capillary suction, because the rock had been at least partly dried before immersion in the sea.

Lehikoinen et al. (1992) describe an investigation where a granite core about 1 m long was obtained which contained old saline water. The core was taken from rock located between two fractures in which, due to the post glacial uplift, fresh water has been flowing for a few thousand years. A very clear salt concentration profile was found which was interpreted was caused by molecular diffusion. It was concluded that the pore system is open and connected for at least one meter over the time period studied. An effective diffusivity of about 10^{-12} m^2/s was obtained. This value is about one order of magnitude higher than expected.

7.2. Time spans of order of million years

Miller at al (1994) and Brandberg et al (1993) cite a number of investigations of rock samples where concentration profiles of different species have been obtained. They include uranium disequilibrium studies in rock samples near uranium ores, Rare Earth Element profiles and other element profiles. One investigation from the Palmottu analogue project (Kumpulainen et al. 1992) showed clear evidence of uranium series disequilibrium in an altered zone over a distance of 2.5 cm in rock adjacent to a uranium mineralization. Smellie et al. investigated samples adjacent to active fractures from Kråkemåla in Sweden, and Böttstein and Grimsel in Switzerland. In the weakly altered granite at Kråkemåla uranium disequilibration at least to depths of 3 cm was found and in the Böttstein and Grimsel cores different elements showed moblisation at distances ranging from 3 to 20 cm. In all cases the samples nearest the fractures showed different degrees of alteration.

Valkiainen (1992) in a compilation of laboratory and field data gives several examples of porosity and formation factor profiles of granite cores as a function of distance from the active fracture. Canadian, Swedish and Finnish rocks are included. Typically the first 2-5 cm have higher values and then they level out at larger distances to 2-3 times lower values than at the surface.

In the cited and most other cases the profiles are erratic and it is difficult to quantitatively evaluate diffusivities with any confidence. One of the problems is that the initial and boundary conditions are often not known. Another problem is that for all sorbing and precipitating species the retardation due to these effects is not known and only the ratio of the pore diffusivity D_p and the retardation coefficient can be estimated at best.

Nevertheless, these observations show that matrix diffusion is active over very long times, thousands to millions of years in granites and gneisses but the evidence is only available for altered rock regions.

Romero et al. (1993) investigated the processes underlying the the formation of redox fronts in an open pit mine at Poços de Caldas, Brazil. The phonolitic host rock is intruded by oxygen by flow with water and also by molecular diffusion in the porous rock matrix. The oxygen oxidizes the pyrite in the rock and very sharp redox fronts are formed and can be clearly seen as the colour change between the originally gray rock and the oxidized reddish rock.The large scale movement of the front is clearly caused by inflow of water. However, in many places on the high vertical walls of the mine and on the flat bottom channels in fractures have been exposed where water has flown. The channels are typically from tens of cm to meter wide and have apertures which are hardly visible by the naked eye. Around these channels in the surrounding gray rock is a zone of cm to tens of cm or more of oxidized red rock. These oxidized channel walls were interpreted to be formed as follows. When oxygenated water flows in the fractures in the rock the flow is confined to a small portion of the fracture, a channel, as is known from other field studies. The oxygen in the flowing water diffuses into the rock matrix over the channel surfaces. Along the channel a thin band of oxidized rock is formed. Eventually the oxygen is depleted as the water has proceeded far along the channel. The channels can extend tens to hundreds of meters into the otherwise reducing rock. Measurements of the matrix porosity and diffusivity and the theoretical calculations indicate that the observed channels are likely to have formed in the described fashion. The availability of reducing minerals to oxidants in a dense rock matrix by diffusion over times of the order of a million years was in clear evidence at this site.

8. Discussion and conclusions

There is ample evidence from laboratory investigations that matrix diffusion takes place in all crystalline rocks investigated so far. Effective diffusivities for nonsorbing species in the range of 10^{-14} to 10^{-13} m^2/s, or larger, are typically found in the low porosity rocks, $\varepsilon < 0.5$ %, and larger values are found for more porous rocks. Laboratory as well as field experiments show that the pore system is connected over distances of at least 0.4 m even at rock stresses comparable to alterations has been found. The pore system has been open for thousands of years over distances of at least meters as seen from salt water profile formed since the latest ice age.

Laboratory experiments show that in some rocks there is clear evidence of ion exclusion of an-ions such as Cl^- and I^- reducing the effective porosity and diffusivity. The opposite has also been observed for the cat-ions Na^+, Cs^+ and Sr^{2+}. For the latter order or orders of magnitude higher effective diffusivities are found than what a neutral species has. This is interpreted as these ions being mobile in "sorbed" state to a high degree. This is called surface diffusion but is not well understood. It is potentially of quite some importance because it can considerably enhance uptake of the nuclides into the matrix, withdrawing them from the mobile water in the fractures. The phenomenon should be further investigated experimentally, theoretically and hopefully by finding some suitable natural analogue.

The observations of uranium series disequilibration in the vicinity of water bearing fractures and uranium mineralizations clearly shows that over times of about one million years uranium migrates by diffusion and sorbs on the minerals either original, or often secondary such as ferric oxy-hydroxides. The disequilibration depths of 3-10 cm is in the range of expected values for such times and diffusivities and sorption coefficients. Often the penetrated regions have been altered by hydrothermal processes and are not representative of undisturbed rock. It need not be concluded that the observed depths are upper limits and that rock must be altered to take up nuclides. There seems to be little long time evidence that sorbing nuclides have been found to have penetrated beyond these distances and it would be valuable if such evidence could be found.

However, already a 3-10 cm penetration depth is in practice sufficient to withdraw and retard all sorbing nuclides of interest for a repository design such as KBS-3 and similar.

The only clear field evidence of low temperature redox front formation by diffusion is found at Poços de Caldas. The rock there is crystalline but more porous than granites and gneisses and the reducing agent, pyrite, is not the same as in the latter rocks. It would be valuable if evidence for these phenomena could be found and quantified in granites and gneisses.

9. Notation

C	Concentration	mol/m^3
C_p	Concentration in pores	mol/m^3
C_s	Concentration sorbed film	mol/m^3
D_a	Apparent diffusion coefficient	m^2/s
D_e	Effective diffusion coefficient in matrix	m^2/s
D_p	Pore diffusion coefficient	m^2/s
D_s	Surface diffusion coefficient	m^2/s
D_w	Diffusion coefficient in water	m^2/s
F_f	Formation factor	-
K	Volumetric sorption coefficient	m^3/m^3
N	Flowrate of dissolved species	mol/s
R_d	Retardation factor	-
t	Time	s
x	Distance into matrix	m
α	Rock capacity factor	-
δ_D	Constrictivity	-
ε	Porosity	-
ε_t	Total porosity	-

η	Penetration depth	m
ρ_p	Density of rock	kg/m^3
τ	Tortuosity	

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IN-SITU DISTRIBUTION COEFFICIENTS DERIVED FROM URANIUM AND THORIUM DECAY SERIES ISOTOPES IN WATER-ROCK SYSTEMS: PROMISE AND PRACTICE

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ABSTRACT

Mass balance theories relating the distribution of radionuclides between groundwater and rock surfaces to activities of uranium and thorium decay series radionuclides in natural water-rock systems are summarized. Interpretation of natural systems using these theories offers the promise of independent, in situ evaluation of laboratory based distribution coefficient data, which are commonly used in performance assessments for geologic repositories for nuclear waste. Selected applications of this approach reported in the literature are summarized. Most applications require numerous approximations and assumptions. Published criticisms of the approach are also summarized. Generally, in situ distribution coefficients can not be regarded as transferable between systems or directly applicable as conservative parameters for performance assessments. Nevertheless, with increasing model sophistication and comprehensive analytical data insights can be provided on the rates and mechanisms of water-rock interactions and chemical transport. Such analyses should provide support for assumptions and approximations associated with performance assessments for nuclear waste repositories, including constraints on important abstracted model parameters.

Introduction

Performance assessments for geologic repositories for nuclear waste generally and conveniently invoke distribution coefficients for individual radioelements to simulate retardation of radionuclide migration. Theories have been proposed relating the distribution coefficient for a nuclide to activities of uranium and thorium decay series radionuclides in natural water-rock systems. The promise of an independent, in situ evaluation of radionuclide transport modeling methodologies and laboratory based distribution coefficient data provides worthy motivation for natural analog studies. However, the practice of interpretation of natural system data is marked by the characteristic complexity of nature relative to our models. This paper offers a brief summary of the promise and practice of the evaluation of in situ distribution coefficient values using natural decay series radionuclides.

The promise

The initial theoretical basis for determination of in situ distribution coefficients and retardation factors using data from decay series isotopes is generally attributed to Krishnaswami et al. (1982). The theory couples equations for mass balance at a point among dissolved and adsorbed radionuclide species in the uranium and thorium decay series. Radioactive decay of the species and their parents, production by alpha recoil, desorption and adsorption kinetics and/or sorption equilibria, and dissolution and precipitation kinetics are treated explicitly in various applications. The theory presented in this paper generally follows the symbolic formalism of Ku et al. (1992), who developed mathematical relations for description of a static system with explicit sorption/desorption kinetics (analogous to Krishnaswami et al., 1982), and relations for the alternate description of a one dimensional transport system with sorption corresponding to local equilibrium (analogous to Davidson and Dickson, 1986).

Static system model

In the absence of transport by advection or diffusion (the static, chemically kinetic model), changes with time of dissolved and adsorbed concentrations are given by

$$\frac{\partial C}{\partial t} = P_r + P_d + \lambda' C' - k_p C - \lambda C - k_1 C + k_2 C_a \qquad (1)$$

and

$$\frac{\partial C_a}{\partial t} = k_1 C - k_2 C_a - \lambda C_a + \lambda' C_a' \qquad (2)$$

where C and C_a represent aqueous and adsorbed concentrations of a dissolved species which both have units of atoms water-volume^{-1}, which results in a dimensionless ratio. Constants k_1, k_2, k_p and λ denote, respectively, first order adsorption, desorption, and precipitation rate constants (assuming applicability of first order kinetics), and the radioactive decay constant for the species (time^{-1}), P_r and P_d represent the supply to the aqueous phase due to recoil (from the bulk solid) and due to dissolution (atoms water-volume^{-1} time^{-1}), and ' (prime) designates the radioactive parent of the species; $\lambda' C'$, the activity of the parent, equals the rate of ingrowth of the species in solution.

Under steady-state conditions the partial derivatives in Eqs. (1) and (2) equal zero, and it follows from these equations that

$$\frac{P_r + P_d + \lambda' C' - k_p C + \lambda' C_a'}{\lambda C} - 1 = \frac{k_1}{k_2 + \lambda\left(1 - \frac{\lambda' C_a'}{\lambda C_a}\right)} = K \qquad (3)$$

Eq. (3) relates the radionuclide concentrations to production rates, and adsorption and desorption rate constants, and the distribution coefficient (K) defined as

$$K = C_a / C \qquad (4)$$

In the development by Krishnaswami et al. (1982), ingrowth in the adsorbed inventory and precipitation were neglected (i.e., $\lambda' C_a' = k_p C = 0$), so Eq. 3 reduces to

$$\frac{P_r + P_d + \lambda' C'}{\lambda C} - 1 = \frac{k_1}{k_2 + \lambda} = K^* \qquad (5)$$

where K* is an approximate value of K. The parameters K, as defined by Eq. (4), and K* are not generally equilibrium distribution coefficients. For example, if λ is significant relative to k_2, then K* in Eq. (5) may vary significantly among different radioisotopes of the same element. In contrast, equilibrium distribution coefficients for isotopes of individual elements of the uranium and thorium decay series depend only subtly on half life.

Transport system model

An alternate model presented by Ku et al. (1992) invokes linear reversible sorption, a conventional approximation adopted in performance assessments. The model also accounts for chemical transport represented by the advection-dispersion equation. This approach follows that of Davidson and Dickson (1986) for distribution of decay series radionuclides with a distributed source. In addition, it takes explicit account of precipitation. The transport equation is written for the species of interest in the combined aqueous and adsorbed states as

$$\frac{\partial(C + C_a)}{\partial t} = D_s\frac{\partial^2 C}{\partial x^2} - V_w\frac{\partial C}{\partial x} + P - k_p C - \lambda(C + C_a) \qquad (6)$$

where D_s stands for the effective aqueous diffusivity (length^2 time^{-1}), V_w denotes the specific discharge (length time^{-1}), P represents the combined production term [$P = P_r + P_d + \lambda'(C' + C_a')$], and x and t stand for length and time.

The transport equation developed by Ku et al. (1992) depends on substitution of Eq. (4) and its derivative with respect to time for constant K in Eq. (6). In this context K is regarded as an equilibrium constant, and the resulting equation is valid only when adsorption and desorption rate constants are sufficiently large that the net sorption reaction is effectively instantaneous relative to other influences on sorbed and dissolved concentrations such as transport or radioactive decay. For example, constant K requires $\lambda\left(1 - (\lambda' C_a'/\lambda C_a)\right)$ in Eq. (3) to be constant or insignificant relative to k_2. Adopting these assumptions and making the noted substitutions, rearrangement of the resulting equation leads to

$$\frac{\partial C}{\partial t} = \frac{D_s}{1 + K}\frac{\partial^2 C}{\partial x^2} - \frac{V_w}{1 + K}\frac{\partial C}{\partial x} - \left(\frac{k_p}{1 + K} + \lambda\right)C + \frac{P}{1 + K} \qquad (7)$$

which is the advection-dispersion equation representing retarded transport properties and source-sink terms involving rates of production, precipitation, and radioactive decay.

For steady state conditions ($\partial C/\partial t = 0$), constant P (i.e., a uniformly distributed source except at the upstream source), and constant V_w, D_s, k_p, and K, for boundary conditions of $C = C_0$ at $x = 0$ and $\partial C/\partial x = 0$ as $x \rightarrow \infty$ (which would represent a contaminant source at the upstream boundary), the solution to Eq. (7) is given by

$$C = \frac{P}{\lambda + \lambda K + k_p} + \left(C_0 - \frac{P}{\lambda + \lambda K + k_p}\right)e^{(-\alpha x)} \tag{8}$$

where α is a constant given by

$$\alpha = \frac{-V_w + [V_w^2 + 4D_s\lambda(1 + K + k_p/\lambda)]^{1/2}}{2D_s} \tag{9}$$

Eqs. (8) and (9) are equivalent to Eqs. (18.5) and (18.7-corrected) of Ku et al. (1992).

Extensions

The promise of this theory is that values for distribution coefficients and related parameters in natural systems may be extracted based on measurements of properties such as aqueous and solid phase radionuclide activities. This prospect is enhanced by the existence in nature of multiple isotopes of individual chemical elements in the uranium and thorium decay series (e.g., Th, Ra, and Pb). Chemical properties such as equilibrium constants, diffusion coefficients, and precipitation rate constants should vary insignificantly among isotopes of the same element. Thus, if applicable, an equation such as Eq. (5) can be written for each of the isotopes, providing multiple constraints on unknown parameters. For example, Ku et al. (1992) present equations relating activities of five radioactive thorium isotopes, which can be solved simultaneously for the five parameters: dissolution rate, precipitation rate, adsorption rate, desorption rate, and surface area.

The practice

In general the application of theories for determination of in situ distribution coefficients has involved identification of particular systems for which the equations may be simplified and some parameters approximated. Valid use of the approach is therefore limited to site specific applications, and results typically depend on numerous assumptions. A classic example from Krishnaswami et al. (1982) illustrates one application. Under circumstances for which Eq. (5) is valid, the problem of determining the in situ distribution coefficient K* reduces to determination of the concentrations C and C' and the production in solution due to recoil and dissolution ($P_r + P_d$). To address this problem, Krishnaswami et al. (1982) presented arguments that production of ^{222}Rn in groundwaters by ingrowth and dissolution is insignificant relative to recoil production to solution by alpha decay of ^{226}Ra in the solids. Ingrowth can be discounted because ^{222}Rn activities in solution commonly exceed ^{226}Ra activities. The short half life of ^{222}Rn (3.82 days) and its negligible sorption suggest that, at steady state, the alpha recoil rate equals the ^{222}Rn activity in solution. Similarly, it was assumed that production of ^{224}Ra in solution is dominated by recoil from alpha decay of ^{228}Th. The recoil efficiency of ^{224}Ra was estimated to be equivalent to that of ^{222}Rn. For these conditions the production of ^{224}Ra by recoil equals the activity ($A = \lambda C$) of ^{222}Rn in solution times the ratio of the activities of their respective parent radionuclides in the solid, i.e.,

$$P_{r224_{\mathrm{Ra}}} = A_{222_{\mathrm{Rn}}}(A_{s228_{\mathrm{Th}}}/A_{s226_{\mathrm{Ra}}}) \tag{10}$$

where A_s stands for the activity in the solid (decays time^{-1} water-volume^{-1}). Measurements of the activity of ^{222}Rn in Connecticut, USA, groundwaters and the ^{228}Th/^{226}Ra activity ratio in corresponding drill hole cuttings permitted Krishnaswami et al. (1982) to calculate the recoil production of ^{224}Ra using Eq. (10), which they took as an estimate of $P_r + P_d + \lambda'C'$ in Eq. (5) by assuming $P_r >> (P_d + \lambda'C')$. Measurement of the activity of ^{224}Ra in the groundwaters yielded λC in Eq. (5), permitting calculations of in situ values of K*, the ^{224}Ra distribution coefficient, which ranged from 4,800 to 123,000 (Krishnaswami et al., 1982).

An example of constraints provided by multiple isotopes of a given element is given in the study of Copenhaver et al. (1993) on the distribution of lead between solid adsorption sites and the aqueous phase in an aquifer in Paleozoic crystalline rocks in Connecticut. Multiple constraints permit estimation of the adsorption and desorption rate constants as well as the distribution coefficient. The study of Copenhaver et al. (1993) adopts the approach of Krishnaswami et al. (1982) summarized in the previous example for a static system with explicit sorption and desorption kinetics. The production of both ^{214}Pb and ^{210}Pb in solution is assumed to equal the activity in solution of ^{222}Rn which is a progenitor of both lead isotopes. Thus, production in the aqueous phase is assumed to predominate over production due to dissolution or alpha recoil from the solid. Also, precipitation, coprecipitation, and colloidal concentrations are assumed to be negligible. Under these circumstances, Eq. (5) can be rearranged for each isotope to give simultaneous expressions of the form

$$\frac{P}{\lambda C} = \frac{k_1}{k_2 + \lambda} + 1 = \frac{k_1 + k_2 + \lambda}{k_2 + \lambda} \tag{11}$$

where P represents the production. Rate constants for sorption and desorption should be nearly identical for each Pb isotope, although their decay constants and concentrations differ. Solutions of simultaneous expressions of Eq. (1) written for each isotope yield equations for k_1 and k_2. The adsorption reaction rate constant (k_1) is given by

$$k_1 = \frac{(\lambda_{210} - \lambda_{214})\left(1 - \frac{\lambda_{210}P_{210}}{C_{210}}\right)\left(1 - \frac{\lambda_{214}P_{214}}{C_{214}}\right)}{\frac{\lambda_{210}P_{210}}{C_{210}} - \frac{\lambda_{214}P_{214}}{C_{214}}} \tag{12}$$

where subscripts 210 and 214 denote values for the ^{210}Pb and ^{214}Pb isotopes. The desorption rate constant is given by

$$k_2 = \frac{\frac{\lambda_{210}P_{210}}{C_{210}}\frac{\lambda_{214}P_{214}}{C_{214}}\left(\lambda_{210} - \frac{\lambda_{214}P_{214}}{C_{214}}\right) + \lambda_{210}\frac{\lambda_{214}P_{214}}{C_{214}} - \lambda_{214}\frac{\lambda_{210}P_{210}}{C_{210}}}{\frac{\lambda_{210}P_{210}}{C_{210}} - \frac{\lambda_{214}P_{214}}{C_{214}}} \quad (13)$$

Eqs. (12) and (13) are equivalent to Eqs. (2) and (3) of Copenhaver et al. (1993). Using isotopic concentrations measured for a granitic aquifer in Connecticut, Copenhaver et al. (1993) obtained values of 0.020 min^{-1} for k_1 and $2.0\text{x}10^{-7}$ min^{-1} for k_2. The corresponding distribution coefficient, which Copenhaver et al. (1993) define to be equal to k_1/k_2, is $1\text{x}10^5$, indicating strong sorption.

Methods to assess a variety of related phenomena have been formalized theoretically and to a lesser extent attempted. Ku et al. (1992) review approaches for making in situ estimates of dissolution and precipitation rates, reactive surface areas, residence times, sorption and desorption rate constants, and retardation factors. Ivanovich et al. (1992) applied a variation of the technique of Ku et al. (1992) for multiple Th isotopes using data from a sandstone aquifer in Great Britain to obtain estimates of adsorption and desorption rate constants, the precipitation rate constant, and retardation factors for ^{238}U and ^{234}U. Ivanovich et al. (1992) did not use ^{222}Rn activity as an indicator of alpha recoil production, but rather estimated it to be equal to the product of the activity of the parent radionuclide in the solid, the recoil efficiency, the recoil range, the surface area of the solid, and the density of the solid. However, many of the data required in the analysis were not directly available and estimates were employed.

Discussion

Numerous complications arise in attempts to extract distribution coefficients from field data. One basic problem is a consequence of limitations in the concept of K_d, the form of the distribution coefficient generally invoked in performance assessment models. Proportionality between adsorbed and dissolved concentrations is likely to be valid under limited circumstances of small concentration ranges (e.g., trace concentrations) and constant water-rock properties such as pH, temperature, and surface area. K_d is conventionally expressed as the concentration ratio of moles (or mass) of adsorbed species per mass of solid to moles of dissolved species per volume of fluid. The surface-specific mechanism (adsorption) generally invoked to control retardation of radionuclide transport makes the mass-based measure of solid-fluid distribution (K_d) dependent on the effective surface area to mass ratio in each system and, therefore, difficult to extrapolate. Furthermore, the adsorbed concentration C_a in the mathematical relations derived above cannot generally be equated to the bulk solid concentration.

The various approximations and assumptions invoked in the use of natural uranium and thorium decay series radionuclides to determine water-rock distribution coefficients have engendered considerable criticism. For example, Rama and Moore (1984) presented analytical data indicating that Rn is released to the bulk solution from nanopores where it is introduced by recoil, whereas other decay series isotopes are retained in the nanopore network and not released. Hence, the ^{222}Rn activity in solution may overestimate the production rate of other isotopes, and values of K* for Ra determined by Krishnaswami et al. (1982) may represent upper limits.

McKinley and Alexander (1992, 1993) levy an assortment of criticisms on the interpretation of natural decay series isotope data, approximations invoked in determinations of in situ distribution coefficients, and applicability of these coefficients in performance assessment calculations for contaminant transport. These critics correctly note the complex variety of processes that control the distribution of chemical species among the aqueous phase, sorption sites, and bulk solids, as well as ambiguities associated with analytical methods. Processes neglected or incompletely represented in various theoretical approaches and interpretations of data include nonlinear sorption, sorption site saturation, precipitation, coprecipitation, colloid formation and transport, and disequilibrium between sorbed species and the bulk solid. In particular, McKinley and Alexander (1992, 1993) warn against potentially dangerous applications of distribution coefficients or retardation factors in performance assessments for radioactive waste disposal systems when the coefficients can not be shown to provide conservative results.

The complexities of nature noted by McKinley and Alexander (1992, 1993) are the same that characteristically limit the ability of performance assessment models based on the K_d concept to provide realistic representations of contaminant transport. If nature is so complex that it is impossible to interpret in situ radionuclide activities in terms of species distributions, then how much confidence can we have in performance assessment models for contaminant radionuclide transport in geologic systems? Complexity and its potential consequences must be recognized, even as models are knowingly generated using grossly simplistic descriptions of natural processes. Some complex natural systems and system components will defy interpretation, and are unlikely to provide useful natural analog information. Natural analog studies in support of performance assessments for nuclear waste disposal should focus on systems that offer reasonable control on important variables, while providing the opportunity to study uncertain processes of significance to performance. Furthermore, theoretical models of increasing sophistication are required to account for nature's complexities, and improvements in the comprehension and accuracy of analytical data will provide finer constraints on natural processes. These advances should aid both the interpretation of natural systems and the accuracy and confidence of projections such as performance assessments.

One such advance in the theory for in situ distribution coefficients was described by Ku et al. (1992), based on work by Hammond et al. (1988), by taking explicit account of precipitation kinetics (i.e., the k_pC term in Eq. (1)). Single component, first order precipitation kinetics is a simplification for general systems, but it has nevertheless found applications in geochemistry, such as in the interpretation of quartz reaction kinetics (Rimstidt and Barnes, 1980). Kinetic precipitation in the formulation of Ku et al. (1992) also leads to a relatively realistic treatment of the dissolution/precipitation reaction rate (for a one component system) as equilibrium is approached. Neglecting radioactive decay and sorption in Eq. (1), the zero order dissolution rate term (which is considered to represent the forward dissolution reaction only) is coupled to the first order precipitation term by

$$\frac{\partial C}{\partial t} = P_d - k_pC \tag{14}$$

The condition of chemical equilibrium for the system is characterized by $\partial C/\partial t = 0$, so it follows from Eq. (14) that

$$P_d = k_pC_e \tag{15}$$

where C_e denotes the equilibrium concentration (or equilibrium constant). Substituting Eq. (15) in Eq. (14) yields

$$\frac{\partial C}{\partial t} = k_pC_e - k_pC = k_p(C_e - C) \tag{16}$$

According to Eq. (16), the net rate of reaction is realistically proportional to the degree of disequilibrium, and goes to zero for the equilibrium state. Multicomponent systems are generally governed by more complex kinetic relations, and steady state concentrations invoked in models for in situ distribution coefficients depend on balancing all sources and sinks including those due to radioactive decay and recoil. Nevertheless, a first order precipitation term may approximately balance production by dissolution, permitting estimations of its significance in interpretations of field data.

Concluding remarks

Uranium and thorium decay series radionuclides provide powerful tools for the interpretation of the evolution of natural systems. Their chemical fractionation in nature together with their differing decay constants permit important temporal constraints to be placed on a variety of geologic and hydrogeologic phenomena. The occurrence of multiple radioactive isotopes of the same element in these series enhances the possibility of quantifying the rates and mechanisms of processes of fractionation such as radionuclide sorption. These species also comprise some of the radioactive waste components for which geologic repositories are being conceived and simulated in computational models. Natural analog research in support of performance assessments for geologic repositories for nuclear waste has made and will continue to make valuable use of natural decay series radionuclide concentrations.

The distribution of radionuclide species among aqueous, sorbed, and bulk solid states is a function of many complicated chemical and hydrologic phenomena in nature and, hypothetically, in geologic repositories. While performance assessments may reasonably rely on conservative simplifications, they generally fail to provide realistic representations of natural processes. Similarly, nature will not easily hand up appropriate parameters for models that are simplistic abstractions of the natural processes. The challenge is to develop increasingly comprehensive conceptual, theoretical, and computational models for chemical interactions in water-rock systems and for transport of chemical species. Applications of these models in interpretations of natural data for well characterized systems should provide insights on the rates and mechanisms of water-rock interactions and chemical transport. Such analyses should provide support for assumptions and approximations associated with performance assessments for nuclear waste repositories, including constraints on important abstracted model parameters.

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GEOCHEMICAL TRANSPORT MODELING

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1. Introduction

Contaminant transport in the subsurface environment involves complex, interdependent processes of hydrology, geology, geochemistry, and microbiology in a heterogeneous medium that is very difficult to characterize. The challenge for disposal of hazardous wastes is to demonstrate that subsurface disposal can be done "safely." Hence, safety assessment has become a major issue for the remediation of contaminated sites and especially for the demonstration of safe containment and long-term storage of everything from organic solvents to nuclear wastes.

Safety or performance assessment of a nuclear waste repository site must make estimates of travel times and paths for long-lived radionuclides. Such an assessment requires knowledge of all important subsurface processes that can mobilize radionuclides over long periods of time. Predicting the future behavior of radionuclides for thousands to millions of years is outside the normal experience of earth scientists and engineers. Predictions of this type cannot be tested before actual disposal takes place. It is common practice to use models for the prediction of radionuclide behavior in both the near-field and far-field, i.e. to model waste dissolution, cannister corrosion, exchange, reaction, and diffusion through cement and clay backfill, solubility and sorption along fractures and pore spaces, travel times and directions for ground-water flow, etc. Geochemical models can provide guidance for some of these performance assessment questions.

This presentation is a brief overview of geochemical transport modeling for the 6th CEC Natural Analogue Working Group Meeting in Santa Fe, New Mexico, September 12-16, 1994. Limitations of geochemical modeling and suggestions for future research are included. It has not been reviewed or officially approved by the U.S. Geological Survey.

2. Origin and evolution of geochemical modeling

Geochemical transport modeling attempts to integrate geochemical reaction modeling with fluid flow or solute transport modeling. However, geochemical modeling has developed separately from flow modeling.

2.1. Geochemical Modeling

Recent reviews of geochemical modeling are available from a variety of sources. Of special note are four recent books: Alley (1993), Appelo and Postma (1993), Chapelle (1993), and Melchior and Bassett (1990). In addition, reviews by Grove and Stollenwerk (1987), Yeh and Tripathi (1989), Mangold and Tsang (1990), Plummer (1992), and Parkhurst and Plummer (1993) are especially noteworthy. These were the primary sources from which the discussion in this paper was distilled.

Geochemical modeling is an outgrowth of applying chemical principles and theories to water-rock interactions. Landmark papers by Garrels and Thompson (1962) on the speciation of seawater, by Garrels and Mackenzie (1967) on mass balances during granitic weathering, by Helgeson (1968) on the theoretical basis for geochemical modeling, by Helgeson, Garrels, and Mackenzie (1969) applying geochemical modeling to simulate natural processes with the aid of computers, and by Helgeson, Brown, Nigrini, and Jones (1970) further extending this computational approach, put geochemical modeling on a firm foundation and inspired the development of many computer codes used today.

Parallel with the development of mass balances in geochemical modeling, Bormann and Likens (1967) and Likens, and others (1977) developed a mass balance (input-output budgets) approach for watershed chemistry, similar in concept to geochemical mass balances but with an emphasis on nutrient cycling.

Several computer codes were developed in the 70's and 80's that could perform speciation and saturation index calculations for natural waters and for synthetic aqueous solutions. Speciation calculations found numerous applications including toxicity studies, bioavailability and bioaccumulation studies, sorption studies, colligative studies, solubility studies, formation of mineral deposits, hydrometallurgical reactions, physiological studies, as well as testing the state or condition of a natural water with respect to mineral equilibrium saturation.

The next major step was the formalization of mass balances (Plummer and Back, 1980) into the "inverse modeling" procedure advocated by Plummer, and others (1983) and Plummer (1985). This simple yet powerful approach to the interpretation of water-rock interactions has become a valuable tool in groundwater geochemistry studies. It will be described in the next section.

2.2. Surface Chemistry Modeling

A fundamental aspect of aqueous geochemistry is surface chemistry and increasing use of sorption models, especially the surface complexation model (SCM), has been readily apparent. The landmark book by Dzomback and Morel (1990) is proving to have considerable influence on sorption calculations in geochemistry. It provides a reasonable basis for making adsorption calculations on hydrated ferric oxides in complicated systems. The three books edited by Davis and Hayes (1985), Stumm (1987), and Hochella and White (1990) constitute an excellent source of information and data on surface chemistry with a focus on water-mineral interfacial processes. Parks' (1990) thorough and concise account of the science of adsorption and Davis and Kent's (1990) comprehensive discussion of surface complexation modeling in aqueous geochemistry are particularly noteworthy.

2.3. Solute Transport Modeling

Solute transport modeling evolved from fluid flow modeling by adding dispersion and chemical reaction terms to the continuity equation. Dispersion is mathematically included by adding a Fick's law term for diffusion, resulting in the so-called advection-dispersion equation. Reaction is included by adding other terms for processes such as radioactive decay, first-order chemical reaction, or sorption (often a distribution coefficient or retardation factor). Solute transport models that include these types of reaction terms are necessarily simplifying the chemistry thereby incorporating ambiguities into the interpretation. Calibration of these models also introduces a kind of simplification because properties and processes are averaged and smoothed. These simplifications make the models much more manageable and may give adequate results for the stated objectives of the investigation but they can be very misleading if taken too seriously.

3. Mechanics of geochemical transport modeling

3.1. General Approaches

Three general approaches have been used to model water-rock interactions: forward modeling, inverse modeling, and statistical. Plummer (1985, 1992) describes forward modeling as that which predicts water compositions and mass transfer quantities resulting from a given initial condition and hypothesized reactions. Forward modeling is also known as simulating geochemical reactions because it simulates the chemical evolution of a water and a rock for a specified set of conditions. Inverse modeling utilizes water compositions, mineralogical data, and isotopic data as constraints on a hypothesized set of reactions. The primary constraints on forward modeling are the assumptions made by the modeler whereas the primary constraints on inverse modeling are the quantity and quality of the field data in addition to the assumptions made by the modeler. In practice, the division between forward and inverse modeling is not so clear. Forward modeling can be constrained by mineralogical data but not compositional data on waters. Inverse modeling requires some minimal data on water compositions but might not be constrained by mineralogical data. Inverse modeling, no matter how complete the data, usually requires some forward modeling and forward modeling would not be of any use to a site investigation without some field data. Both approaches use a chemical model with speciation and mass transfer capabilities and both can utilize thermodynamic and kinetic properties.

The third approach uses statistical analysis to look at associations among dissolved constituents or between environmental variables such as temperature, climate, relief, lithology, and dissolved constituents. Statistically significant sets of parameters may be found to have a reasonable basis in terms commonly known reactions or processes. Correlation analysis, multivariate analysis, and factor analysis have all been used in geochemical studies. One advantage of the statistical approach is that no thermodynamic or kinetic data is explicitly needed. Knowledge of hydrogeochemical processes, however, is needed and this usually presumes some knowledge of the physico-chemical properties of water-rock interactions. Good discussions on using a statistical approach can be found in Drever (1988) and Puckett and Bricker (1992).

3.2. Mathematics

The mathematics of the geochemical equilibrium problem for speciation and mass transfer involves solving a set of nonlinear algebraic equations derived from substituting mass balance equations for the components of the system into the mass action expressions for chemical equilibrium. The same procedure can be used for sorption calculations as long as the database has a uniform system of standard states and stability constant expressions.

The mathematics of solute transport involves solving a set of partial differential equations. The difficulty of combining transport modeling with geochemical modeling translates into solving both partial differential equations and non-linear algebraic equations which has both mathematical and computational challenges. Finding a mathematical solution is not straightforward and depends upon the type of chemical reactions being considered

(Rubin, 1983). However, even if the mathematics are solved, the huge matrix of equations and parameters results in such huge storage requirements and computer time that more efficient algorithms are needed. Any approach that simplifies the problem (e.g. by reducing the number of chemical parameters without deleting anything important) is also helpful. Rubin (1990) discusses the feed-forward simulation method as another approach to formulating solute transport equations with reaction that not only improves efficency but also demonstrates exclusion of certain types of reaction in a network so that not all possible reactions have to be included.

Yeh and Tripathi (1989) describe three approaches in current use: (1) the mixed differential and algebraic approach (DAE), (2) the direct substitution approach (DSA), and (3) the sequential iteration approach (SIA). The DAE approach attempts to solve both differential and algebraic equations in a single matrix. This approach has only succeeded on relatively simple transport problems and is not practical for full-scale site modeling with all of the relevant chemical variables. In the DSA approach the chemical equations are substituted into the transport equations resulting in a set of nonlinear partial differential equations. This approach suffers from some of the same problems as the DAE approach, the mathematics are difficult and the computer time is formidable. The more popular and more successful approach has been the SIA method in which the transport equations are solved for one cell volume and then the geochemical model is solved iteratively. The next step is to move forward along the flow path to the next cell and repeat the iterative calculation. Whether the transport equations or the chemical equations are solved first seems to make little difference. The SIA is the most efficient of the three approaches.

3.3 Examples

Four prominent and different examples of geochemical transport modeling are those of Appelo and Willemsen (1987, 1990), Liu and Narasimhan (1989a,b), Lichtner and Waber (1992), and Frind and Molson (1994). Appelo and Willemsen (1987) developed a one-dimensional mixing-cell model to simulate advection and dispersion. The geochemical code PHREEQE was then coupled iteratively to the transport code (PHREEQM) and applied to geochemical transport of salt water intrusion. Liu and Narasimhan (1989a) developed the transport code DYNAMIX which is a sequential coupling of the PHREEQE geochemical code to the TRUMP transport code and includes redox calculations. This code was used to simulate supergene enrichment of ore at Butte, Montana (Liu and Narasimhan (1989b). Lichtner and Waber (1992) considered one-dimensional advection in a pure homogeneous medium but used reaction kinetics for the geochemical model in a code called MPATH.

They applied this approach to the interpretation of a moving redox front at the Poços de Caldas Natural Analogue site in Brazil and constrained the results with detailed mineralogical data. Frind and Molson (1994) describe a coupled transport-reaction code called MINTRAN which uses MINTEQ for the reaction code and a transport code that includes advection, dispersion, and diffusion. The code has been applied to the simulation of contaminant plumes below mill tailings impoundments in Canada. This application appears to be one of the most sophisticated uses of geochemical transport modeling yet published.

4. Limitations

Modeling is performed for three major objectives today: (1) to understand better the geochemistry of our environment (basic research), (2) to assist site characterization (applied research), and (3) to demonstrate compliance or the probability of compliance with regulatory requirements for disposal and management of hazardous wastes. The first objective strives to improve the models in all important and relevant respects so that they reflect better our knowledge of hydrogeochemical processes. The second objective seeks to apply hydrogeochemical knowledge to the description of a particular site. The third objective attempts to show through critical analysis of the hydrogeochemical environment what the travel paths and times for contaminants are likely to be as part of an overall safety assessment of a contaminant site. The regulatory requirements for a high-level radioactive-waste repository are the most challenging because calculations are being used to assess the safety over periods of thousands to millions of years in the future. There are three approaches to this problem: (1) scenario analysis, (2) time-dependent probabilistic analysis, and (3) natural analogue studies (Chapman, 1994). Since model calculations done now cannot be checked for their reliability, "scenario" development is a more appropriate word to use. Model deductions can only be tested over very short time frames relative to the long time frames indicated for radioactive waste disposal. The limitations described here refer to the application of geochemical models to site characterization and natural analogue studies.

Models are limited by two types of input, human and basic data. The human input or the knowledge and creativity that a geochemist brings to bear on any particular problem is more important than any other limitation. The investigator who works on a site should be aware of the hydrogeochemical complexities and the need for multiple alternative working hypotheses. Computer codes are helpful for bookkeeping and managing data, testing out possible hypotheses and conceptual models, and performing uncertainty analyses. Computer codes are tools that make modeling more efficient but they cannot replace the modeling process.

Models are used to gain a greater understanding of phenomena that are not well-known. Models begin as ideas and opinions that develop into testable hypotheses. If these hypotheses have deduced consequences that are corroborated by further evidence and stand the tests of criticism over time, then they gain in credibility and enjoy long survival. They may still be incorrect (indeed all models are incorrect in some respects), but some of them may be useful. Models might be described as useful fiction. Some models are known to a greater degree of certainty than others. How useful they are is not easy to say for it depends upon the objectives (often a moving target), the practical applications (which are not always predictable), the thoroughness with which the model has been developed and tested, and the insight obtained (a subjective aspect). It may take considerable time to assess the usefulness of a model.

Limitations imposed by the basic input data includes the applicability and assumptions of the basic physical and chemical principles for the problem at hand, the uncertainties associated with the database (thermodynamic, kinetic, and transport parameters), the uncertainties associated with the field and analytical parameters for the gound waters and the mineralogy, and the uncertainties associated with the geological and geochemical heterogeneities within the aquifer system. The extreme difficulty with obtaining adequate compilation of field data and the associated uncertainties usually means that there is no unique model solution to geochemical transport at any specific site. Another limitation emphasized by Bethke (1992) is the non-uniqueness of geochemical computations that appear to be adequately specified but in fact are not. Hopefully, the major features of transport and geochemistry can be delineated for the purposes of site investigation such that uncertainties do not overwhelm the main conclusions. This outcome is always sought but not always achieved in a thorough analysis (Chapman, 1994).

5. Future Research

I should like to suggest two productive avenues for research related to building confidence in geochemical transport models. One direction is for continued work on testing and comparing models with experimental data on colligative properties such as osmotic coefficients, activity coefficients, solubility data, redox and acid-base titrations, and electrochemical data. An important challenge when making model comparisons with experimental data is not only the reliability of the experimental data but also what degree of uncertainty on the experimental data is acceptable for the purposes of geochemical modeling. Uncertainty analysis will have to be done by propagating errors for chemical property data (thermodynamic and kinetic data) through speciation and mass transfer computations to determine what amount of error is acceptable. Furthermore, performance assessors will have to make decisions on what are reasonable goals for propagated errors. These decisions should be made in collaboration with experienced geochemical modelers who have been involved with site interpretation studies, i.e. modelers whose primary experience is with quantitative application of geochemical models to field sites. These evaluations should be done in a systematic manner interactively with international consortiums that are routinely involved with the evaluation and compilation of chemical property data such as CODATA (Committee on Data for Science and Technology) and the IUPAC (International Union of Pure and Applied Chemistry).

The other important direction for future work should be on a point nicely emphasized by Plummer (1992): "apply inverse modeling to hydrochemical systems, and then test the inverse results in forward simulations that take into account uncertainties in reaction kinetics, mineral thermodynamics, and hydrologic properties of the system." This approach has tremendous potential applications but has been little utilized. The main challenges for the future of geochemical modeling lies in availability of adequate chemical and hydrologic data, not so much in the sophistication of the modeling codes. Important data that are usually lacking or inadequately known include mineralogy and its spatial variation, surface areas of the most reactant minerals and their distribution, chemical and isotopic compositions of reactants and products, hydrology of the system, the extent to which the system is open or closed and with respect to the important mobile components, temporal variations of these properties. "Our development of efficient and sophisticated computer software capable of treating existing theories, concepts, and data, has out-paced research in the fundamental geochemical processes controlling the evolution of water-rock systems" (Plummer, 1992).

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CONCEPTUALISATION OF HYDROGEOCHEMICAL SYSTEMS

UNCERTAINTY, BIAS AND SUBJECTIVITY

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INTRODUCTION

Evidence that a radioactive waste disposal system will not give rise to unacceptable health risks in the future is derived from a variety of sources, principally post-closure performance assessments, small-scale laboratory or field tests and studies of natural geological systems. Each of these, in isolation or collectively, provide no surety of waste containment but do generate confidence that performance targets will be met. The mechanistic treatment of phenomena traditionally followed in the geological sciences tends not to sit easily with probabilistic safety assessment methods which highlight uncertainty at each stage of the investigation (Thompson and Sagar (in press)). This is perhaps surprising as geologists are used to dealing with information at levels of detail ranging from the highly quantitative to loosely descriptive. It is rare, however, to find examples in the literature where one conceptualisation of a geological system is discussed in terms of plausible alternatives or the uncertainty associated with the preferred interpretation is explored. This paper constitutes an attempt to formalise the earth scientist's 'rule of thumb' in terms of the uncertainty and bias procedures germane to any performance assessment.

The views of Popper (1972, 1982) are frequently cited in the context of model validation but are equally valuable when addressing model formulation. For example, he states (Popper,

1982) "the method of science depends on our attempts to describe the world with simple theories..... Science may be described as the art of systematic over-simplification: the art of discerning what we may with advantage omit." The complexity of the natural environment necessitates a simplified representation whether for performance assessment or any other purpose. Though probabilistic risk assessment (pra) models are usually supported by more detailed calculations of, for example, the hydrogeological regime, the latter, in turn, contain many approximations, assumptions and caveats. Typically, we plead for more data as the system is "insufficiently characterised" without admitting that this will always be the case. Indeed, in assessing a potential waste disposal site, there is a risk that too exhaustive a sampling programme will compromise future safety. Recognising these basic tenets, HMIP among others have developed a generalised procedure for treating uncertainty and bias throughout the various stages of an assessment (Thorne, 1992). Aspects of this procedure are discussed below, followed by a section which examines the problem of reconciling the disparate and often conflicting approaches to treating information in performance assessments and conventional scientific investigations, respectively. Emphasis is placed on geochemical processes, models and data as these invariably make a significant contribution to estimates of the overall risk.

PERFORMANCE ASSESSMENT ISSUES

The central purpose of pra is to devise a protocol which can account explicitly for the uncertainty inherent in long term prediction. It should address the extent to which the initial state of the system can be specified in addition to placing confidence bounds on the features governing future evolution. In this context the following definitions apply:

uncertainty	reflects our incomplete knowledge of parameter values, both spatially and temporally (parametric uncertainty) together with deficiencies in our conceptualisation of the system (model uncertainty)
bias	results from prejudicial selection of models, parameters or data owing to incomplete definition of the disposal system and/or limitations in calculation methods.

Identifying sources of uncertainty can often be facilitated by considering four distinct stages within the assessment; conceptual model development, selection of model parameters, selection of key data and mathematical modelling (Read *et al*, 1993). Expert elicitation is frequently used for the first two of these and also for data estimation where direct measurements are lacking. It has clear advantages in that 'scientific judgements' can be recorded and assumptions made explicit. However, the application of Delphi methods involving expert groups is characterised by a tendency towards consensus. Safeguards are needed to ensure a diversity of opinions, where appropriate, as this can improve decision-making through increasing possible options and challenging accepted conventions. Parametric uncertainty is usually incorporated into a risk assessment by using statistically defined distributions of parameter values. Conceptual model uncertainty is addressed in most countries by considering a range of possible 'scenarios', as discussed elsewhere (Thompson and Sagar, in press).

Quantification of bias is more difficult and, here, the choice of conceptual model can exert an over-riding influence on all subsequent calculations (Mackay, 1993). Alternative conceptualisations of a system may have been overlooked even though they may be consistent with available information from a site. Model results tend to be presented with a narrow (or more often zero) range of error implying a very high accuracy of prediction; that is, a degree of belief which may not be justified. Relatively few attempts have been made to address this issue in the field of geochemistry, but those studies which have been undertaken follow two distinct routes:

- a top-down approach (eg. Read, 1991) in which the results of predictive modelling are assessed by retrospectively analysing each component of the modelling procedure.

- modular construction, ie a 'bottom-up' approach (eg. Bonano *et al*, 1988).

Both involve a certain degree of subjectivity. In the case of the former, one may derive a false sense of security from apparent conformity in predicted and measured results when the actual processes operating and associated boundary conditions are not sufficiently well understood. Similarly, for the modular approach, an assurance is needed that all of the necessary components of the system are represented and that their interactions are explicit. Thus, while the advantages of expert systems, for example, are readily apparent (Pearson *et al*, 1990), they may be negated if deployed in an uncritical manner.

The use of subjective judgements is, of course, unavoidable and recognition of this reduces the problem to one of recording sensitive decisions and deciding at what level such judgements should be made (Scholten and van der Tol, 1994). For example, we may choose to include or omit a process from our model eg. equilibrium sorption, represent the process in a variety of ways (ion-exchange, surface complexation) and sample or assign parameter values.

Subjectivity is accepted as an integral part of performance assessment but is rarely acknowledged in traditional geochemical investigations where an individual researcher is prone to advocate only his interpretation of observed features. There is much to be gained from applying performance assessment techniques to studies of natural geochemical systems. This need not detract from our attempts to develop an in-depth understanding of the mechanisms operating. On the contrary, emphasis should be placed on ensuring model adequacy, ie whether the model can simulate the relevant processes and model reliability, ie whether the output matches system behaviour (Figure 1).

CONCEPTUALISATION OF GEOCHEMICAL SYSTEMS

The tenet of the geological sciences 'the present is the key to the past' has been adopted enthusiastically by the waste disposal community and extended to the maxim 'the past is the key to the future'. Inherent in this statement is an appeal to the geosciences to provide assurance regarding the future performance of a natural system. Such assurance is far in excess of the demands normally imposed on earth scientists and tends not to reflect the provisional nature of geological understanding. Clearly, there are practical limits to the confidence which can be gained from either 'natural analogues' or 'predictive modelling'. Thus, rather than strive to 'validate' waste disposal concepts using these methods; an impossible task, a more realistic aim would be to employ models in testing plausible hypotheses of natural system evolution in a structured manner. One might, for example, make alternative selections of the processes thought to dominate, examine a variety of boundary conditions and re-assess interactions between the hydrogeology and geochemistry of the site or region. The application of these methods when considering data selection and the modelling process, itself, has been described in an earlier paper (Read *et al*, 1993). The discussion below focuses on the selection of 'dominant' processes in developing a conceptual model and choice of model parameters.

As an illustration of the former, consider a clay-dominated aquitard behaving as a semi-permeable membrane, separating saline water from fresh. If one postulates osmosis as a dominant mechanism (Alexander, 1990), concentration gradients within the aquitard will result in the movement of groundwater up the concentration gradient. The transport of radionuclides present as charged ions, complexes or colloids will be impeded and, consequently, these species may accumulate at the edge of, or within, the aquitard where salinities are high

(Figure 2a). If, however, the semi-permeable behaviour of the aquitard is neglected, purely diffusive gradients for individual ions promote mixing, thereby producing a range of overall solution compositions (Figure 2b). The conceptual models for each of the above situations are very different. Osmosis tends to enhance radionuclide concentrations whereas diffusion tends to reduce them. Speciation and sorption behaviour will reflect the variable solution compositions at the interface or along the diffusive gradient, respectively.

Osmosis is only one of a large number of processes which are all too often ignored by researchers simulating chemical transport. Reference is made to Fargue *et al* (1988) for a discussion of other potentially important mechanisms including the temperature-dependent Soret Effect (Bierlein, 1954) and thermogravitational settling (Figure 3).

By far the most contentious assumption in geochemical modelling is the attainment of equilibrium, particularly when discussing solid-solution partitioning according to idealised distribution coefficients (Kd). It is generally accepted that many rock-water systems are not at equilibrium. Equally, it is recognised that the use of purely empirical Kd data is extremely difficult to justify when presenting transport calculations. It is often found (eg. Mackay, 1993) that parameter values which previously produced an acceptable fit to a model and, hence, were used in the initial calibration are no longer compatible with new data sets. Attempts to overcome this problem may result in a compromise fit being advanced which matches neither observation (von Maravic, 1992), when clearly the requirement is for a re-examination of the underlying basis of the model.

Examples of the above abound in the literature and generally reflect the fact that the concepts advanced, parameters chosen or both do not represent the processes occurring. The case study below illustrates the inadequacy of an 'equilibrium sorption' approach for treating actinide migration on the laboratory scale. The implications of the findings are then discussed from the viewpoint of performance assessment.

CASE STUDY

Colloids are ubiquitous in natural waters and effectively control the speciation of many trace contaminants in high oxidation states (O'Melia, 1987). Electrophoretic measurements for a variety of groundwater colloids have yielded large negative mobility functions (Longworth *et al*, 1989) and from these and related evidence it has been inferred (eg. Kim *et al*, 1994) that colloids can exist in stable suspension over a wide range of conditions. Despite these observations, the potential role of colloids tends to be ignored in modelling-based risk assessment studies (Sumerling, 1992). The latter consider only aqueous transport and retardation via sorption coefficients, estimated or measured in batch experiments.

A programme of research is underway to investigate the colloid-mediated transport of actinides through diverse matrices. The results presented here address thorium bound to silica colloids (Read *et al*, in press) but comparable data exist for other systems (Table 1). Thorium is characterised by a low thermodynamic solubility and a strong affinity for mineral surfaces. It is widely assumed to be 'immobile' in natural waters. In order to test this assumption for a simple system, the transport of thorium in 'true' solution (<2 nm) and bound to a colloid feed (75 nm) was studied on two identical, pre-equilibrated columns packed with silica beads. The results are discussed in detail elsewhere (Read *et al*, in press) and summarised in Figure 4.

In the case of the ultrafiltered system, no evidence of breakthrough was found in samples collected over the 660 hour period of the experiment confirming the anticipated low mobility of aqueous thorium. By contrast, in the second flood thorium was detected simultaneously with colloid breakthrough after 17 hours providing clear evidence that thorium was transported in association with the colloidal phase (Figures 4a, b). Further, the thorium loading on the colloids was virtually quantitative and appeared not to be affected by passage through the column. This migration behaviour can only be explained by rapid thorium attachment and imperceptibly slow desorption on the experimental timescale. It would not be accounted for by a rock-water distribution model. Employing a local equilibrium model in which metal ions are free to exchange between the colloidal phase and the matrix (Kim *et al*, in press) would also give a markedly different profile as shown in Figure 5. Similar results have been observed by other laboratories working on different systems (Table 1), emphasising the need to develop a phenomenological understanding of radionuclide transport in the presence of colloids.

At present, there is no evidence to suggest that the above findings would be valid on the field scale. Equally, however, there is no evidence to the contrary. For this reason, illustrative simulations have been performed to demonstrate the possible influence of colloidal transport on the outcome of risk assessment calculations (Tyrer *et al*, in press). On the basis of the experimental data summarised in Table 1, radically different predictions emerge regarding the radionuclides which contribute most to dose and risk. The pre-eminence of iodine-129 is supplanted by the actinides, including plutonium and thorium, which are precluded from consideration in most published assessments (eg. SKB 1992) by their 'low solubility and high sorption'.

One may choose to dismiss the colloid-mediated transport model on the grounds that upscaling in this way is unrealistic. Before doing so, however, it is worth bearing in mind the tacit assumptions and hidden bias implicit in the conventional approach to radionuclide transport which include, *inter alia:*

- colloids are absent or play no significant part in radionuclide speciation;
- uptake and desorption from the surface are instantaneous and reversible;
- the adsorption process is independent of solution chemistry.

For the reasons discussed above, it is essential that all potentially significant processes be addressed when constructing conceptual models of natural system behaviour, even if only in a simplistic manner. Treatment of uncertainty and bias is required at each stage of the modelling procedure, as propagated errors of judgement cannot always be eradicated by Monte Carlo simulation of aggregated system parameters in pra (Mackay, 1993). That is to say, sampling from a wide distribution of parameter values will not compensate for the fact that the parameter itself, misrepresents the effects of the dominant hydrogeochemical controls.

DISCUSSION

This paper has briefly highlighted efforts made to distinguish between alternative models of geochemical behaviour. The case study presented examines the null hypothesis implicit in almost all geochemical modelling exercises that the system is in thermodynamic equilibrium and, in addition provides a clear demonstration of the inadequacy of conventional methods for quantifying actinide transport. Despite the widely held belief that science advances by invalidating concepts rather than validating them (Popper, 1982), such approaches are still relatively rare. The argument may be true but, in the interim period, strenuous efforts are often made to arrive at a 'consensus' description of a site, experiment or process even where substantial discrepancies in the underlying data exist. In the international Alligator Rivers Analogue Project, for example, attempts to continually fit observed trends as new data became available led to the postulation of models which were deemed to be physically unrealistic by independent workers (von Maravic, 1992). This serves to emphasise the need for formalised model and data elicitation prior to performing numerical calculations, followed by critical peer review subsequent to completion.

At a practical level, the ambiguities in interpreting contaminant transport behaviour can only be resolved satisfactorily for simple systems such as those discussed above. Reconstructing the geological history of natural systems is an intractable problem as the contemporary boundary conditions are unknown. Thus, we are faced with the reality that we cannot generate definitive interpretations of 'analogue' sites nor, in making predictions of future evolution, can we eliminate ambiguity (Beck, 1994). We are left with a set of possible alternative models which require evaluation. One method suggested for ranking alternatives and, hence, reducing uncertainty and bias at the conceptualisation stage might function by posing a series of logical questions to explore the limitations associated with each model. The strength of a conceptual model could then be quantified in terms of the amount and quality of data available to support it. This does not mean, of course, that the preferred model is 'correct' but it does make explicit the factual basis of the model and the robustness of the arguments advanced.

Ultimately, advances in hydrogeochemical modelling can only be made by applying the models to real systems and continually refining our approach. Well designed laboratory experiments are an essential adjunct in that they allow quantitative testing of hypotheses under controlled conditions. The application of established judgemental techniques to both field and laboratory investigations would make these studies more accessible to those engaged in performance assessment and help counter accusations concerning their relevance in a waste disposal context.

CONCLUSIONS

Essentially, there are two main approaches to developing models of natural systems; one conditioned by the available data, and the other by expressing an understanding of the processes operating. The latter, often termed a 'first principles' approach may appear weaker to the observer owing to the high degree of subjectivity involved. This is not necessarily the case as it helps ensure that all potentially significant processes are considered and that alternative conceptualisations of the system are documented together with their associated assumptions. Consensus need not be sought. Rather, formal treatment of uncertainty and bias is required at each stage of the investigation in order to avoid the situation whereby a single favoured model, often without firm basis, is adopted to the exclusion of plausible alternatives.

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COLLOID	METAL	MATRIX	METAL UPTAKE	RECOVERY	BREAKTHROUGH RELATIVE TO TRACER
Silica	Th	Packed silica	Quant Irrevers.	100%	x5
Latex	-	Triassic Sst	-	80%	x10
Humic	Eu	Packed sediment	Major	<92%	x1
Humic	Am	Packed sediment	Major	<79%	x1
Humic	Np	Packed sediment	Major	63%	x1
Humic	Th	Packed sediment	Quant	68%	x2
Humic	U	Packed sediment	Minor	10%	x1

Table 1 Summary of colloid mediated transport experiments

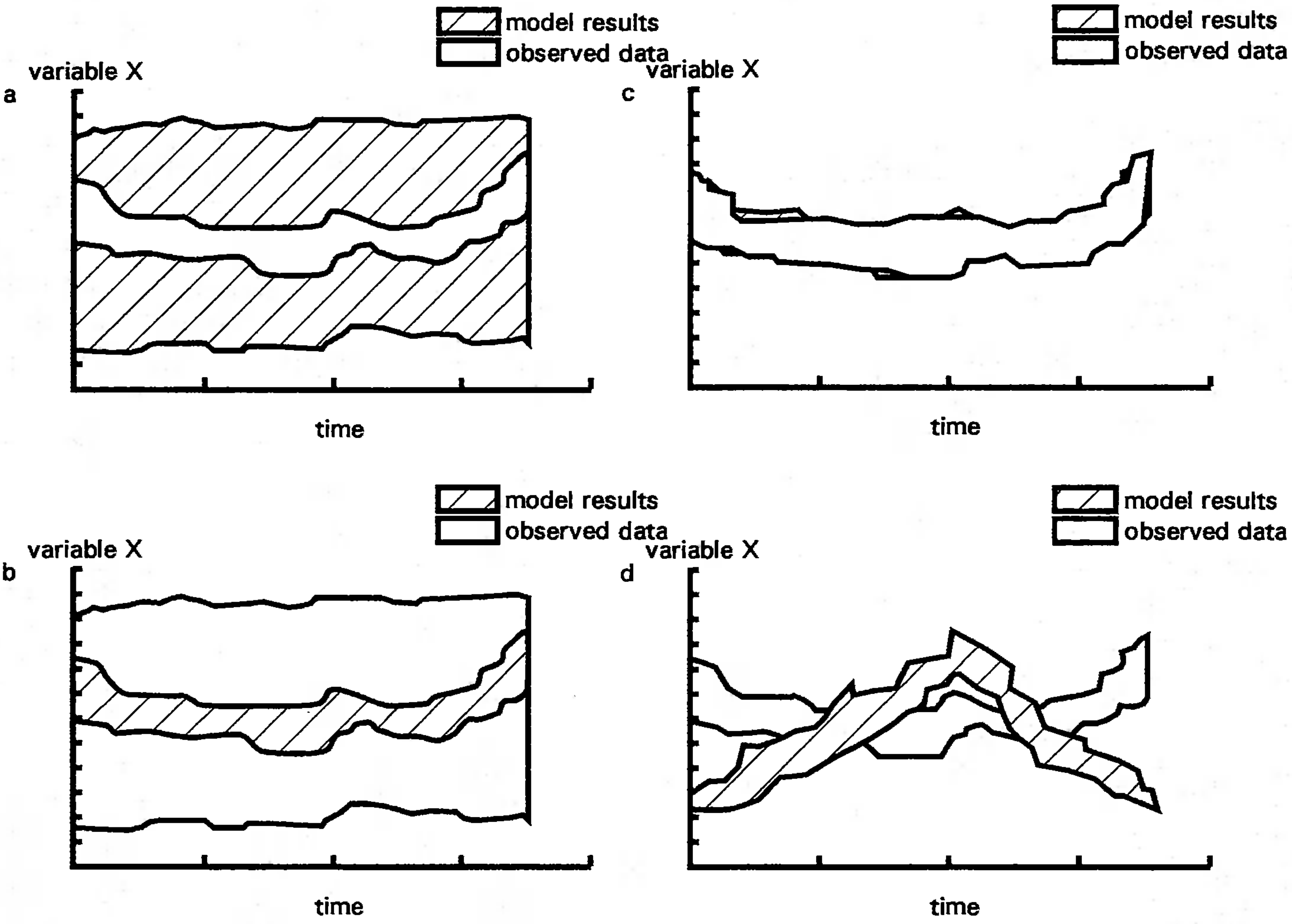

Figure 1 Models with high degree of adequacy and low reliability (a), low adequacy, high reliability (b), high adequacy, high reliability (c), low adequacy, low reliability (d) from Scholten and van der Tol (1994)

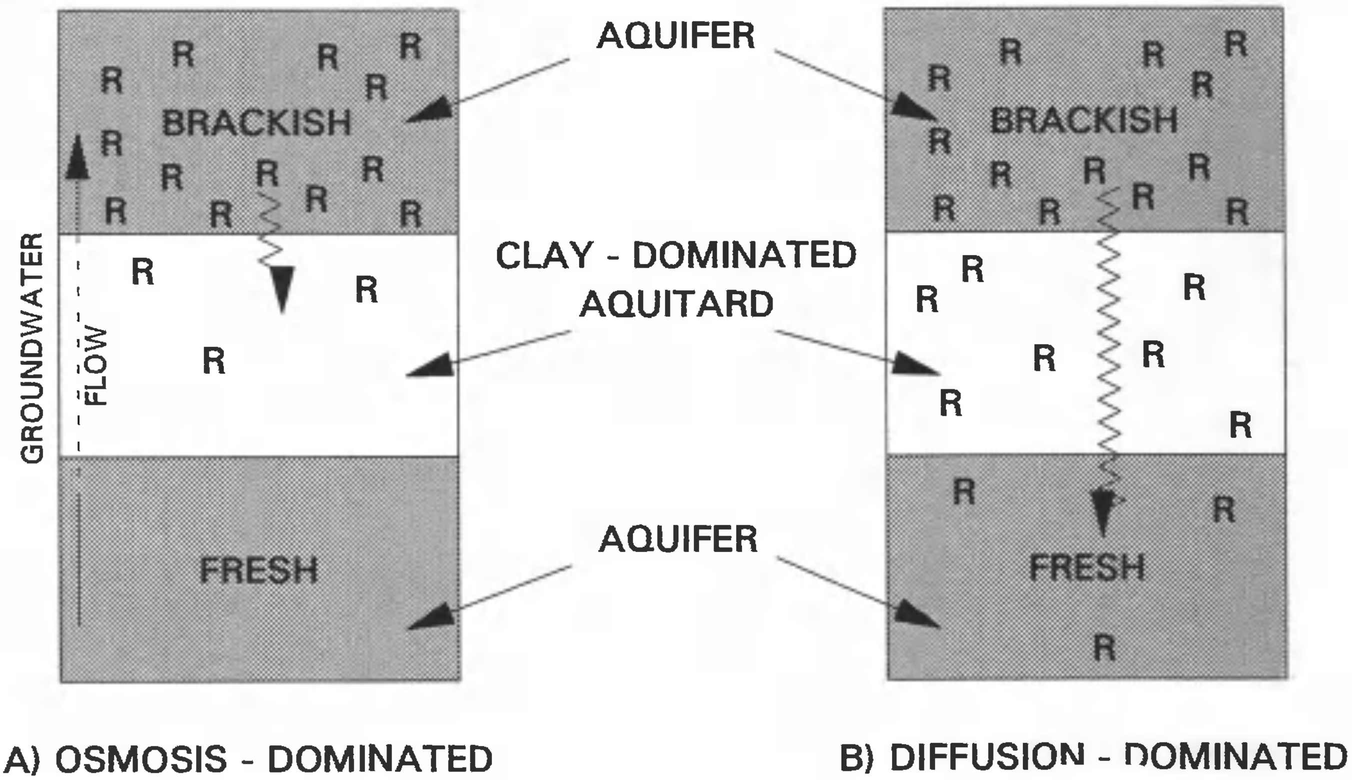

Figure 2 Alternative conceptual models of radionuclide transport at a salinity interface

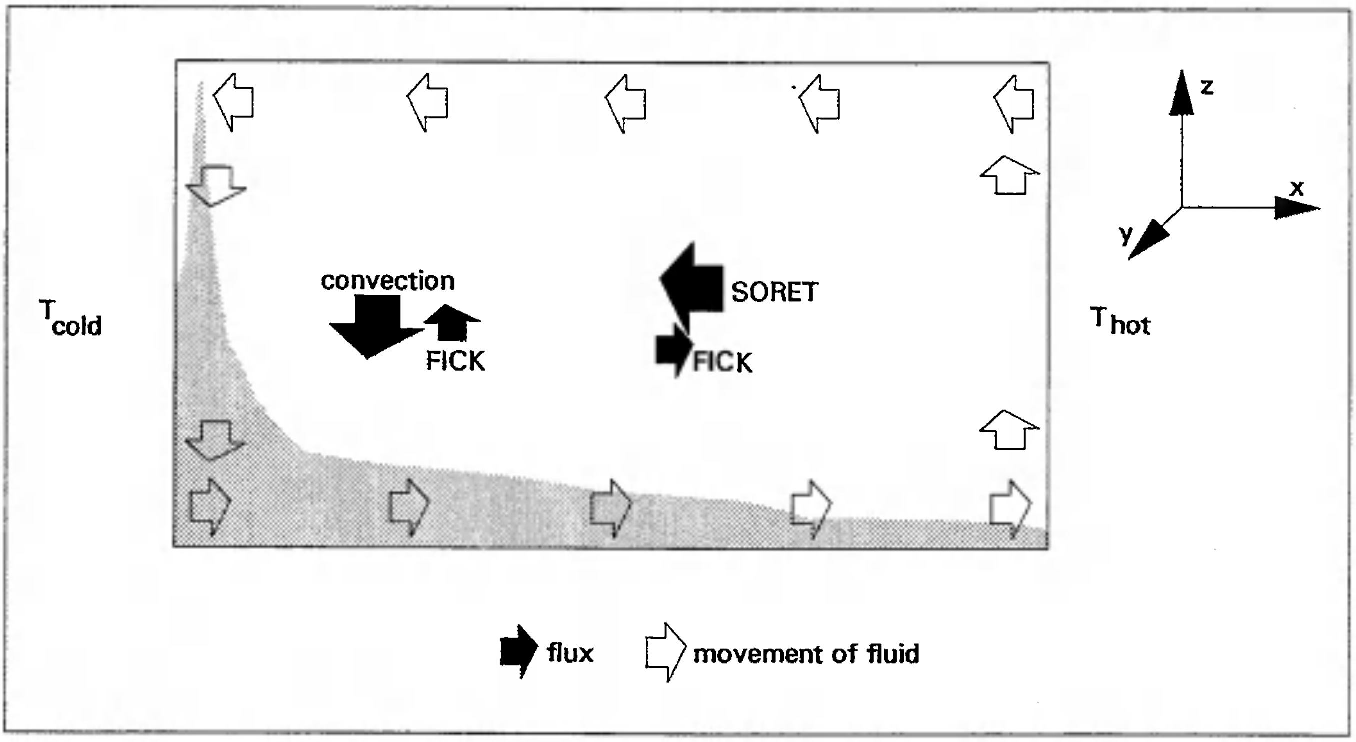

Figure 3 The effect of gravitational settling

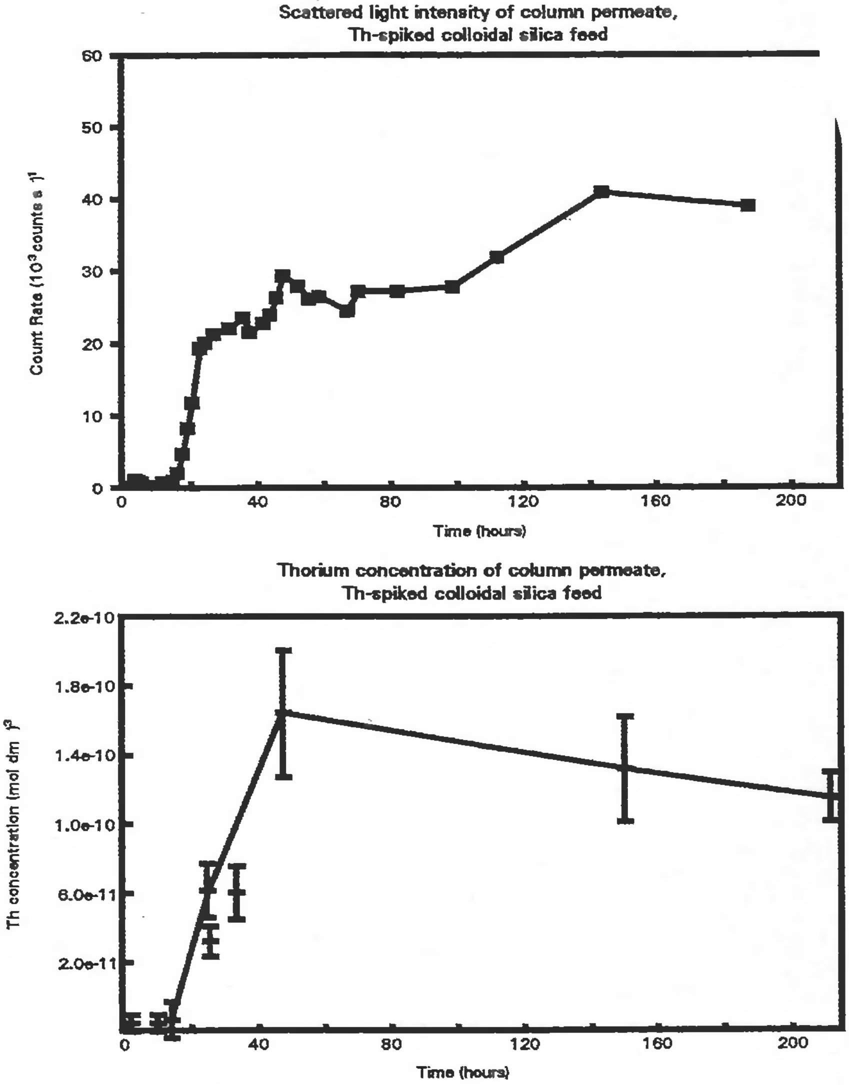

Figure 4 Breakthrough profiles for thorium and silica colloids. Note the coincidence of the time at which both thorium and colloid breakthrough occurs.

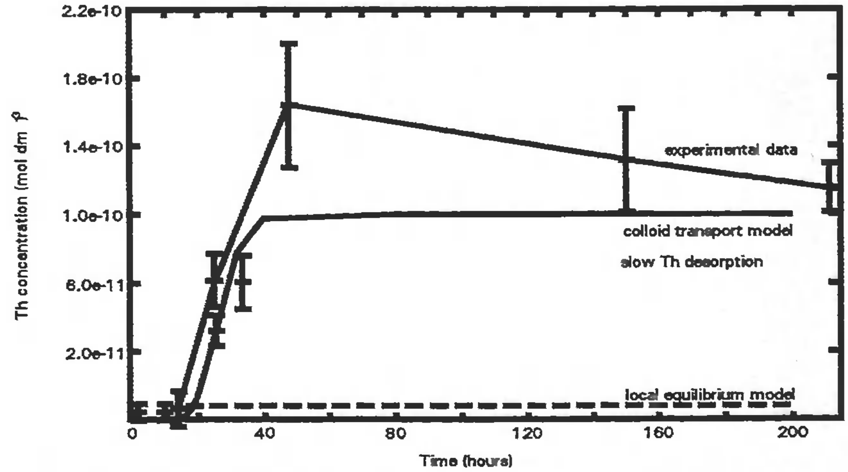

Figure 5 Comparison of modelling results for thorium breakthrough with experimental results from the second column. The experiment results can be explained by the transport of thorium bound to the silica colloids if little thorium desorption occurs during the experiment.

SESSION 4: NATURAL ANALOGUES AND PERFORMANCE ASSESSMENT

Chairpersons: I. Neretnieks (S), L. Kovach (USA)

The uses of natural analogue input in repository performance assessment: an overview	I. McKinley et al. (CH)
The use of natural analogues in public relations	J. Lindqvist (S)

The uses of natural analogue input in repository performance assessment: an overview

Ian G. McKinley[1], *W.Russell Alexander*[2]

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1 Introduction

In this paper we review both the extent to which natural analogue studies carried out to date are relevant to radioactive waste performance assessment and the degree to which recently published performance assessments have utilised/acknowledged analogue input. The review concentrates on the particular case of deep disposal of radioactive waste in a terrestrial environment (with particular emphasis on the Swiss Kristallin-I assessment) and hence does not directly consider either near-surface disposal or disposal on or under the sea-bed.

It should be emphasised from the outset that the paper is intended to serve as a focus for discussion and hence tends to concentrate more on potential areas of controversy than those in which a reasonable consensus exists. The review also selects particular analogue studies/performance assessments as examples when making both positive or negative points. It should not be assumed that these examples are the best (worst) of their type - merely that they are particularly well known to the authors.

2 How could natural analogues contribute to performance assessment?

A number of areas in which natural analogues could provide input to performance assessment have been identified in past reviews (e.g. Chapman et al., 1984; McKinley, 1989; Miller et al., 1994), i.e.

- Repository system design
- Conceptual model development
- Mathematical model development
- Providing input data
- Testing models
- Putting results in perspective

[• Presenting results to the general public]

These are now considered further in sequence, except for the last topic which is the subject of another paper at this workshop (Lindquist et al., these proceedings).

Repository system design

In principle, observations from nature could be used to provide input towards designing specific repository systems but, to our knowledge, this has never been seriously considered. Alternatively, observations of natural systems could be used to support a particular design selected; the best example of such an analogue is probably Cigar Lake (c.f. Cramer, these proceedings).

Conceptual model development

For specific processes, observations of analogue systems could be an important component of developing the conceptual models used to examine them. This probably occurs tacitly in many cases, as the experts involved in developing such models do so on the basis of their cumulative experience in the topic involved (e.g. models of engineered barrier degradation would consider evidence from relevant archaeological samples). The process of conceptual model development is, however, rarely documented in detail in primary performance assessment reports and may even be difficult to trace in the supporting grey literature.

Mathematical model development

The transmogrification of a descriptive conceptual model into a quantitative mathematical model is a rather subjective process and a single conceptual model may result in a range of quite different mathematical representations. Natural analogues do not contribute directly to this process, but the experience in developing mathematical models for analogous natural processes could be transferable to the repository situation. This, again, probably occurs tacitly when staff with experience in modelling natural systems are drafted into nuclear waste management programmes.

Providing input data

It has often been claimed that natural analogues can provide data applicable to long timescales and averaged over large spatial distances - which could not be obtained in any other way. There are very few cases where such data have ever been usefully derived and many of the extravagant claims made have been subsequently debunked (e.g. "in situ Kds").

Testing models

The output from safety assessment analyses is presented over timescales of up to 10^6 years or more and the only way such analyses can be realistically tested is via natural analogues. Especially for particular sub-components of the model chain, such testing has been relatively successful and is often acknowledged in the main performance assessment reports. Less often acknowledged is the associated testing of modellers - which is an equally important aspect of such studies. This is especially useful when such modellers come from a pure science background (as is often the case) and have little feeling for the complexity of natural systems.

Putting results in perspective

Calculated consequences from performance assessments are often extremely low doses (or risks) arising in the distant future. The plausibility of such global results can be assessed by a semi-quantitative, or even qualitative, evaluation of natural systems.

In terms of the usual definition of natural analogues (Chapman et al., 1984; Miller et al., 1994), the last 3 areas are where most analogue studies are expected to be focused - especially for established programmes where repository systems have been already designed and performance assessment methodology and tools are in place.

3 How are natural analogue studies actually focused?

To be quite blunt, it is probable that at least 50 % of all reported "natural analogue" studies do not contribute to performance assessment (or any other aspects of waste management) in any way whatsoever and hence are misnomers. The basic work carried out may well be academically sound, but is has no relevance to any existing repository project. Examples of such studies include most analyses of elemental release/immobilisation processes under hydrothermal conditions and studies of the behaviour of exotic elements at sub-trace concentrations. Some specific examples are listed in Table 1. The source of the problem is generally the unfamiliarity of the workers involved with nuclear waste management programmes, but this is confounded by poor control by funding bodies and even poorer standard of review by the organisations publishing such work.

Of the remainder of analogue studies which have a relevant goal and involve appropriate systems, we would estimate that about half involve some aspect of testing models (or training-staff!), a quarter involve attempts to derive data and the rest are more involved with putting results in perspective or direct public relations.

It should be noted that these estimates are based on studies producing data directly; in terms of publications, a sizeable proportion are reviews of primary studies. These reviews are of variable usefulness depending on whether they critically appraise the relevance of primary studies or not (e.g. compare Pearcy & Murphy, 1991 with Miller et al. 1994).

Table 1: Examples of irrelevant "analogue" studies

Topic	Reference	Comments
a) Studies of radio-iodine at Alligator Rivers	1	Irrelevant source term, irrelevant chemistry, irrelevant concentration range
b) Studies of rôle of bitumen at Oklo	2	Irrelevant material, inappropriate conditions (ludicrous conclusions!)
c) Trace element mobilisation during igneous intrusion	3	Irrelevant temperature range, inappropriate conditions
d) U migration at Alligator Rivers	4	Irrelevant source term, inappropriate conditions
3) Retardation in aquifers	5	Irrelevant source term, inappropriate conditions

1= Fabryka-Martin & Curtis, 1994
2= Nagy et al., 1991
3= Brookins, 1986
4= Golian & Lever, 1994
5= Krishnaswami et al., 1992

4 How useful are such studies for performance assessment purposes?

Model testing

There have been a number of good studies demonstrating that the models used for the quantification of materials degradation (e.g. steel, copper, glass, cement, etc.) are consistent with observations of archaeological artefacts over periods in the 10^2 - 10^3 year scale. Longer timescale studies involving natural systems are generally less useful, as the materials examined are less relevant and both the chemical environment and the period of interaction are less well defined (e.g. Petit, 1991; Apted, 1991). Although lots of work has been reported on the alteration of natural uraninite, for example, it would appear that little of this is of much relevance to performance assessment for given spent fuel disposal concepts.

As solubility and sorption of nuclides are key constraints on the releases for many types of waste, testing the geochemical models used to derive (or support the derivation of) such parameters has been a focus of many analogue studies. These studies have been most useful in highlighting inappropriate/incorrect data contained within such models and areas where thermodynamic models break down (e.g. where kinetics or microbial catalysis may play dominant rôles). This allows the limitations of the models used to be assessed and priorities set for improvement of these models or their associated databases. Cases where the performance assessment model predictions - made within a rigorous, blind-testing framework - are consistent with field observations are, however, a very important component of building confidence in the use of such models.

The third main group of models tested in analogue studies are those which quantify radionuclide transport. Although the focus of many studies, the difficulty in characterising natural solute transport over long timescales has greatly limited the applicability of results produced (c.f. review by Alexander & McKinley, 1992). Analogue systems in which solute transport occurs by diffusion have been somewhat more successful (e.g. Hooker et al., 1985) but, even here, the systems studied tend to be near surface with potential complications due to inappropriate chemical gradients and biological activity.

Apart from the major components of the performance assessment model chain, supporting models have also been tested within analogue studies with a degree of success which is related to the performance assessment experience of the workers involved and the simplicity of the system studied (cf. examples in Table 2).

Data production

Cases where data usable in performance assessment have been derived from natural analogue studies are very rare. The few values so derived (e.g. matrix diffusion depths in crystalline rocks from natural series profiles) may be very important to the building of a safety case when (as in this instance) the process involved performs an important barrier rôle and the data set derived are more robust than those obtained by alternative methods.

Table 2: Examples of tests of supporting models

Model	Example	Reference	Comment
1) Spent fuel radiolysis	Oklo	1	System extremely old and complex, results ambiguous
2) Microbiology - redox front	Poços de Caldas	2	Database very limited, results semi-quantitative
3) Hydrothermal flow	Poços de Caldas	3	System very complex, analysis over-simplistic, results ambiguous
4) Colloid transport	Poços de Caldas	4	Database limited, results qualitative, analysis simplistic
5) Sorption mechanisms	Alligator Rivers	5	Database limited, results ambiguous
6) High pH plume	Jordan	6	System very complex, models semi-quantitative
7) Microbiology - high pH	Jordan	7	Database extensive, simple model tested

1= Karlsson et al., 1994
2= West et al., 1992
3= Cathles & Shea, 1992
4= Mikeley et al., 1992
5= Bennet & Read, 1994
6= Alexander, 1992
7= West et al., 1994

In general, however, the value of "data" derived from analogue studies is rather limited and, in many cases, data may be worthless or, even worse, misleading (cf. the "in situ Kd" fiasco documented by McKinley & Alexander, 1992; 1993). Apart from problems caused by inconsistent nomenclature and misunderstanding of performance assessment database requirements, a major limitation is the inherent complexity of natural systems and the limitations of the analogy involved. Thus, the processes involved in alteration of natural glasses or uraninite may be similar to those influencing borosilicate glass/spent fuel in similar environments, but the rates of alteration are likely to be very different.

Performance assessment models require data which are averaged over large spatial and temporal scales which **might be** obtainable from natural analogue studies, but extraction of such data generally requires more detailed analysis of good analogue systems than has been attempted to date. Such an analogue study would be rather expensive compared to prior projects but certainly not when compared to the extremely high costs of field characterisation (much of which yields no performance assessment relevant data).

Results in perspective

Presentation of the results of an integrated performance assessment to the general public (or even a technical audience from outside the waste disposal community) is extremely difficult - especially due to the long timescales involved and very high level of safety required. Oklo is undoubtedly one of the most convincing arguments for the basic feasibility of long-term containment, but other relevant ore bodies (e.g. Cigar Lake) can also be very useful in this regard.

A pitfall in using analogues in this way is the danger of over-interpretation; Oklo only proves that disposal of high-level waste is feasible in principle, it is far too old and complex to allow anything to be said about the safety of any particular disposal concept. Indeed, the lack of fossil reactors at other sites strongly suggests that Oklo is an anomaly and hence must be treated with care.

Care must also be taken when interpreting provisional data. Examination of the Poços de Caldas data to provide support for the Kristallin-I performance assessment focused on the rôle of redox fronts as potential traps of a range of trace elements (McKinley et al., 1992). Due to the limitations in this database, however, this process was not taken into the basic safety case (Nagra, 1994) - which is lucky as re-examination of the samples indicates that many of the data may be artefacts (Hofmann, pers. comm.). Nevertheless, other information exists to support the idea of redox traps (e.g. redox halos, roll front deposits), but the case must be made carefully before it can be used to support a specific disposal concept.

5 General overview of the treatment of analogues in performance assessment

Given that there are a number of ways in which natural analogue studies could contribute to performance assessment and that a fair amount of relevant work has been published, how much evidence is there for direct analogue input to recent major performance assessment projects? Major performance assessments produce a vast volume of documentation, so a comprehensive review is not possible. Nevertheless, focusing on the main performance assessment summary reports in recent analyses leads to the general observations summarised in Table 3.

Table 3: Use of analogues in recent performance assessments

Assessment	Reference	Comments
SKB-91	SKB, 1992a	Direct reference to analogues to support radiolysis calculations and bentonite longevity
TVO-92	TVO, 1992	Analogues to support radiolysis calculations with reference to SKB-91
PNC-H3	PNC, 1992	Reference to analogues to support low canister corrosion rates and bentonite longevity
Nagra Kristallin-I	Nagra, 1994	Extensive reference to analogues in scenario analysis and model validation sections
SNL Yucca Mountain TSPA-1993	Wilson et al., 1994	No direct mention found of natural analogue studies
AECL-EIS	Goodwin et al., 1994	Use of analogues appears to merit only one sentence in a 700 page report

Although SKB, TVO and PNC each have natural analogue programmes, there is relatively little mention of them in the main performance assessment reports. Particular direct mention of analogues tended to focus on justifying the longevity of engineered barriers and assessment of the significance of radiolysis on near-field performance. This low profile of natural analogues could be contrasted with their prominence in R&D programme overviews (c.f. the SKB R&D programme 1993-1998 which has a chapter on natural analogues and also Karlsson et al., 1994). The Kristallin-I performance assessment contains somewhat more extensive documentation on the use of natural analogues and is discussed further in the next section.

By contract, the use of natural analogues is not mentioned at all in the Yucca Mountain Total System Performance Assessment and has a very low profile in the AECL-EIS. One characteristic of both of these analyses is that they focus very much on the use of probabilistic modelling methods. The use of analogues seems to be less developed (or inherently less applicable) to such an approach. It should, however, be noted that, within AECL supporting documents, the use of natural analogues (particularly Cigar Lake) is more evident. By comparison, as far as the authors can see, analogues are completely ignored in the performance assessment carried out by the US DOE and its contractors.

6 The specific case of the Kristallin-I performance assessment

Natural analogue studies have featured prominently in the Nagra R&D programme for the last decade - resulting in about 100 papers and reports on this topic. From the beginning, the rôle of analogues in performance assessment was emphasised and the report summarising the Project Gewähr 1985 assessment (Nagra, 1985) has an extensive section considering both their use to support estimates of engineered barrier longevity and to validate models of radionuclide release and migration through the geosphere. Project Gewähr 1985 also included an assessment of natural sources of radiation in the environment in order to put the results of the entire performance assessment model chain in perspective.

In the more recent Kristallin-I assessment of HLW disposal in the crystalline basement of Northern Switzerland, use of natural analogues is more integrated within the overall performance assessment (Nagra, 1994). The use of natural sources of radioactivity to demonstrate the plausibility of global results is, however, included in a separate "Results in Perspective" report (Neall, 1994). The Kristallin-I performance assessment is more formally structured than previous Nagra analyses and is based on a painstaking scenario analysis procedure. Even at the base level of describing the "FEPs" (features, events and processes) which comprise the evolving repository system, evidence from natural analogues is often included to demonstrate the occurrence of such FEPs in nature and to suggest how they may be combined into "scenarios" for quantitative analysis. Within specific scenarios, natural analogues are often used to support model assumptions - particularly for the case of engineered barrier longevity. Natural analogues are not used to provide input data - with the notable exception of the distance of connected porosity around fissures in crystalline rock. This parameter plays a critical rôle in defining the extent of matrix diffusion which, in turn, is one of the most important characteristics of the geosphere barrier. Although diffusion distances can be measured via laboratory or field experiments, these are inherently limited by the possibility (or probability) of experimental artefacts. Measurement of natural series disequilibrium in core profiles, however, provides an unambiguous measure of the minimum extent of such connected porosity.

Model testing - including verification and validation - is prominently discussed in Kristallin-I. Although "validation" is a very controversial topic at present (e.g. Bredehoeft & Konikow, 1993), as defined within the Swiss programme it is an achievable aim (McCombie & McKinley, 1993) in which analogues play an important rôle. (It may be noted that the Swiss position here seems to be supported by the US Courts - c.f. Blair, 1994.)

A conclusion of Kristallin-I is that the near field engineered barriers comprise the "robust" component of the overall repository system. To a fair extent, this robustness is derived from the considerable analogue support for the models (and databases) used to quantify engineered barrier degradation and the associated release and migration of radionuclides. Remaining uncertainties in the analysis allow priorities for further analogue studies to be identified - assessing long-term rheology of compacted bentonite (canister sinking), trapping of radionuclides at redox fronts and further testing of models/databases used to assess solubility limits for a few key elements.

7 Conclusions

In this brief review it is noted that natural analogues are used within performance assessments to a varying degree. The extent to which analogues support assessments may not, however, be clearly represented by the extent to which they are documented in major performance assessment publications (e.g. compare SKB, 1992a with Karlsson et al., 1994). Nevertheless, the main areas of use seem to be supporting assumptions of engineered barrier longevity with much less direct use reported for model/database validation. The most complete integration of analogue studies within a major performance assessment project to date seems to be represented by Kristallin-I whereas least use of analogues is apparent in probabilistic performance assessments - particularly those carried out for the Yucca Mountain project.

8 Acknowledgements

Many of the ideas presented in this paper arose out of discussions with the "hard core" (or is it "soft centre") of the NAWG. Andreas Gautschi and Charles McCombie are thanked for their support of the Nagra natural analogues programme and their tolerance of our rather blunt approach to the presentation of controversial topics in the open literature. It is not our intention to offend anyone, but the topic of performance assessment relevance of natural analogue studies seems to be an omelette which cannot be made without cracking quite a few eggs!

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The use of Natural Analogues in Public Relations

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"Som ni alla vet, måste vi använda säkerhetsanalys för att utvärdera den långsiktiga säkerheten i ett djupförvar för använt kärnbränsle."

This was an introduction in swedish, a language most of You don´t understand. My guess is that between 5 and 10 percent of the participants at this meeting, the Swedes and some Finns, understood it, and I think that equals the percentage of the general public that would understand a description of safety analysis.

As you all know, we must rely on safety analysis methods when it comes to long term safety for disposal of spent nuclear fuel. But when it is so difficult to explain this methods to the majority of politichians, journalists and general public, who don´t have the basic scientific knowledge needed, how can we provide them with something that indicates that it isn´t impossible and completely ridicolous to talk about isolation of dangerous materials for thousands of years? As we right now are close tho the end of a conference about natural analogs, You all know the answer: natural analogs.

For me, who actually started with physics but now works with public relations, the natural analogs is a link, making it possible for the general public to get a little more understanding for the long term processes in nature, studied and analysed by the scientists. I will later return to how SKB uses the analogs, and the reactions among the general public.

I´d like to continue with some words about public relations. The purposes of the public relations programme performed by SKB are to increase knowledge among the general public and selected target groups about the nuclear waste, the handling of it and the disposal, but also to manage and reinforce SKB:s capital of confidence, to gain acceptance for operation of existing facilities and acceptance to site, construct and operate the final, Deep repository for spent nuclear fuel.

There are three obvious difficulties when talking about the radioactive waste:

- There is a general lack of knowledge about radioactivity, and for many people, radioactivity is an emotionally charged question.

- People seldom realizes that the waste do exist and must be handled, no matter the future for nuclear power. Some people even compare the risk of the nuclear waste with nuclear weapons.

- Finally, the very long times the waste must be isolated are so far from human experiences.

Well, radioactivity can be explained. SKB and others inform about the natural radioactivity around us, how we quite easy can measure radioactivity, what contamination means and how the radiation can be shielded off. We can also explain that the waste exists today and must be taken care of, and that there is no risk of nuclear explosions in the waste.

Finally, the time scale is the problem. Of course we can tell people about the results from the safety analysis, even though the analysis itself is difficult to understand. But when we tell people that a copper canister, embedded in clay 500 meters down in the bedrock will withstand corrosion for 30 million years (and that includes the influence of the germs in the bedrock), they get a funny look in their eyes. This doesn´t relate to his or hers own experience, and at the best, they feel sorry for us, at the worst they think we are trying to fool them. In any case, it doesn´t create any confidence in SKB or the scientists.

Now You all know what I´m going to say. To show some of the natural analogs, for example a piece of wood from Dunarobba, more than one million years old, gives a hands-on understanding that things, under the right circumstances, can be isolated for a very long time in nature.

But we, who work with public relations, must be very careful when describing the use of analogs. It´s important to stress that the existence of natural analogs doesn´t prove, and must not be presented as a proof, that the repositories planned by the scientists really will work as intended. The natural analogs helps the scientists to understand the slow, long term processes in nature that can´t be tested in a laboratory. The analogs can also be used for validation of theoretical calculations, for example the long term solubility of uranium in ground water.

It´s obvious that in public relations work, as in the scientific work, some analogs are better than others. For me, a good analog is an analog that gives the hands-on feeling that nature can provide isolation, like Dunarobba, the cannon from the warship Kronan or pieces of native copper. Others, like Pocos de Caldas, are more theoretical.

In my company, the SKB, I get the feeling that the scientists are interested in fewer and more theoretical analogs than the information department. But our scientists, and I would specially like to mention Per-Eric Ahlström and Fred Karlsson, do have a good understanding for the public relations aspect of natural analogs. They know that SKB never will get the permission to site, build and operate the facilities needed if we don´t create confidence also outside the scientific society. This is one important reason why SKB is paying for research in the natural analog area.

I promised to show you how SKB uses the analogs in our public relations work. Actually, the first presentation material we used were produced by NAGRA in Switzerland. They made a very interesting broschure we got their permission to translate and print in Swedish.

Now the analogs are included in much of our printed material. I´d like to show you a pocket-size broschure, named "About Sweden´s radioactive waste". It was intended as a argument guide for people working in the nuclear industry, but is now also distributed after lectures and discussions in schools, at fares, exhibitions at power plants etc. Here, we have gathered the basic facts, describing the waste, the legislation, the research and the existing facilities. You will also find the principles, or the ethical arguments, guiding our work, and the plans for the future that is the result of the facts and the principles. Among the principles, we refer to natural analogs; "The methods of radioactive waste management have to be compatible with the law of nature. The methods are therefore based on research on natures chemical and physical environments. The results of these scientific studies show that, given certain conditions, nature itself has isolated radioactive substances from the surrounding environment for millions of years.

We also describes natural analogs in our company presentation produced each year, and gives a little deeper explanations in a fact sheet (only produced in swedish). Also the general set of SKB transparancies includes some of the natural analogs.

One of the biggest public relations activities performed by SKB, is the Sigyn summer tour, in harbours all along the swedish coast. SKB owns a specially built transport ship, the M/S Sigyn. Each summer she is converted to a floating exhibition, with 600 square meters of equipment, models, posters, and videos in the cargo hold, normally visited by some 75 000 people each summer.

The exhibition is manned mainly by SKB staff, including everyone from the lady working in the switchboard to the scientific experts. This has several advantages. The best way to tranfer facts together with confidence is eye to eye. The public meets the people who really work with the waste, and our scientists understands what really concerns the public.

Of course, a large part of the exhibition presents some of the natural analogs. Here, we try to explain the time scales with natural analogs from the past, giving better safety analysis for the future. Our message is: no, we can´t look into the future, but we do analyse different scenarios and how they would affect a Deep repository for spent nuclear fuel, and we can look back in time, millions of years, to get a better understanding of what can happen during the following ten tousands of years.

Last summer, we used Oklo, Cigar Lake, Dunarobba and the copper cannon from the Kronan. Our experience is that these analogs really fascinates people, giving them an understanding for the geological time scales.

During the conference, many of you saw a video about natural analogues. It´s a coproduction between NAGRA, SKB, EC, UK NIREX, ENRESA US DOE, AECL and ONDRAF. There are two messages included in this video: the first and obvious is that natural analogs helps us to understand the processes in nature that´s important when constructing final repositories for long-lived wastes, processes that thanks to the analogs can be studied after thousands of years. The other message is in the coproduction: scientists around the world has a common view on the issue, there is an extensive knowledge about the methods for long term safe disposal deep underground.

I would like to end with the statement that the three strongest factors in the PR work of SKB is: meeting people eye to eye, the ethical arguments and the natural analogs.

APPENDI

Some posters presented at the meetin

Influence of the alteration processes on the U-Th-REE minerals in the El Berrocal granite (Spain): an example of analogue processes	L. Pérez del Villar et al. (
The Tono natural analogue rogram	H. Yoshida et al. (JAP)

INFLUENCE OF THE ALTERATION PROCESSES ON THE U-Th-REE MINERALS IN THE EL BERROCAL GRANITE (SPAIN): AN EXAMPLE OF ANALOGUE PROCESSES.

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ABSTRACT

The hydrothermal and weathering events that affect the U-Th-REE accessory minerals in the El Berrocal granite have been studied in relation to the natural radionuclide migration/retention processes in a fissured granitic environment.

The available data, obtained by inclusion fluid studies, stable isotopes, scanning electron microscopy and whole rock chemical analyses, show that the uranium has been mobilized in a broad temperature range from 350°C to ambient temperatures, provided oxidizing conditions are present. Nevertheless, uranium is readily retained mainly by precipitating anions and, in less proportion, by adsorption onto Fe oxyhydroxides.

The first two high-temperature hydrothermal processes identified have been considered as analogue processes to those that can occur in a high level radioactive waste repository taking into account the temperatures that would be attained in the near field, according to certain national conceptual models. The third low-temperture hydrothermal process and weathering have been considered as low-temperature analogue processes to those that could be expected in the far field of a high level radioactive waste repository.

INTRODUCTION

Research on different geological environments are being carried out in Spain within the framework of the analysis of the safety assessment of high level radioactive waste (HLRW) repositories. In order to address this problem, an international, multidisciplinary project on U migration was undertaken in 1991 in a fissured granitic environment, the El Berrocal pluton (Fig. 1A). This granite is the host rock of a U mineralized quartz vein, both forming the so called Berrocal granite/U-bearing-quartz-vein system (Fig. 1B).

El Berrocal pluton is mainly constituted by an alkaline-feldspar granite with two micas, muscovite being dominant, and a very complex accessory mineral association formed by: corundum, andalusite, zircon, ilmenite, niobite, monazite, xenotime, apatite, uraninite, cassiterite, gold, bismutinite, arsenopyrite, sphalerite, chalcopyrite, galena and pyrite. Fluorite and anatase are secondary minerals. From a geochemical point of view, the El Berrocal granite is highly evolved, rich in SiO_2,(74.5%) and P_2O_5 (0.4%), peraluminous

(13.5%), hypocalcic (0.5%) and enriched in incompatible elements like Li, F, Sn and U [1]. The high U content (X = 16.3 ppm), the value of the U/Th > 2 and the presence of uraninite as accessory mineral, which holds approximately 63% of the total U of the rock, allow its classification as a so called "U fertile granite" [2, 3]. These mineralogical and geochemical characterisitics are typical of the S-type granites [4].

The U mineralization is hosted in a sulfide-bearing quartz vein, and is formed by pitchblende, Mn-rich carbonates, minor pyrite (melnikovite) and barite [5].

Though the granite/U-mineralization system cannot be globally considered as a natural analogue [6], the alteration processes which affected the granite, including those that originated the U mineralization, as well as the past and recent-past weathering, can be considered "a priori" as analogous processes to those that could occur both in the near and far field of a HLRW repository.

Four alteration events have been established in the El Berrocal granite (Table 1), based on the structural, mineralogical and textural features of the granite [6], as well as the thermometric data obtained from fluid inclusions in quartz from the granite [7], and from stable isotopes determined on quartz from the mineralized vein and near-by carbonates [8, 9].

The objectives of this work are: i) to establish the influence of the alteration events on the U-Th-REE accessory minerals in the granite and on the U ore body; ii) to deduce the physico-chemical conditions of these events based on the mineral transformations and new formations, and iii) to establish the analogies between these processes and those that can occur in a high level waste repository.

EXPERIMENTAL

The samples studied come from the reference granite (RG) intersected by borehole B-16 and from the access gallery of the U mine. The samples of the hydrothermally altered granite (HAG) were taken from core B-13 between 85 and 182m deep, at both sides of the U-mineralized quartz vein. Samples of weathered granite (WG) were collected from the upper part of B-16 between 5 and 18m (Fig. 1B).

The mineralogical studies have been performed by optical and scanning electron microscopy (OM and SEM), the latter coupled to an energy dispersive X-ray analysis system (EDX). Secondary and backscattered electron images (SE and BSE, respectively) were taken. The chemical composition of whole rocks has been determined combining inductively couple plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry (XRF) for SiO_2, U and Th, atomic absorption spectrometry (AAS) and flame atomic emission spectroscopy (FAES)(Fig. 2).

RESULTS AND DISCUSSION

First hydrothermal event

This hydrothermal event (310-350°C), defined as deuteric and/or early post-magmatic, since a clear distinction between them is difficult to establish, affects the El Berrocal granite pervasively though incipiently to a depth of 609m. This granite is the least altered in the pluton and it is referred to as reference granite (RG).

Among the transformations affecting the essential and accessory minerals, the following can be highlighted: 1) *Pervasive chloritization of biotite with release of* TiO_2 *and* Fe_2O_3 *and new formation of K-feldspars*; 2) *Muscovitization of biotite;* 3) *Sericitization of albite*; *4) Transformation of ilmenite into anatase; 5) Partial dissolution of apatite and* 6)*Partial destabilization of uraninite and monazite.*

Concerning the new formed minerals, the main mineralogical processes are: 1) *Interstitial albitization* and 2) *New formation of fluorite.*

All these alteration processes on the whole rock originate an average oxidation degree (Ox°) of 0.45 ($Ox^{\circ}=Fe^{3+}/Fe^{3+}+Fe^{2+}$, [10]), and their pervasive, though incipient intensity, suggests a low water/rock ratio.

The most important mineralogical processes concerning the remobilization, migration and retention of the U, Th and REE are the new formation of fluorite and the destabilization of apatite, uraninite and monazite. Secondary fluorite mainly occurs as in-fills of pit etching in albite (Fig. 3a), voids in the rock and, occasionally, surrounding the uraninite crystals. Primary apatite is often partially dissolved (Fig. 3b).

The presence of uraninite is constant in all the RG studied to 609m in depth. It occurs as idiomorphic [100] [111] crystals ranging in size from 5 to 100μm, and is included in all the essential minerals of the granite and in intergranular positions. Uraninite is generally coated by pyrite and shows only minor alteration along microfissures (Fig. 4a). The chemical composition of this unaltered uraninite obtained from a uraninite concentrate is:

U_3O_8 = 95.12%; ThO_2 = 0.96%; PbO = 3.54%; Ce_2O_3 = 0.18% and Y_2O_3 = 0.19% [2].

When uraninite is included in albite, the former can be coated by secondary fluorite.

In this case, the uraninite crystals are almost always totally altered to a U-Si-P-Al-K-Ca-Na complex compound with S traces, except for the core, which remains as unaltered uraninite. In zones adjacent to the altered crystals, U from uraninite is precipitated along the microfissures affecting the host mineral (Fig. 4b), indicating a short distance of mobilization. If the alteration is extremely strong, boxworks of uraninite surrounded by fluorite with relicts of pyrite and U compounds are observed (Fig. 4c).

Similarly, when monazite is surrounded by secondary fluorite, skeletal textures, due to partial dissolution of the former, are produced. These relicts, lacking in REE, are composed of: ThO_2 (55.6%), CaO (8.5%), Fe_2O_3 (3.5%), P_2O_5 (18.8%) and SiO_2 (12.5%), their composition being close to that of auerlite (Fig. 4d).

There are clear evidences that the U has migrated far from uraninite, precipitating in the following ways: a) surrounding chloritized biotite, along the cleavage planes of muscovite and filling microfissures in quartz (Fig. 5a); b) coating anatase and partially-dissolved apatite (Fig. 5b); c) coating pyrite and secondary fluorite and filling voids in albite (Fig. 5c); and d) coating idiomorphic crystals of arsenopyrite (Fig. 5d). In all the cases the U precipitates as U silico-phosphates, except in arsenopyrite where U precipitates as uranyl arseniates. On the contrary, Th from monazite remains immobile, and no secondary REE minerals have been found.

Some of the mineral transformations described indicate oxidizing conditions, specially those related to the alteration of uraninite, though significant free oxygen is unlikely to exist in deep-seated hydrothermal fluids [11]. However, fluorine from the residual magmatic fluids can cause the complete oxidation of U^{4+}, transforming uraninite into clarkeite following this reaction [11]:

$$\begin{aligned}&14UO_{2+x(cr)} + 6Na^+ + 14(1\text{-}x)F_{2(aq)} + (10\text{-}14x+n)H_2O \rightarrow \\ &\quad \rightarrow Na_6U_7O_{24}\bullet nH_2O_{(cr)} + 7(UO_2)^{2+} + 28(1\text{-}x)F^- + 2(10\text{-}14x)H^+ \qquad (1)\end{aligned}$$

In the El Berrocal granite, though the existence of F is supported by the constant presence of secondary fluorite, clarkeite has not been identified. However, the formation of uranyl fluoride complexes and their migration through the rock are confirmed by the precipitation of secondary fluorite in pit etching in albite together with U silicate compounds (Fig.6 a,b). Similarly, U-silico-phosphate compounds, filling microfissures and cleavage planes and coating pre-existing minerals, could have also precipitated after uranyl fluoride destabilization had taken place, favored by the high activity of SiO_2, P_2O_5, Na and Ca, since partial dissolution of albite and apatite also took place.

Since the samples studied do not present other alteration events other than the deuteric and/or late magmatic processes, the alteration of uraninite by fluorite is considered to have taken place in a temperature range between 350-315°C. Though this temperature is way above the upper temperature limit of the stability of the uranyl silicates (uranophane), if the data given by [12] on the thermal decomposition of uranophane were considered, Bayushkin et al. [13] have obtained a dehydrated uranyl silicate between 300° and 600°C from Na-boltwoodite. These last data would support the formation of silico-phosphates from uraninite in the temperature range 350-315°C.

Second hydrothermal event

This second process is related to the most important fracture zones (N80°E and N110°E) and the main mineralogical transformations in the granite are: *1) Sericitization of chloritized biotite and 2) The almost total sericitization of albite and K-feldspar* according to the following reactions:

$$3\ \text{Albite} + K^+ + 2H^+ \rightarrow \text{Sericite} + 6SiO_2 + 2Na^+ \quad (2)$$

$$3\ \text{K-feldspar} + 2H^+ \rightarrow \text{Sericite} + 6SiO_2 + 2K^+ \quad (3)$$

All these processes originate a Ox° of the whole rock which varies from 0.6 to 0.8, and the strong intensity of the alteration observed suggests a high water/rock ratio, favored by the strong tectonization of the granite.

The influence of this second process on the U-Th-REE-Zr accessory minerals and on fluorite are: *1) Total destabilization of primary uraninite and secondary fluorite and 2) Partial destabilization of primary apatite and accessory Th-REE-Zr-bearing minerals.*

The mineralogical evidences of U-Th-REE-Zr mobilization and precipitation are: i) the presence of U silico-phosphate coating and filling intracrystalline fissures in primary pyrite (Fig. 7 a,b); ii) precipitation of botryoidal mineraloids whose chemical composition varies from U-Th silico-phosphates to Th-U-silico-phosphates (Fig. 7 c,d); iii) existence of Th-phophates coating primary chalcopyrite and presence of Th and Zr-silicates filling microfissures in quartz (Fig. 7e) and iv) new formation of complex Al-phosphates with Sr, Ca, S, La, Ce and Nd, probably florencite (Fig. 7f).

From a geochemical point of view, these mobilization/precipitation processes are supported by a general increase of the contents of U, Th, Ce, La, Y and Zr in the HAG in relation to the RG. Furthermore, a similar distribution of the highest contents of these elements occurs in the HAG intersected by B-13, whose normalized values are represented in Fig. 8.

This process is similar to the deuteric and/or early post-magmatic process but more intensive due to a stronger tectonization of the granite and greater water/rock ratio. The oxidizing and dissolving agent can be fluorine from the destabilization of fluorite, and the transport of U, Th and REE would also take place as F^- complexes.

Third hydrothermal event

This proccess, which took place within a temperature range of 170°-60°C, is divided in two phases separated by a tectonic event.

Phase A was developed at the higher temperature, during an extensional regime, originating the principal sulfide-bearing quartz veins (N110°E and N80°E). The quartz comes from the SiO_2 released by the alteration of feldspars in the second hydrothermal process, and the sulfides come from the dispersed primary sulfides existing in the RG. This phase is barren in U.

Phase B was developed at the lower tempertures, after the tectonization of the sulfide-bearing quartz veins, originating the El Berrocal U ore body within the N110°E quartz vein, and composed of pitchblende, Mn-rich carbonates, and minor pyrite (melnikovite) and barite [5]. The values of δ ^{13}C (-7 to -16‰), determined in the Mn-rich carbonates, indicate that the C has an edaphic origin [9], and the co-existence of pyrite and barite suggests that the precipitation took place between -200 to -300mV [14]. All these data suggest, in turn, that the mineralizing process can be divided in a downward and upward step.

During the downward step, weakly acid meteoric waters enriched in HCO_3^- of edaphic origin would oxidize and remobilize the primary uraninite of the RG, transporting the U as uranyl-carbonate complexes. After being reheated in depth by tectonic events, these solutions would move upwards by convective flow, water/rock interaction phenomena and a drop in T and P being produced. Probably, after the destabilization of the uranyl carbonate complexes and the UO_2^{2+} reduction by H_2S, pitchblende, Mn-rich carbonates, pyrite and barite were precipitated.

An approach to the geochemical model of both steps can be the following:

Downward step:

$UO_2 + 2H_2O \rightarrow UO_2^{2+} + H_2O + 2e^-$; $UO_2^{2+} + 3H_2O \rightarrow UO_2(OH)2H_2O + 2H^+$ (4 , 5)

$UO_2(OH)\,2H_2O + H^+ \rightarrow UO_2(OH)^+ + 2H_2O$; $UO_2(OH)^+ + HCO_3^{1-} + H_2O \rightarrow UO_2(CO_3)_2 2H_2O^{2-}$ (6, 7)

The uranium dicarbonate complex is stable in weakly acid and alkaline solutions between 25 and 200°C [15].

Upward step:

$UO_2(CO_3)_2 2H_2O^{2-} \rightarrow UO_2^{2+} + 2CO_3^{2-} + 2H_2O$; $UO_2^{2+} + H_2S \rightarrow UO_{2+x} + SO_4^{2-}$ (8, 9)

($CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3^{*}$; $SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4^{**}$; $H_2S + 2Fe^{2+} \rightarrow Fe_2S^{***}$ (10 , 11, 12)

(*calcite; ** barite; ***pyrite)

Weathering

The past and recent-past weathering processes on the U orebody and the granite have different intensities due to the varying flow of the meteoric waters, the alteration being extremely strong and deep (≈ 100m) in the U orebody, gradually less intense in the HAG and still less intense and more superficial (18m) in the RG. Furthermore, the percolating meteoric waters present different physico-chemical conditions in these environments, being very acid (pH=3) in the U orebody due to sulfide oxidation, and weakly acid (pH=6-7) in the HAG and RG. The pH of the waters gradually increases with depth to weakly alkaline in all the cases.

The effects of the weathering processes on the orebody are: i) dissolution of the Mn-rich carbonates and oxidation of pyrite, forming Fe-Mn oxyhydroxides; ii) frequent oxidation of pyrite to jarosite, indicating a very low pH of the percolating waters and oxidation of chalcopyrite to covellite and calcocite (Fig. 9a); iii) oxidation of pitchblende and "in situ" transformation to uranyl phosphates: uranocircite (Ba), torbernite (Cu) and autunite (Ca) (Fig. 9 b,c). Barium, Cu and Ca come from the destabilization of barite, chalcopyrite and carbonates, respectively, and P comes from the destabilization of apatite, which is very abundant in the whole granite/U-mineralization system. iv) formation of uranyl phosphates, frequently coated by collophorm Fe oxyhydroxides with traces of U and P, filling microfissures in quartz and indicating precipitation processes (Fig. 9d).

These weathering effects on the orebody constitute a typical example of the oxidation and cementation of a sulfide-U-bearing vein, related to the percolating waters and the fluctuations of the water level.

Weathering in the granite is represented by the transformation of the feldspars to sericite, disappearance of chlorite, formation of smectite and a general oxidation. The effects of this process on the U-Th-REE minerals is fundamentally focused on uraninite, which in the most superficial zones of the granite can be totally dissolved or not, depending on the nature of its host mineral. Thus, if uraninite is included in quartz, it is usually protected from the oxidizing percolating waters (Fig. 10a). On the contrary, if uraninite is hosted by feldspars, the former is generally dissolved, ocassionally showing the cube-octahedral outline of the original crystal. The existence of original crystals of uraninite is also supported by the presence of alteration halos, formed by chlorite-type phyllosilicates, as well as the existence of microfissures in the host mineral due to tensional effects. Uranium from uraninite was precipitated both outside the original crystal and filling near-by fissures as U phospho-silicates, whereas Th remained inside the original crystal as Th-Ca phospho-silicates with minor U (Fig. 10 b,c,d).

The downward migration of U, as well as its retention by precipitation and adsorption onto the Fe oxyhydroxides, is supported by the existence of microfissures and voids filled by uranyl phospho-silicates and Fe oxyhydroxides with traces of U and P. The adsorption process is shown in Fig. 10e, f and Fig. 11, the latter representing the vertical variation of the contents of U, Th, P_2O_5, Fe_2O_3 and FeO in the weathered granite.

ANALOGY WITH THE MIGRATION/RETENTION PROCESSES AROUND A HLRW REPOSITORY.

The El Berrocal granite/U-mineralization system cannot be considered as a natural analogue of a HLRW repository for several reasons. One of the most important is the existence of two sources of U, one, the granite itself, and the other, the U orebody. This fact hinders the delimitation of the dispersion halo of the U from the second source. However, the hydrothermal processes recorded in the granite, including the one that formed the U vein, as well as the past and recent-past weathering processes that affected the whole system, can be considered as remobilization, migration and retention processes of U, Th and REE analogous to those that could occur in a HLRW repository.

The two first hydrothermal events recorded took place at a temperature (350° and 250°C) far higher than the temperature ($\approx$100°C) expected shortly after burial in the near-field of a repository, if the conceptual models of almost all the countries involved in this problem were taken into account. However, in some of the current French concepts in granitic rocks, temperatures in the range of 200-300°C would be attained in the near-field [16]. Similarly, in the USA conceptual model (Yucca Mountain), temperatures as high as 250°C and the possibility of mobilization of halogen elements from the volcanic storage rock are expected [17, 18]. Consequently, the two high-temperature hydrothermal processes identified in El Berrocal granite, in which uraninite and F were involved as source term and oxidizing and mobilizing agent, respectively, can be considered as analogue processes to those that could occur shortly after burial in the near-field, if this high temperature range was expected. The different water/rock ratio in the two natural processes would help to understand what would happen in a repository if varying amounts of water reached it.

The low-temperature hydrothermal process, responsible of the formation of the U vein-type orebody, whose source was the uraninite in the granite, can be also considered as an analogue process to those that could occur in the far-field of a repository. Thus, the mobilization of U was produced by percolating, more or less acid meteoric waters enriched in HCO_3^- of edaphic origin, quite similar to the current percolating meteoric waters through some granitic massifs, covered by organic soils [19]. The tectonic events in the natural system produced the reheating of these uraniferous solutions, while in the artificial system, the radiogenic heat from the canister would be responsible of the reheating of the percolating meteoric waters. Similarly to the natural process, convective flows through fractures are to be expected in the artificial system. The precipitation of U and other analogue radioelements would be produced in the fractures by solutions/fissure fillings interaction, drop of temperature and pressure and favored by the presence of precipitating chemical and physico-chemical agents, like H_2S , pO_2, PO_4^{3-}, SiO_4^{4-} etc. The only difference between the natural and artificial systems is that, in the former, the U from disperse uraninite in the granite was concentrated by natural hydrothermal process, while, in the latter, the artificial hydrothermal processes would tend to disperse U and other analogue radioelements from a concentrated source, the canister [1, 20].

The weathering processes observed both in the U-quartz vein and in the RG can be also considered as analogue processes at ambient temperature. Under the conditions in which these natural processes took place (oxidizing percolating waters with variable acidity), it is evident that the U^{6+} migration from the two sources of the system (pitchblende and uraninite) occurs, but it is also evident that its precipitation, as uranyl phosphates and/or phospho-silicates, and its adsorption onto Fe oxyhydroxides, is easily produced close to the source terms.

Finally, all the natural alteration processes, hydrothermal and weathering, observed in the El Berrocal system indicate that U can migrate in a broad temperature range, provided oxidizing conditions are present. However, U is readily retained either by precipitation or adsorption, due to rapid changes of the physico-chemical conditions of the uraniferous solutions or to the presence of uranyl precipitating and adsorbing agents .

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Table 1. Physico-chemical conditions of the alteration events and mineral transformations in the El Berrocal granite

EVENTS	PHYSICO-CHEMICAL CONDITIONS	MINERAL TRANSFORMATIONS & NEWFORMATIONS
1) Deuteric and/or early post-magmatic processes	T= 315-350°C P= 410-900 bars $H_2O + CO_2$ [7]	BIOTITE→CHLORITE ILMENITE→ANATASE APATITE:partially dissolved FLUORITE:Newformed
2) Hydrothermal process related to fractures	T = 240-260°C H_2O [7]	FELDSPARS→SERICITE
3) Low-T hydrothermal process (Phase A)	T = 120-175°C H_2O [7, 8]	FORMATION OF THE SULFIDE-BEARING Q VEINS
3) Low-T hydrothermal process (Phase B)	T = 60-85°C H_2O [8, 9]	FORMATION OF U OREBODY
4) Weathering	Ambient. Acid waters in sulfide-U-quartz-vein. Weakly acid (pH:6-7) waters in the superficial zone of the granite.	SERICITE→ILLITE→ SMECTITE→KAOLINITE (occasionally) GENERAL OXIDATION

FIGURE CAPTIONS

Figure 1. **A)** Geological setting of the El Berrocal granitic pluton. **B)** Cross section of the El Berrocal granite/U-bearing-quartz-vein system, and situation of the U-mine gallery and sampled boreholes B-16 and B-13.

Figure 2. Flowchart of the studies carried out in the granitic samples.

Figure 3. **a)** Secondary fluorite (Fl) filling pit etching in albite (Ab). **b)** Pit etching in apatite (Ap) included in K-feldspar (K-Fd). B-16, 105m deep. BSE images.

Figure 4. **a)** Unaltered uraninite (1) coated by pyrite (2 &3). Zr = zircon; Q = quartz; KFd = K-Feldspar. B-16 , 105m deep, (RG). **b)** Uraninite (1) partially altered to U silico-phosphate (2,3, 4 & 5) by fluorite (Fl). Notice the U migration near the source and along the grain boundaries and microfissures. Ab = albite; Q = quartz; Zr = zircon. B-16, 105m deep, (RG). **c)** Uraninite boxwork surrounded by fluorite (Fl) with rests of pyrite (Py), and U silico-phosphates (U) outside the boxwork. Plag = albite. U mine gallery (RG). **d)** Destabilization of monazite by fluorite (Fl), remaining Th-Ca phospho-silicates (1). Chl = chlorite; Ap = apatite; Py = pyrite; Zr = zircon; TiO_2 = anatase. B-16, 105m deep (RG). All the figures correspond to BSE images.

Figure 5. **a)** U silico-phosphates (U) precipitated in the boundary between biotite (Biot) and quartz (Q), and in the cleveage planes of muscovite (Mus). TiO_2 = rutile. B-16, 105m deep, (RG). **b)** Idem in the boundary among the accessory minerals. Notice the pit etching in apatite (Ap). TiO_2 = anatase; Mz = monazite; Py = pyrite; Ab = albite. B-16, 105m deep, (RG). **c)** U silico-phosphates surrounding primary pyrite (Py) and secondary fluorite (Fl). Ab = albite. B-16, 21.7m deep, (RG). **d)** Idiomorphic crystal of arsenopyrite partially coated by uranyl arseniate. U mine gallery (RG). All the figures correspond to BSE images.

Figure 6. **a)** Secondary fluorite (Fl) filling voids in albite (Ab). Notice the microfissure (?) network inside the fluorite with higher electron density. Mus: muscovite. **b)** Idem magnified. (1) coresponds to U silicates. B-16, 105m deep. BSE images.

Figure 7. **a)** U silico-phosphates (1) coating primary pyrite (Py) and filling intracrystalline fissures. Mus: muscovite. HAG intersected by B-13, 84m deep. **b)** Idem, magnified. **c)** Precipitation of botryoidal U-Th silico-phosphates (1) varying to Th-U silico-phosphates (2) Biot:biotite; Zr:zircon; Py:pyrite; Chp: primary chalcopyrite. HAG intersected by B-13, 84m deep. **d)** Idem, magnified. Notice the botryoidal texture of U-Th silico-phosphates (1) in contrast with the more compact texture of the Th-U silico-phosphates (2). **e)** Primary chalcopyrite (Chp) partially coated by Th-phosphates. Notice Th and Zr silicates filling microfissures in quartz (Q). HAG intersected by B-13, 86m deep. **f)** Secondary Al-phosphate-complex compound with Sr, Ca, S, La, Ce and Nd (1) (probably florencite). Mus: muscovite; Q:quartz. HAG intersected by B-13, 84m deep. **(a)** to **(f)** correspond to BSE images.

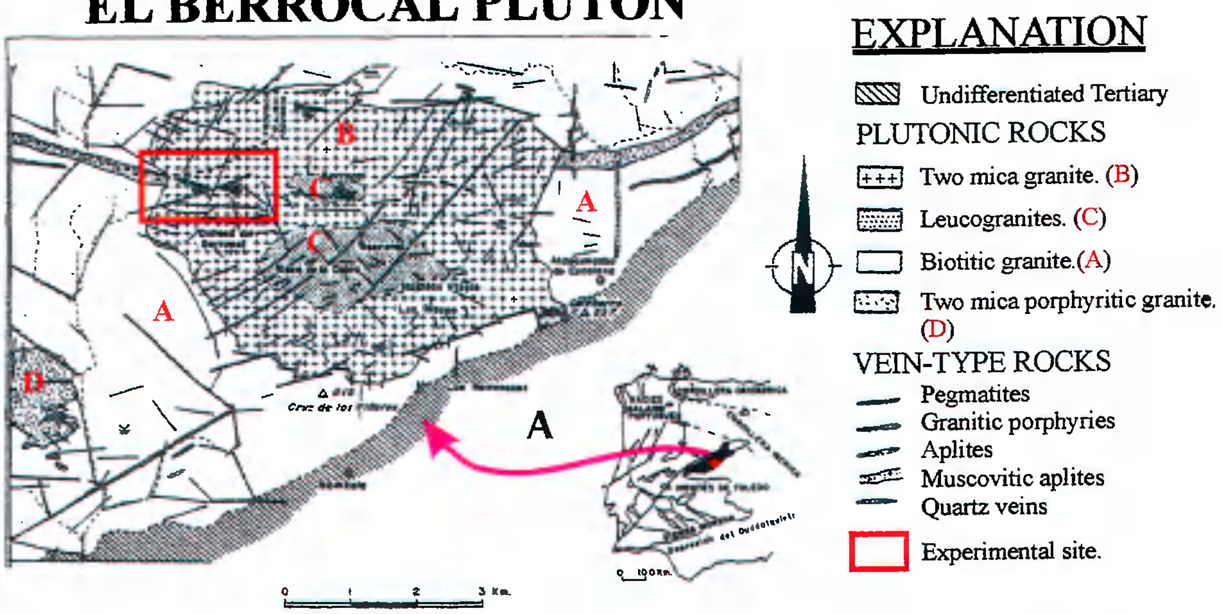
Figure 8. Distribution of the normalized values of U, Th, Ce, La, Y and Zr along the HAG intersected by B13. The values are normalized with respect to the average content of these elements in the RG. In general, the anomalies of all the elements coincide in the same sampling point, indicating that all these elements were mobilized and reprecipitated at once. The number of chemically-analyzed samples are 78 situated from 85 to 122m in depth.

Figure 9. **a)** Euhedral pyrite (Py) included in anheudral chalcopyrite (Cpy) partially altered to chalcocite and covellite. The euhedral pyrite is coated by K-jarosite (1), indicating the low pH (between 3 and 4) present during weathering. **b)** Collophorm and spherulitic pitchblende (1) being transformed into uranocircite (2) and autunite. **c)** Idem, magnified. 1: pitchblende; 2: uranocircite; 3: autunite. **d)** Torbernite (1) filling a fissure in quartz and coated by a collophorm band of Fe-oxyhydroxides (2) with adsorbed traces of P and U.
The sample corresponds to the U quartz vein intersected by B-13 at 87m deep. BSE images.

Figure 10. **a)** Crystal of primary uraninite shielded by quartz. SE image. B-16, 18m deep. **b)** Totally dissolved euhedral uraninite crystal, showing an alteration halo (B) formed by chlorite-type phyllosilicates, and the original outline of the crystal with immobilized Th-U-Ca phosphosilicates inside (A). Notice U phospho-silicates filling microfissures (C) and the microfissures due to tensional effects in the host mineral (3). 1: quartz; 2: albite; 3: K-feldspar; 4: apatite. **c & d)** Idem, magnified. 1 & 2 in **d**: chlorite-type phyllosilicate; 3 in **d**: Th-U-Ca phospho-silicate; 4 & 5 in **d:** U-Th-Ca phospho-silicate. B-16, 6m deep. **e & f)** Fe oxyhydroxides with P and traces of U filling microfissures and voids in albite (Ab). Sample in **e & f** corresponds to B-16, 9m and 18m deep, respectively. **(b) to (f)** correspond to BSE images.

Figure 11. Vertical variation of U, Th, P_2O_5, Fe_2O_3 and FeO in the WG from B-16. Notice the high U concentration close to the limit between the WG and RG, which coincides with a higher content of Fe_2O_3.

EL BERROCAL PLUTON



EL BERROCAL GRANITE-URANIUM-BEARING QUARTZ VEIN SYSTEM

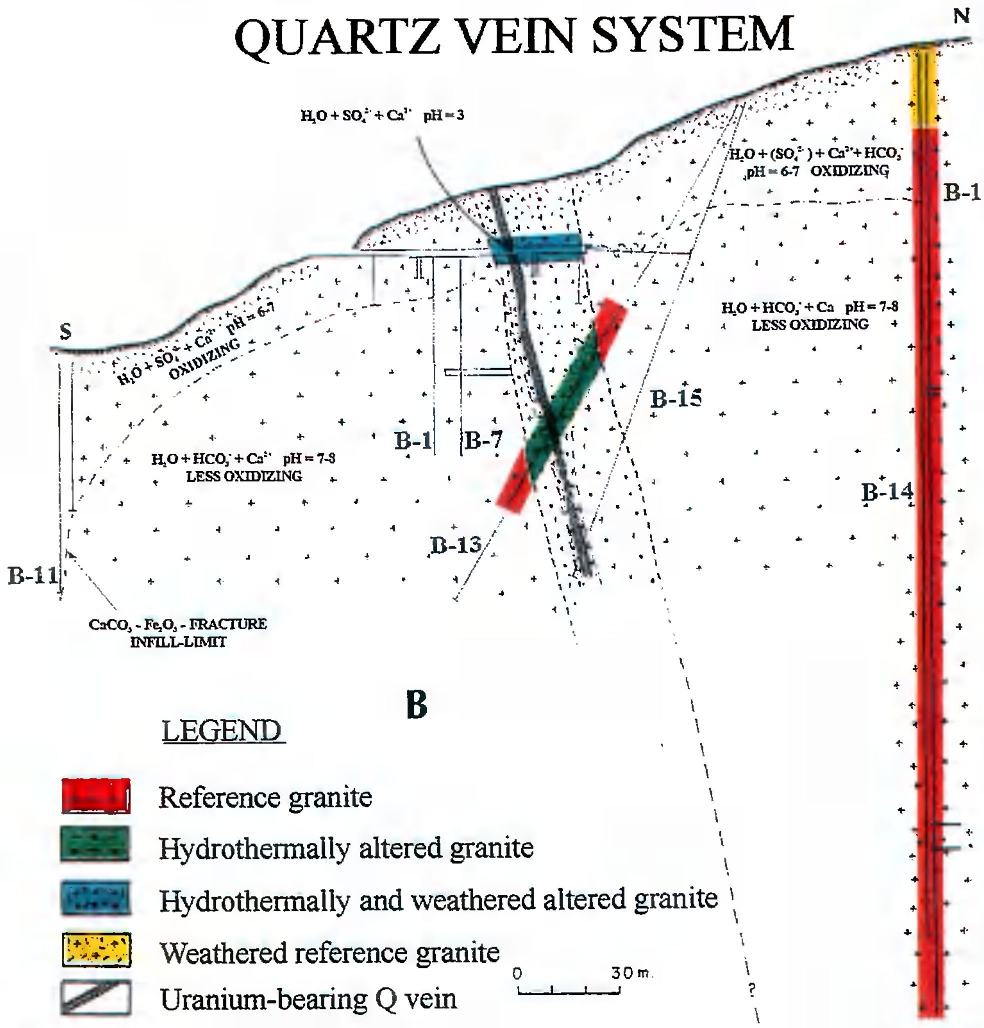
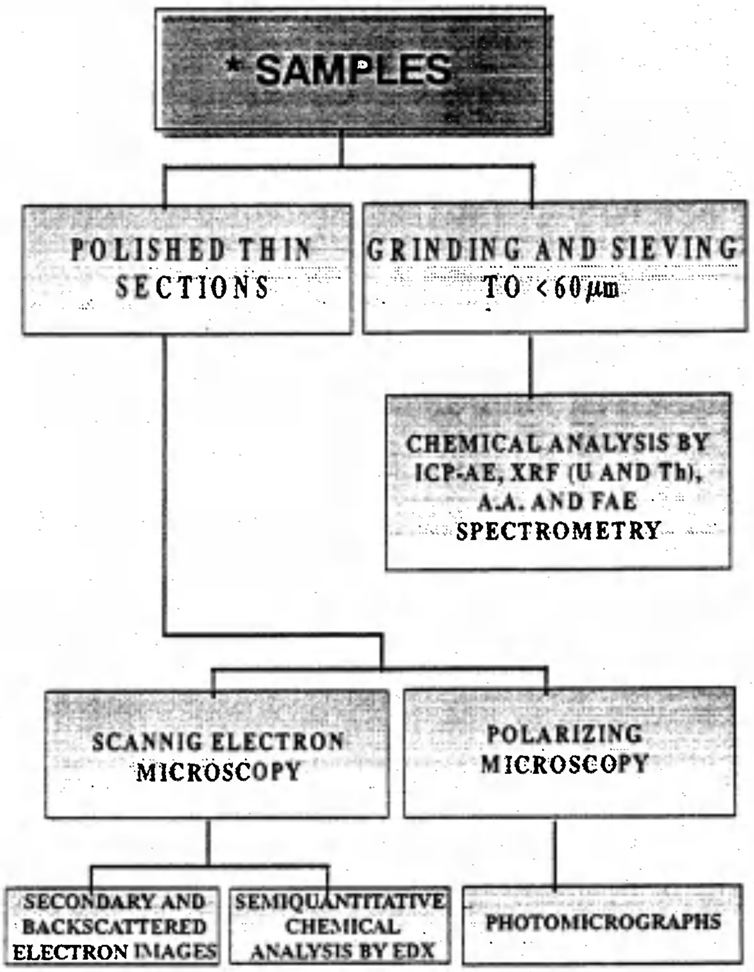


Figure 1



*** From Boreholes 16 (Reference and Weathered granite), 13 (Hydrothermally altered granite), U Mine gallery (Reference Granite) & U-Ore deposit (Uranium Ore)**

Figure 2

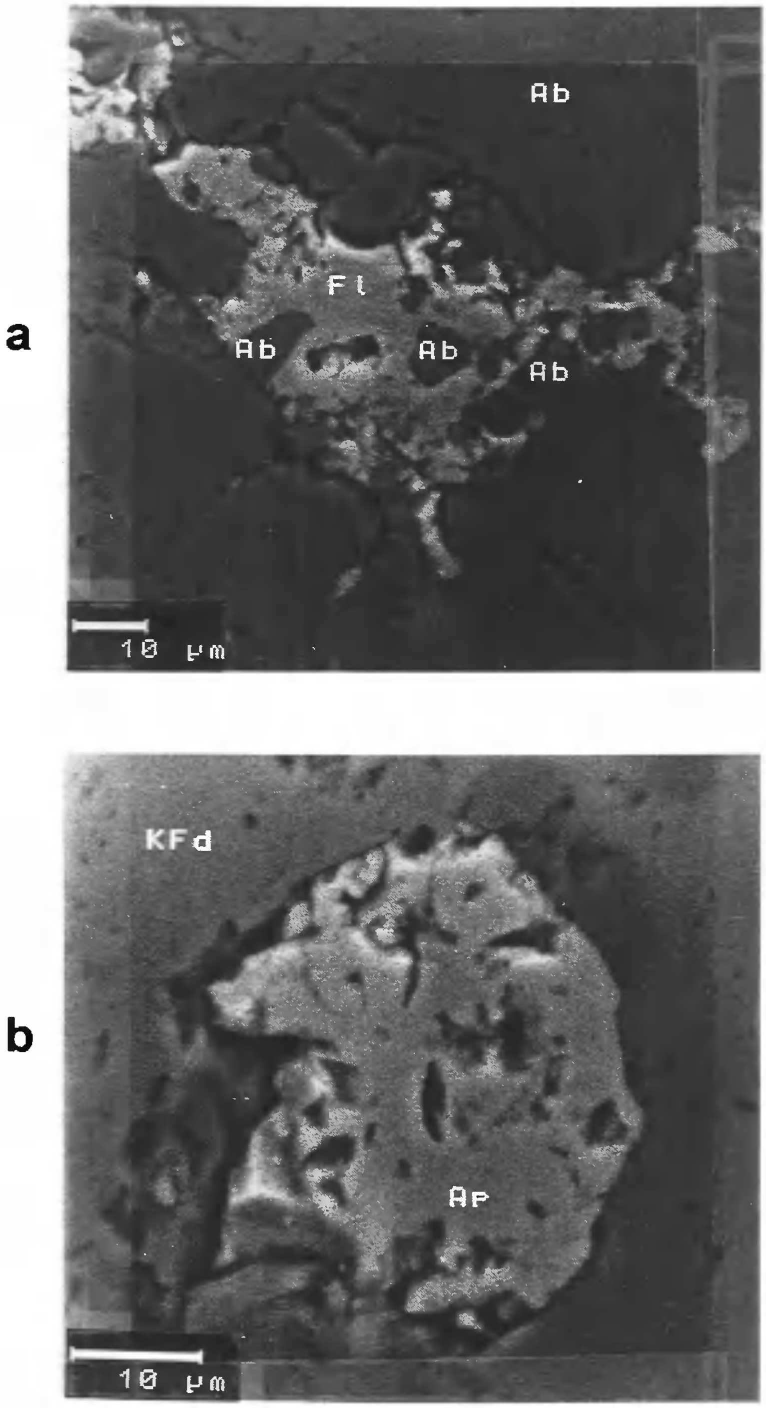
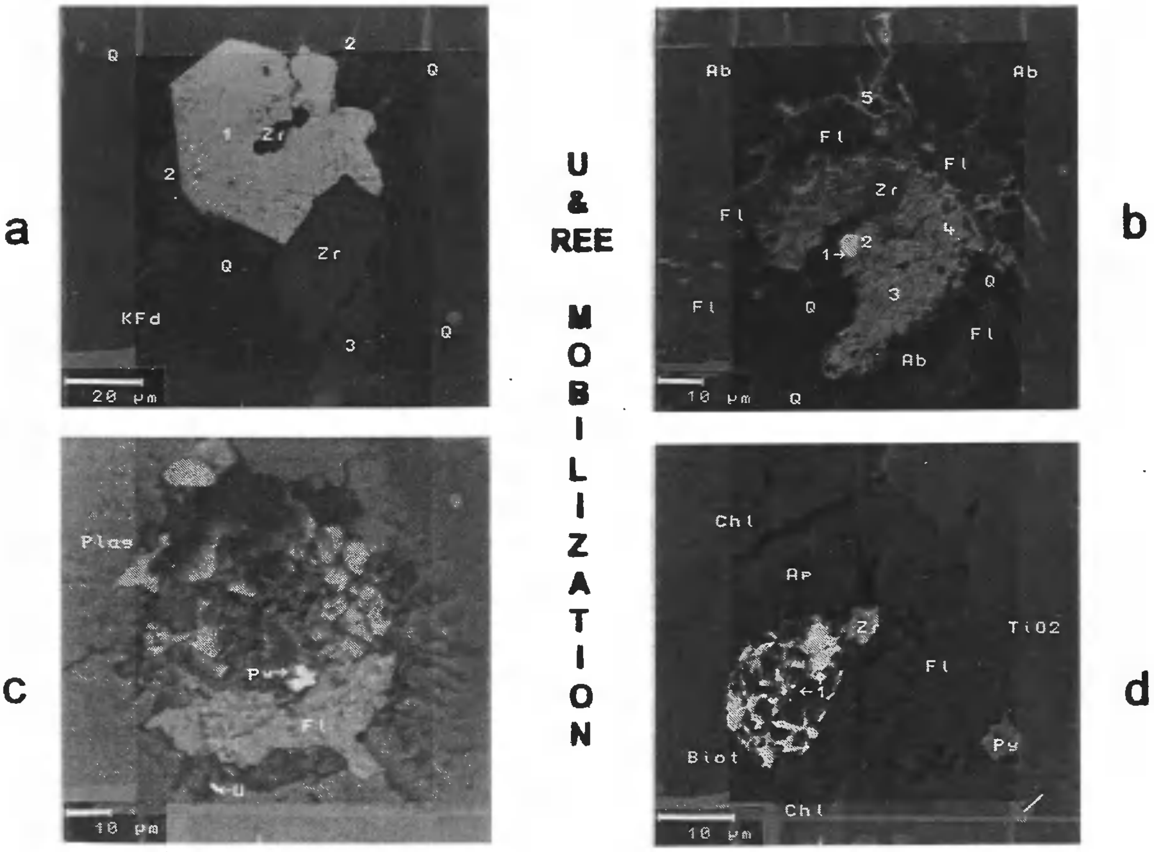


Figure 3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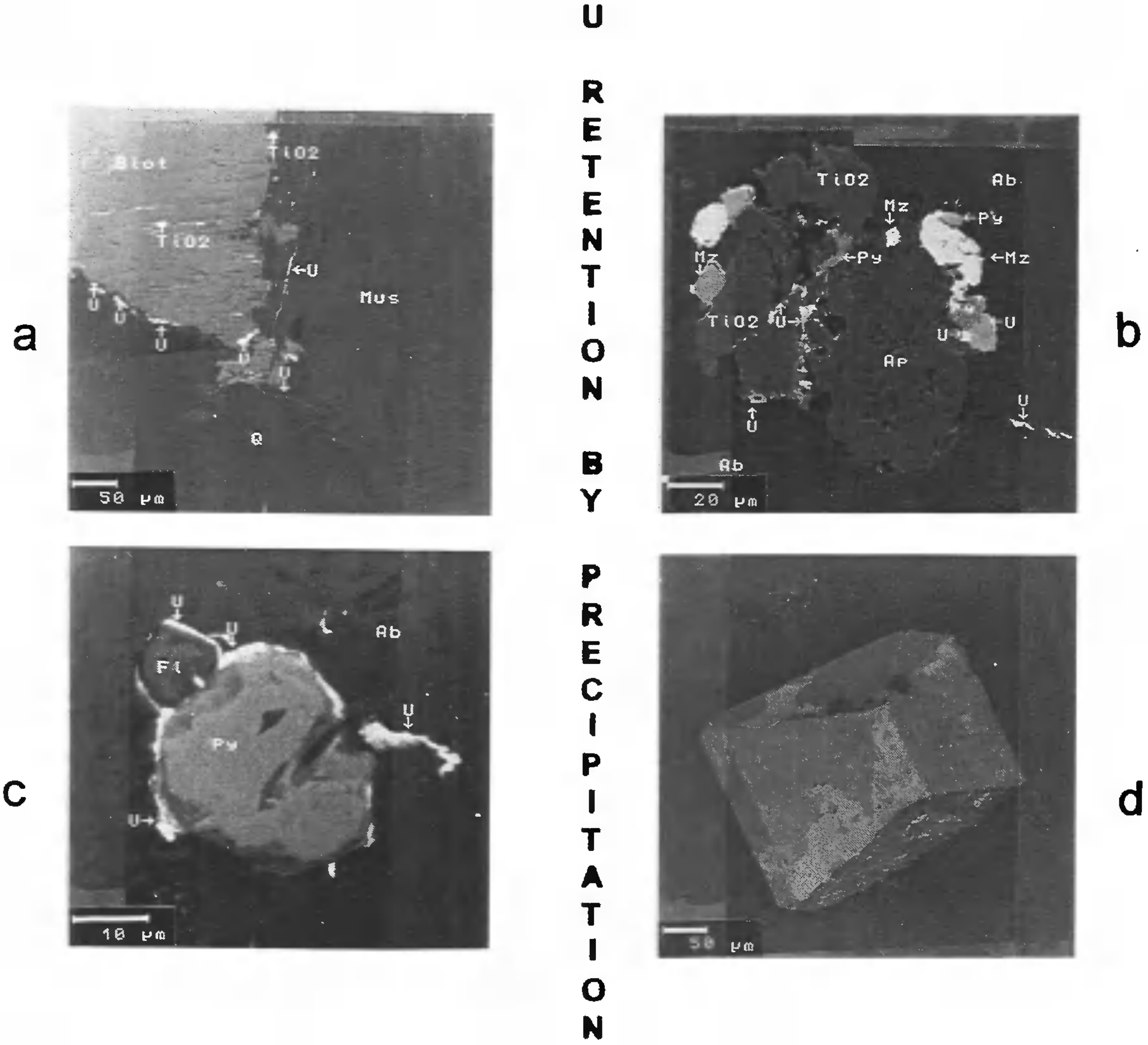
Zr
TiO2
Fl
←1
Py
Biot
Chl
10 µm

Figure 4



U RETENTION BY PRECIPITATION

Figure 5

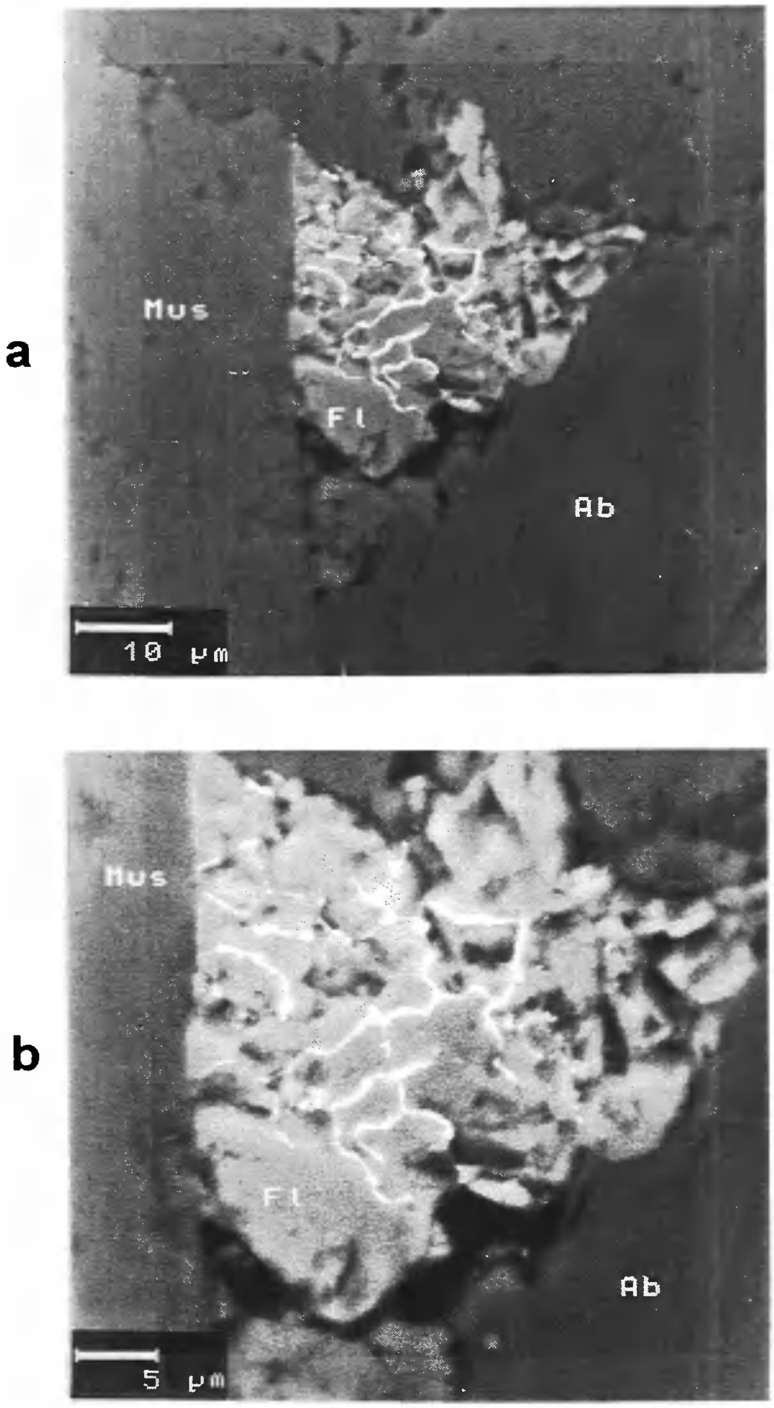


Figure 6

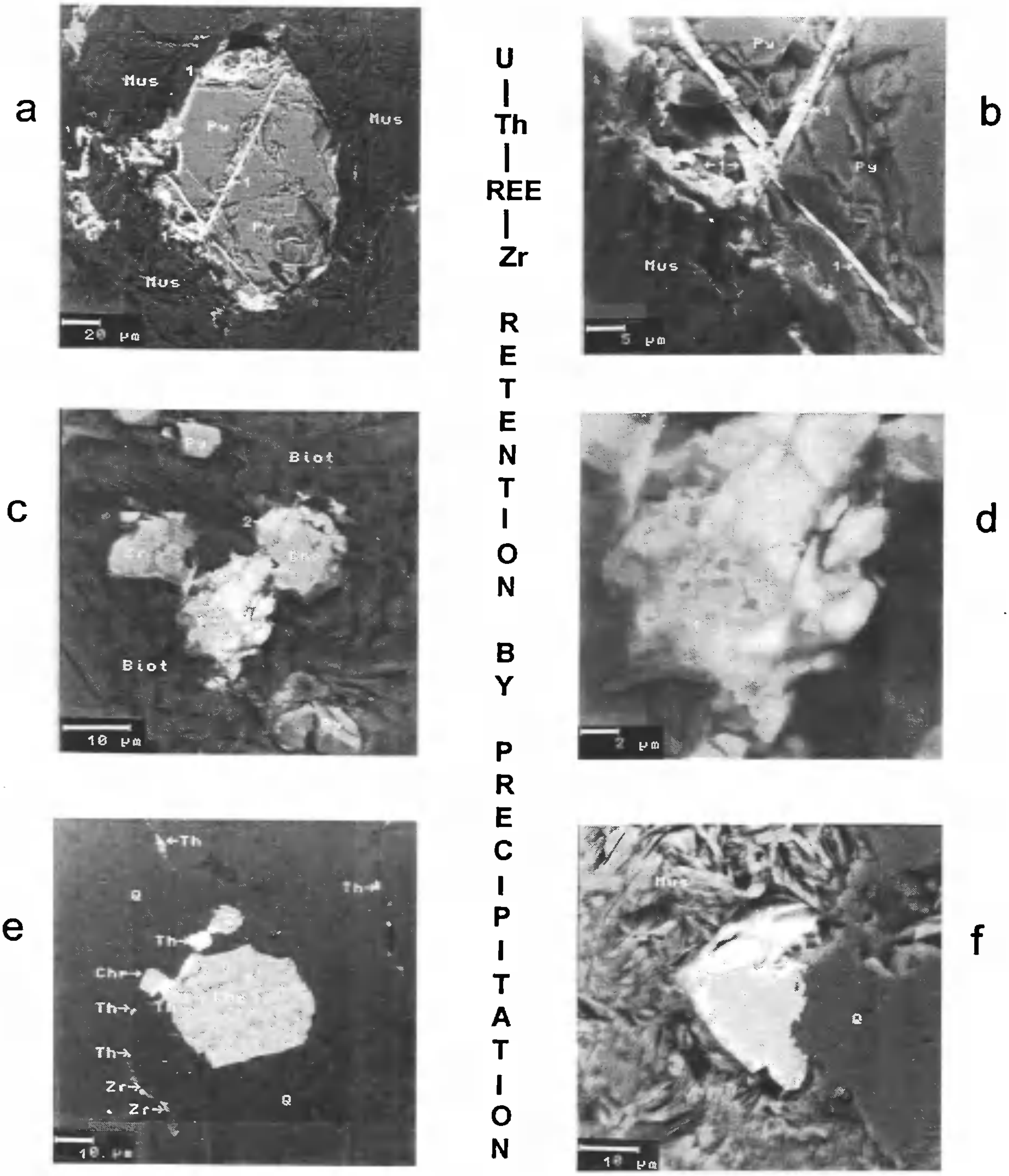

a
Mus
1
Py
Mus
1
1
Py
1
Mus
20 µm
U
|
Th
|
REE
|
Zr
RETENTION
BY
PRECIPITATION
b
Py
Py
Mus
1
5 µm
c
Py
Biot
2
Zr
Biot
10 µm
d
2 µm
e
←Th
Q
Th
Th
Chr→
Th→
Th→
Zr→
Zr→
Q
10 µm
f
Mus
Q
10 µm

Figure 7

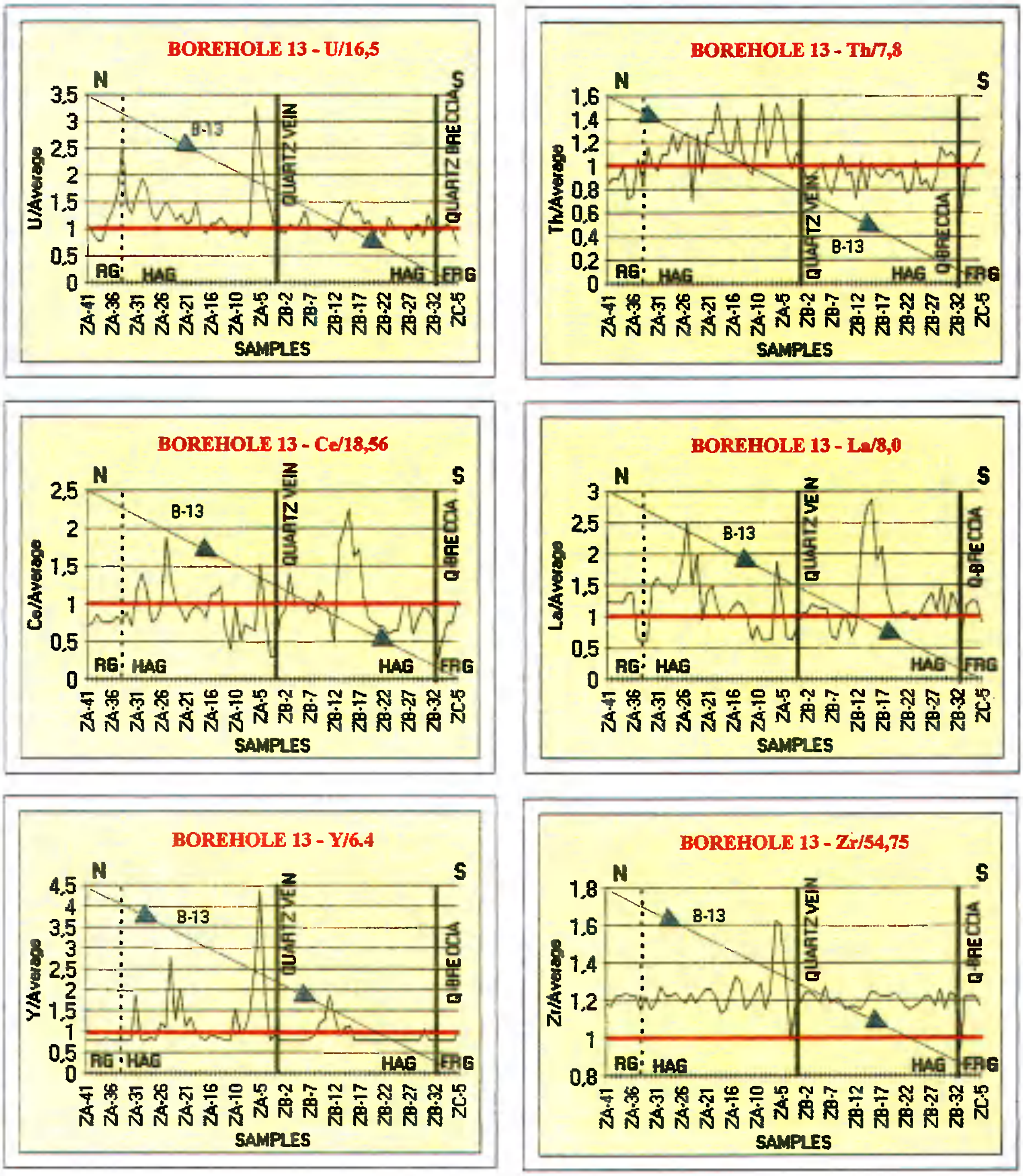

BOREHOLE 13 - U/16,5
U/Average
3,5
3
2,5
2
1,5
1
0,5
0
N
S
B-13
QUARTZ VEIN
QUARTZ BRECCIA
RG
HAG
HAG
FRG
ZA-41
ZA-36
ZA-31
ZA-26
ZA-21
ZA-16
ZA-10
ZA-5
ZB-2
ZB-7
ZB-12
ZB-17
ZB-22
ZB-27
ZB-32
ZC-5
SAMPLES
BOREHOLE 13 - Th/7,8
Th/Average
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
N
S
B-13
QUARTZ VEIN
Q BRECCIA
RG
HAG
HAG
FRG
SAMPLES
BOREHOLE 13 - Ce/18,56
Ce/Average
2,5
2
1,5
1
0,5
0
N
S
B-13
QUARTZ VEIN
Q BRECCIA
RG
HAG
HAG
FRG
SAMPLES
BOREHOLE 13 - La/8,0
La/Average
3
2,5
2
1,5
1
0,5
0
N
S
B-13
QUARTZ VEIN
Q-BRECCIA
RG
HAG
HAG
FRG
SAMPLES
BOREHOLE 13 - Y/6.4
Y/Average
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
N
S
B-13
QUARTZ VEIN
Q BRECCIA
RG
HAG
HAG
FRG
SAMPLES
BOREHOLE 13 - Zr/54,75
Zr/Average
1,8
1,6
1,4
1,2
1
0,8
N
S
B-13
QUARTZ VEIN
Q BRECCIA
RG
HAG
HAG
FRG
SAMPLES

Figure 8

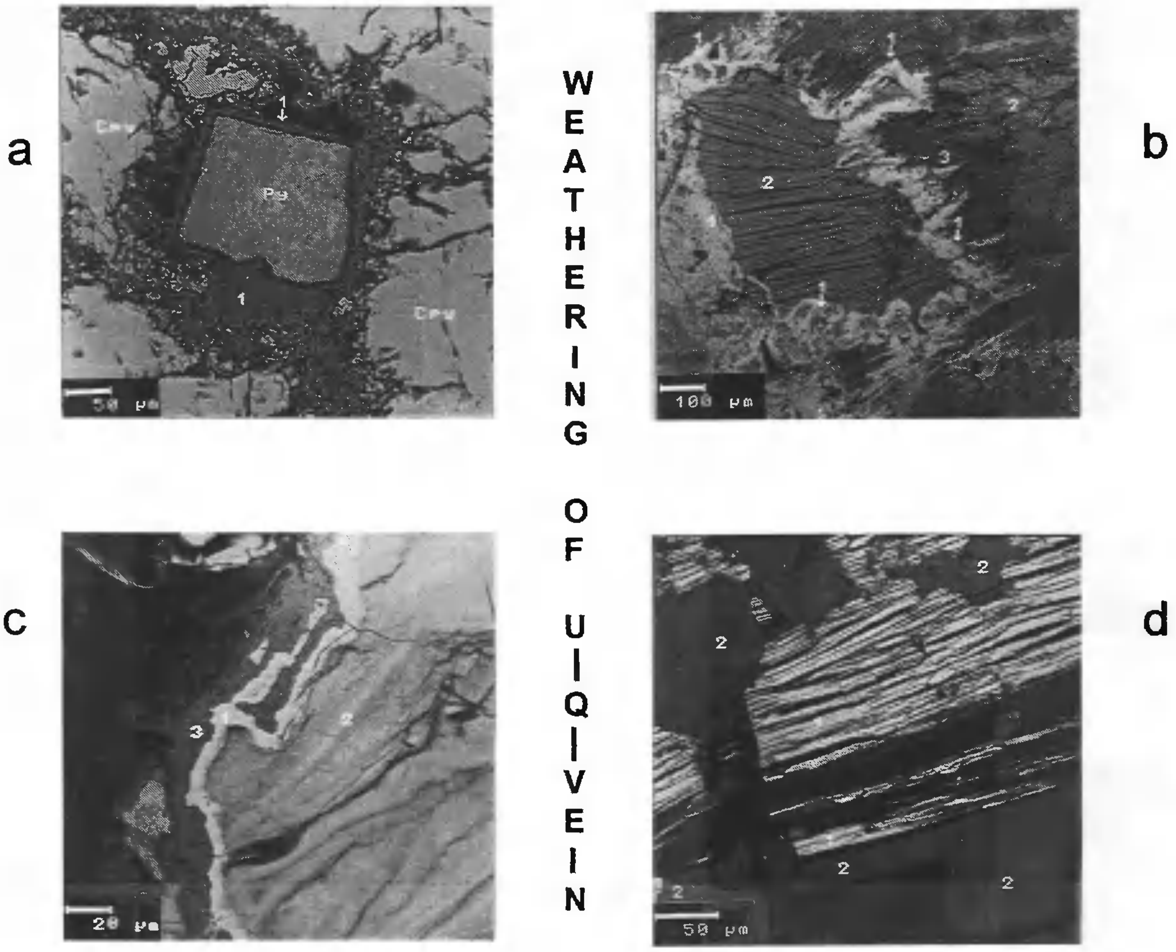

a
Cpy
1
Py
1
Cpy
50 µm
b
1
1
2
2
3
1
1
100 µm
WEATHERING OF UIQI VEIN
c
3
2
20 µm
d
2
2
2
2
2
50 µm

Figure 9

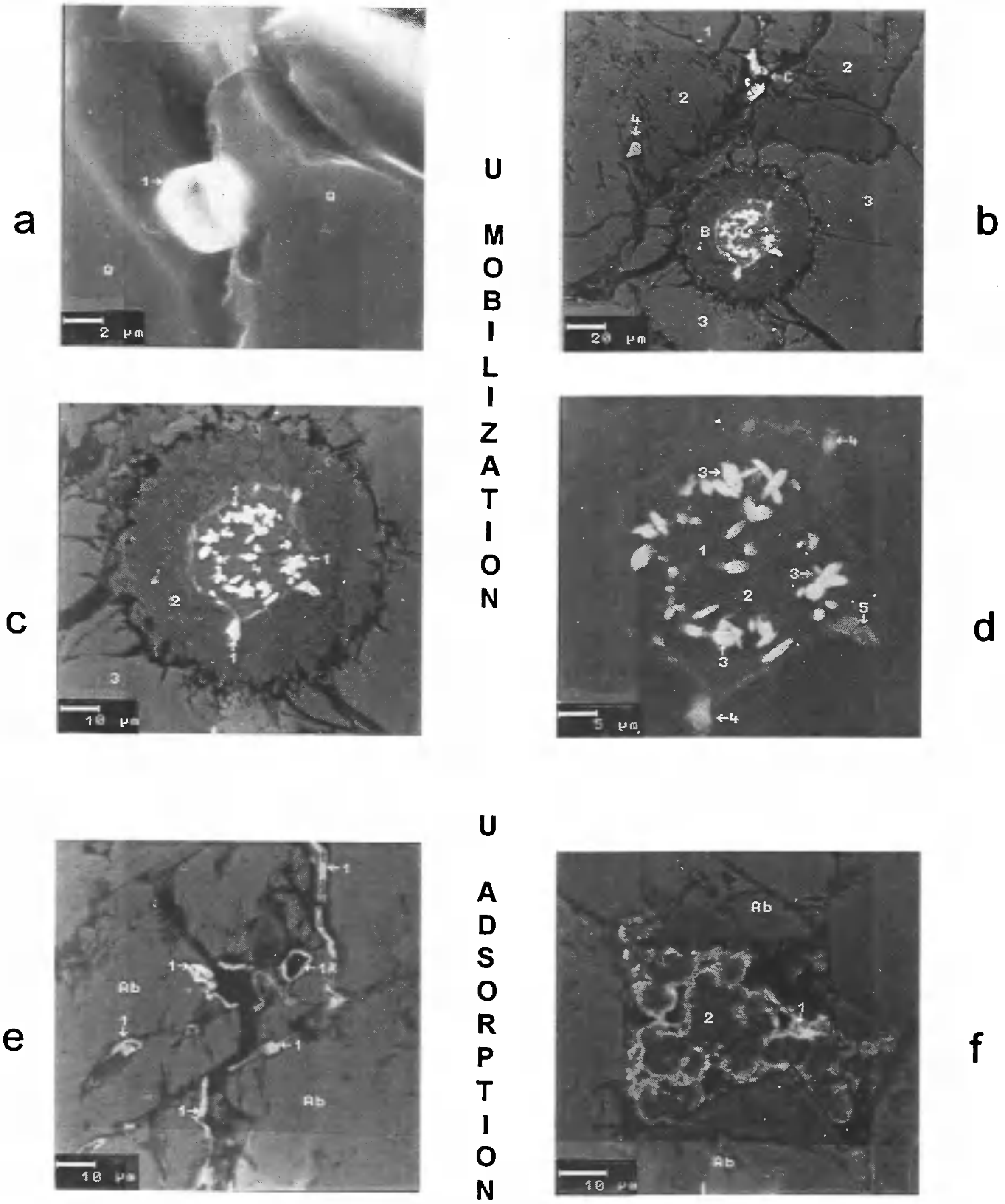

a
b
c
d
e
f
U MOBILIZATION
U ADSORPTION
1→
Q
Q
2 μm
1
2
2
C
4
B
3
3
20 μm
1
1
1
2
3
10 μm
4
3
1
3
2
5
3
4
5 μm
1
Ab
1
1
1
1
1
Ab
10 μm
Ab
2
1
Ab
10 μm

Figure 10

GEOCHEMICAL LOGS OF THE WEATHERED GRANITE (BOREHOLE 16)

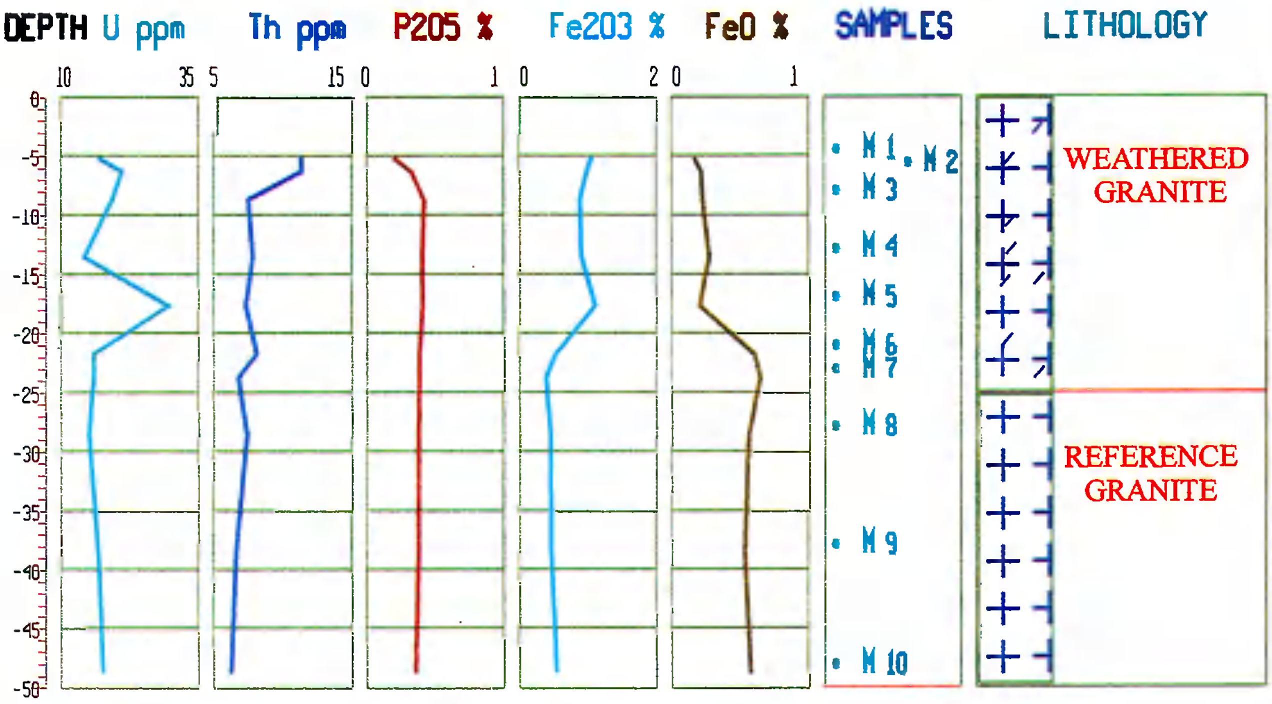


Figure 11

The Tono Natural Analogue Study Program

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INTRODUCTION

The Tono Natural Analogue Study has been performed in the Tono uranium mine located in the central Japan. An exploratory shaft were excavated and gallery has been extended at a depth of 130m since 1972. However, due mainly to the economical reasons there has been no commercial operation. Advantage of this mine as an analogue study site is its relatively undisturbed nature.

In 1986, PNC initiated in-situ geoscientific research program which involves the characterization of groundwater chemistry, hydrogeology and the natural analogue study of uranium transport and retardation processes in and around the mine (e.g. Yoshida,1994). The geoscientific research also includes regional hydrogeological investigations with the development of techniques for deep borehole testing which provides background information for the analogue study. PNC's Tono Geoscience Center (formerly called PNC Chubu Works) is the base for these research activities.

SITE DESCRIPTION

The Tono uranium deposit is hosted in Tertiary sedimentary sequences composed of conglomerate, sandstone and tuffaceous rocks deposited in palaeo-channels in the erosion surface of the basement granite (e.g. Doi et al.,1975) (Figure 1). The uranium mineralization occurs as a stratiform body with an averaging depth of 130 m. Dating by fission track method shows that the mineralization is estimated to be approximately 10^7 years old (Ochiai et al.,1989). The uranium mineralization occurs in a

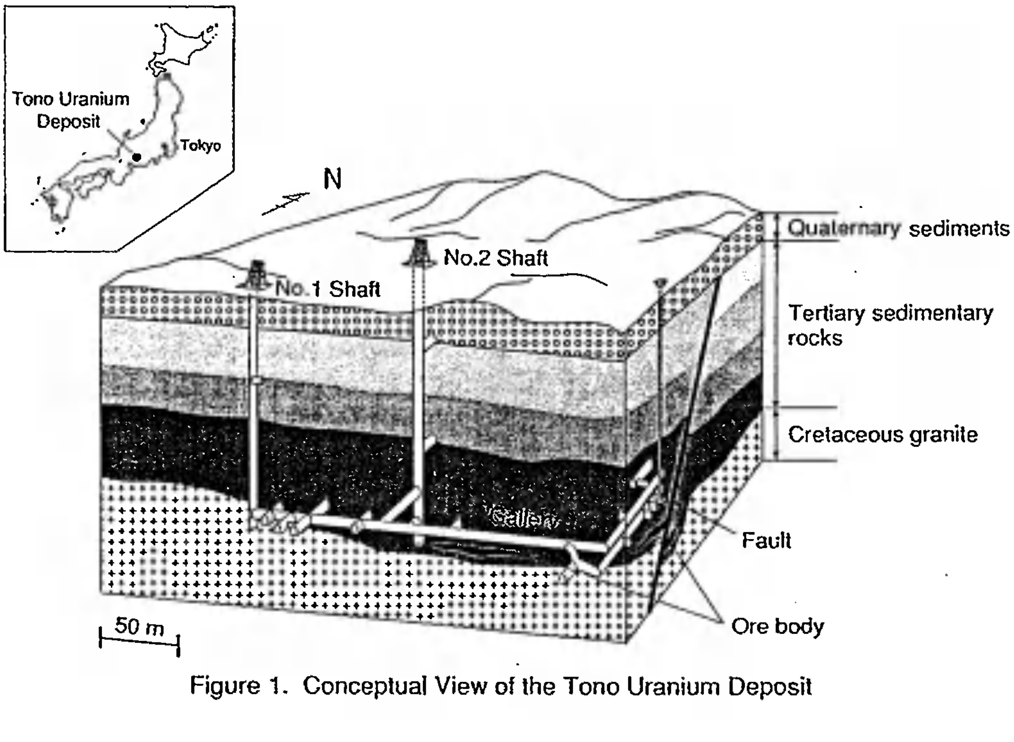

Figure 1. Conceptual View of the Tono Uranium Deposit

fluviolacustrine, lignite-bearing formation which was deposited on a granitic basement. Detrital carbonaceous materials and secondary minerals, such as pyrite and carbonate, are present in the lower part of the Tertiary sequence. The uranium mineralization occurs immediately above the unconformity over an area of several hundred meters wide, 2-3km long, and a few meters thick (Yamakawa,1991). The groundwater chemistry in the Tono uranium deposit is reported by Seo and Yoshida (1992). Groundwater samples were taken from the mineralized zone by a double-packer system in a borehole in the mineralized area of the deposit. The water samples were stored under N_2 atmosphere before transfer to the laboratory. Eh, pH and electric conductivity were measured in-situ by a monitoring system. The results are shown in Table 1.

Table 1. Physico-chemical Characteristics of the Groundwater from the Tono Uranium Deposit

Sampling level: -153 to -155 m								
Temperature	Eh	pH	DO	EC				
18.5°C	-300 mV	8.9 to 9.2	0.0ppb	168μS/cm				
Concentration (ppm)								
Si	Al	Fe^{2+}	Fe^{3+}	Mn^{2+}	Mg^{2+}	Ca^{2+}	Na^+	K^+
8.1	<0.02	<0.02	<0.02	<0.01	0.02	1.98	45	0.29
F^-	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	U (ppb)			
4.1	1.06	1.26	79	8.0	0.06 to 0.2			

DO; Dissolved oxygen EC; Electric conductivity

TONO NATURAL ANALOGUE STUDY

The main technical goals of the Tono Natural Analogue Study are:

- determination of trace-element solubility and speciation in reducing conditions, and testing geochemical thermodynamic databases.
- chraracterization of retardation properties of the sedimentary rock and testing nuclide migration model in a reducing environment.
- characterization of geochemical disturbances around the gallery caused by excavation.
- characterization of colloid species in groundwater and testing colloid transport model.

At present, the Tono Natural Analogue Study has four study areas in relation to the technical issues relevant to the performance assessment and will be conducted mostly within PNC's co-operative framework with Nagra (Swtizerland) and CEA (France).

(1) Solubility and speciation of trace elements in reducing conditions (PNC/Nagra)

PNC is developing a quality assured geochemical thermodynamic database (TDB) for performance assessment (PA). The Tono Natural Analogue Study offers an opportunity to test the PA-TDB relevant to simulated repository conditions.

A suite of safety relevant trace elements (such as U, Th, Pd, Sn, Ni, Co, Sr, Cs, Ra, Se and REE) will be examined in the ore-body and in the host sedimentary rocks and underlying granite. The study will be carried out in collaboration with Nagra. The procedure will be proceeded by the method of examination of the TDB being assessed with comparison of the predicted trace element concentrations and speciations with the field data.

(2) Retardation properties of the sedimentary rock (PNC/Nagra)

Uranium retardation in the sedimentary rock hosting the uranium deposit has been examined as a part of the Tono Natural Analogue Study (e.g. Yoshida, 1994). This work will be continued with the several new boreholes, both from the mine galleries and the surface. A detailed program of data aquisition from the new borehole is planned with the objective of testing a small-scale (area of meters) uranium transport model in the sedimentary rock. The study of regional retardation of uranium in the Tono area also will be considered as a large-scale (area of kilometers) program.

In the small-scale, the work will attempt to elucidate the retardation mechanisms more precisely within the rock matrix and in specific flow structures (sandstone channels, fracture system etc.) (Figure 2), while the study of large-scale will examine the long-term stability of the uranium ore-body under reducing conditions.

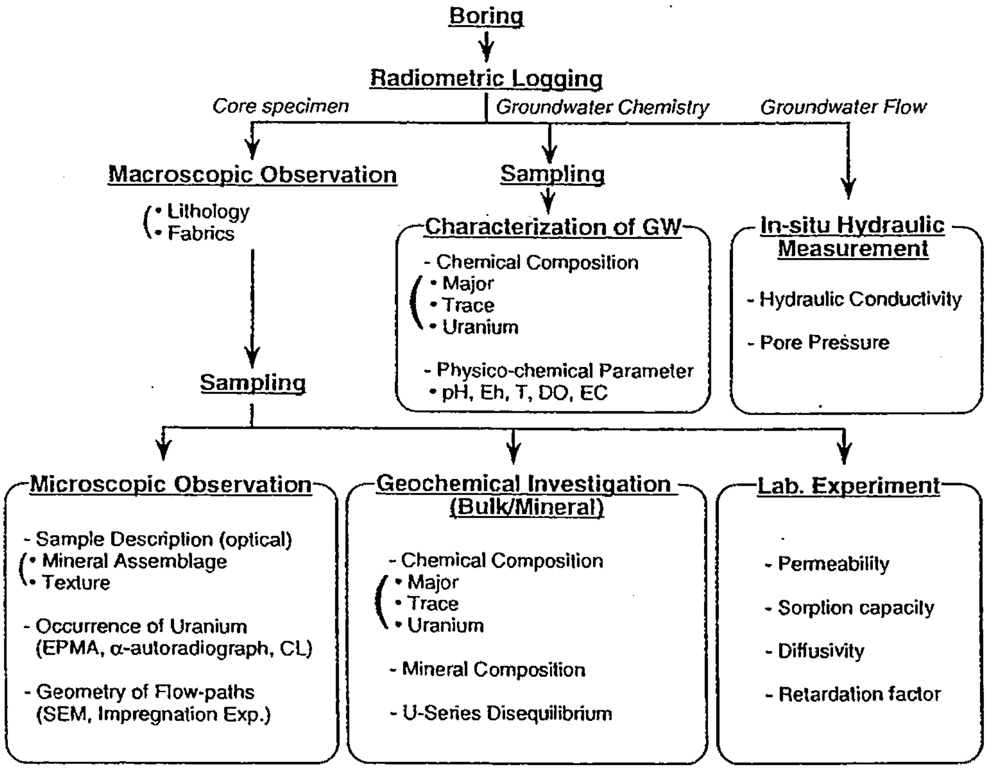

Figure 2. Investigation Procedure of Small-Scale Retardation Properties in the Sedimentary Rocks

(3) Characterization of geochemical disturbance around the gallery (PNC)

Two independent studies have been suggested in this item. One is to understand the geochemical disturbance by excavation of the rock surrounding the drift to support the evaluation of the perturbations to nuclide migration. The other is to characterize the buffering mechanism of specific mineral in the rock surrounding the drift. The Tono mine provide an appropriate analogue in this respect, owing to a relatively lower flux of groundwater.

(4) Characteristics and transport properties of colloids in reducing groundwater (PNC/CEA)

PNC and CEA have recently initiated an examination of the colloid population and its characteristics in the groundwater in the Tono mine. To date, samples have been taken from the ore-body in the mine. The work is planned to examine the samples from unmineralized zone in the Tono area. In addition, the attempt will be expanded to describe the migration behaviour of colloid with the appropriate transport models.

It is expected that the Tono Natural Analogue Study will provide an excellent opportunity to built our confidence in nuclide migration models and geochemical codes.

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European Commission

EUR 16761 — Sixth EC Natural Analogue Working Group Meeting
Proceedings of an international workshop held in Santa Fe, New Mexico, USA on 12-16 September 1994

H. von Maravic and J. Smellie (Editors)

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The six Natural Analogue Working Group meeting was held at Santa Fe, New Mexico, USA on 12-16 September 1994 and was jointly organized by the Los Alamos National Laboratory and the European Commission.

About 50 participants from 13 countries and international organizations (EC, IAEA) attended the meeting which was hosted by Los Alamos National Laboratory (USA) and co-sponsored by US-DOE, EC, LANL and US-NRC. Their support and cooperation are gratefully acknowledged.

The present proceedings include the scientific results of the 25 papers and some posters presented at the workshop which are devoted (i) to reviewing the present status of the various national NA programmes, (ii) to addressing the state of the art of several key issues in near-field and far-field processes and their importance to performance assessment (PA), (iii) to arrivving at a general consensus for each issue and (iv) to providing guidelines as to the future importance of each issue in NA studies and their eventual use in PA and public relations.

The members of the NAWG core group summarized the main conclusions from the workshop and issued a statement outlining the present status of NA studies and future direction of NAWG.

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