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Microbiology in nuclear waste disposal: interfaces and reaction fronts

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Abstract

It is now generally acknowledged that microbial populations will be present within nuclear waste repositories and that the consequences of such activity on repository performance must be assessed. Various modelling approaches – based either on mass balance/thermodynamics or on kinetics – have been developed to provide scoping estimates of the possible development of these populations. Past work has focused on particular areas of the repository which can be considered relatively homogeneous and hence can be represented by some kind of ‘box’ or ‘mixing tank’. In reality, however, waste repositories include a range of engineering materials (steel, concrete, etc.) which are emplaced at depth in a rock formation. Strong chemical gradients – of the type which may be exploited by lithoautotrophic microbial populations – are likely to be found at the contacts between different materials and at the interface between the engineered structures and the host rock. Over the long timescales considered, solute transport processes will cause the locations of strong chemical gradients to move, forming reaction fronts. The high-pH plume resulting from the leaching of cement/concrete in some repository types is a particularly important example of such a reaction front. Redox fronts, which may occur in different areas of all kinds of repositories, also play an important role and would be locations where microbial activity is likely to be significant. In this paper, the key microbial processes expected at (or around) interfaces and fronts will be discussed, with particular emphasis on the development of quantitative models. The applicability of the models used will be tested by considering similar fronts which can be found in natural systems.

Keywords: Nuclear waste; Biodegradation; Energetics; Microbial population

Contents

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1. Introduction

The safety of deep repositories for nuclear waste needs to be demonstrated for very long periods of time. For high-level waste (HLW), in particular, massive engineered barriers have been designed which, in an appropriate geological setting, should provide the required assurance of safety. Confidence in such disposal concepts is based on extensive performance assessment – evaluating how geological, hydrological, physical, chemical, thermal and mechanical processes will influence the system. It is implicitly recognised that many relevant processes may actually be catalysed or otherwise influenced by microbial activity. Nevertheless, when explicitly studying the consequences of microbiological processes, they are generally regarded as perturbations on the 'reference' evolution scenario, ideally shown to be insignificant relative to abiological processes. Defining the constraints on microbial activity is, however, a rather tricky problem.

Initial hopes that the environment of a nuclear waste repository would be too harsh for microbial life were dashed at a fairly early stage for both low- and intermediate-level waste (L/ILW) [1–3] and HLW [4–6]. In the interim, not only have many more studies confirmed and extended this early work, but an entire branch of study of 'extremophiles' has evolved [7]. Similarly, assumptions that autochthonous microbial populations would not exist at depth were disproven by studies of rocks under investigation in national repository programmes [8,9]. Again, over the last decade, the study of deep subsurface microbiology has developed into a significant area of study and, indeed, is the focus of the International Sub-Surface Microbiology (ISSM) symposium series.

An alternative approach to determine the constraints on microbial growth involved mathematical modelling of the limitations set by available substrates for growth in the extremely oligotrophic environment of the deep subsurface. Two main types of modelling approach have been applied to repository systems – one involving a mass balance/chemical thermodynamic approach [10,11] and the other involving a more fundamental analyses of the kinetics of microbial growth [12]. The former approach seemed to have the advantages of simplicity and conservatism (even if not strictly correct, it should
predict microbial activity levels). A decade ag
naively assumed that we could reasonably well
the bioavailability of essential elements and
useable energy sources for microbial growth. I
interim, the ingenuity of lithotrophic organism
been demonstrated to be much greater than we
dreamed (see, for example, papers in this issue
15]).

This paper examines the principles of the
balance/thermodynamic modelling approach an
lustrates its application for the Swiss HLW rep
tory concept. The development of the simple m
to allow consideration of microbial activity at r
tion fronts is also discussed for the particular c
of redox fronts from HLW and high-pH fronts f
L/ILW.

2. Principles of the modelling approach

The deep geological formations selected as pote
tial hosts for nuclear waste repositories tend to
characterised by their tectonic stability, very lo
fluxes of groundwater and, generally, chemically r
ducing conditions. They also tend to be extreme
oligotrophic and the expected levels of microbial a
tivity would be very low. The maximum activity po
sible will be established either due to the availabili
of essential elements or useable energy. Both of thes
constraints can be quantified – the former by a sim
ple mass balance and the latter by use of a chemica
thermodynamic approach.

The elemental mass balance currently considers only major elements essential for cell growth – C, N, S and P. For the 'wet' rocks considered here, availability of water would not be a limiting factor and elements such as Na, K, Ca and Cl are relatively freely available. Growth limitation due to availability of essential trace elements (e.g., Se, V, etc.) has not been examined directly, but is considered unlikely.

The mass balance considers two sources of supply, groundwater and degradation of repository materials. Generally, the flux in groundwater can be considered to be constant for very long periods in the stable environments selected for nuclear waste disposal, but material degradation will tend to be a rather complex function of time. Fluxes of the ele-

Table 1
Conversion factors for mass balance calculations[a]

a	Microbial composition (dry weight)	$C_{160}(H_{280}O_{80})N_{30}P_2S$
b	Water content	99% by weight
c	Average microbial volume	1.5×10^{-13} ml

[a] Values used in past studies [10,35,37,38]. Considerable variation may, however, be expected in specific environments depending on the microbes present and their nutritional status. For example, the water content and volume of *E. coli* are reported as 70% and 9.5×10^{-13} ml, respectively [24].

ments considered can be put in context by considering their relative molar concentration in a typical organism (e.g., C:N:P:S ~160:30:2:1; [16]) which allows the element which is potentially limiting to be identified. The composition of organisms may vary significantly depending on type and nutritional state. The variation in the ratio of particular elements is, however, expected to be small relative to other uncertainties in the calculational procedure. The limiting element flux (mol year^{-1}) can be converted into other units using the conversion factors shown in Table 1.

These conversion factors are very simplistic values which can be used for scoping calculations; they should be reassessed for relevance to more specific applications.

The evaluation of available energy for the organisms which form the base for microbial communities established in such environments is somewhat more difficult. The approach adopted has been based on the assumption that all useable energy is derived from redox processes (cf. [17]; the few exceptions of ADP phosphorylation driven by catabolic reactions of organic substrates are ignored, but this might need reconsideration for wastes with high organic contents). The first stage of the energetics assessment is thus to list the inventories and fluxes of all redox active substrates in the system considered. From such a list, redox half-reactions can be associated with free energies of reaction and redox pairs selected which maximise energy production [18–20]. In principle, such an approach is only applicable when the concentration of all reactants are known, but a fair approximation can be obtained by ignoring the concentration term for all reactants except the proton (cf. [20]; Section 2.3 of Chapter 7 for further discussion of such approximations). The importance of the concentration of protons in the determination of energetics is illustrated in Fig. 1 which shows the variation in free energy of reaction of selected redox couples with pH. For this limited set of reactants, it can be seen that O_2 is the strongest potential oxidant but the most favourable reductant is elemental Fe at very low pH, pyrite (FeS_2) at intermediate pH values and Fe^{2+} under alkaline conditions.

Fig. 1 plots free energy of the redox half-reaction normalised to production or consumption of one electron and hence the free energy produced per electron transferred can be read off the plot directly for a given redox pair and pH. For very low free energy production values, the question arises of whether this can actually be utilised for microbial activities or if a minimum 'energy quantum' exists. Although a potential limitation on energy utilisation has been considered to be the free energy needed to drive ATP production from ADP (~45 kJ mol^{-1} under in vivo conditions), Thauer and Morris [21] have shown that chemotrophic anaerobes utilise reactions producing only about a third of this free energy per mol of substrate. For the purposes of the current models, therefore, a limit on useable energy is taken to be 15 kJ per mol of electrons transferred. Formally, the free energy of exoenergetic reactions is taken to be

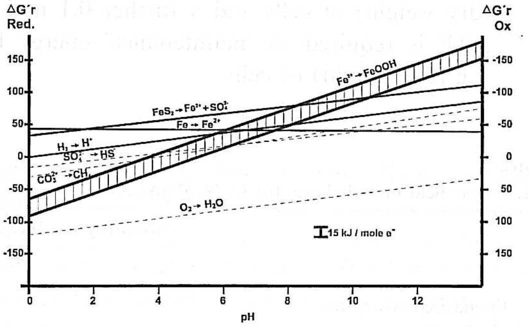

Fig. 1. Diagrammatic illustration of the variation of the free energy of potential oxidation and reduction half-reactions as a function of pH. The reductions (dashed lines) refer to the scale on the left side while the oxidations (solid lines) relate to the right hand scale. Note that the reactions are not balanced, the differences in $\Delta G_r'$ are exaggerated to separate the sulfate and carbonate reduction lines and that the effect of deprotonation as a function of pH (e.g., $H_2CO_3 \rightarrow HCO_3^- \rightarrow CO_3^{2-}$ is not illustrated). The shaded zone illustrates the range in FeOOH data resulting from varying assumptions about the crystallinity of this phase.

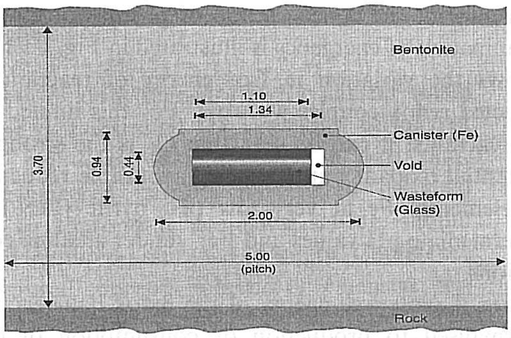

Fig. 2. HWL emplacement geometry (dimensions in metres [25]).

negative. As this paper focuses on formally reversible reactions, however, it is more convenient to simply specify the magnitude of free energy of reaction unless a specific reaction direction is noted. Such a low value is consistent with reactions attributed to methanogens using either H_2 and CO_2 or Fe and CO_2 (~17–17.5 kJ mol electrons^{-1} at pH 7 [22]).

The energy requirements for synthesis and maintenance of microbial cells are difficult to specify, especially for the very low rates of growth expected in extremely oligotrophic environments. From the paper of Thauer et al. [17] the following average data are derived:

1. 0.1 mol of ATP is required to synthesise 1 g (dry weight) of cells and a further 0.1 mol of ATP is required as 'maintenance' energy for 1 g (dry weight) of cells
2. Microbial production of ATP from ADP quires 45 kJ mol^{-1} (under in vivo conditio for anaerobic bacteria; N.B.: a lower value 32 kJ mol^{-1} was used in some of our earl studies)
3. The efficiency of microbial utilisation of che ical reactions is 10% (considered in [17] to a maximum value for all material synthesis)

i.e., production and maintenance of 1 g (dry) of ce requires 90 kJ. This simple conversion allows a estimate of microbial constraints on growth. F more detailed analysis, the effect of low energy su ply rates (starvation conditions) and the ener needs for maintenance of very slowly growing ce need to be considered (cf. [23]).

3. The Swiss concept for HLW disposal in crystalline rock

The near field of the planned Swiss HLW repo tory is rather simple (Fig. 2) and consists of thr main components – vitrified high-level waste fro reprocessing of spent fuel, a massive cast steel ove pack and a surrounding backfill of compacted be tonite clay [25]. Each single waste package compris about 400 kg of waste-containing glass, surround by 8000 kg of steel canister and about 100 000 kg bentonite. For planned disposal at a depth of ~1 k below surface, water flow rates are very low a

Table 2
HLW near field mass balance for C, N, P and S

		Inventory (mol)/package				Corrosion rate (year^{-1})
		C	N	P	S	
a	Engineered structures					
	HLW: Borosilicate glass	–	–	17	–	10^{-5}
	Steel canister	1×10^3	–	85	90	10^{-4}
	Bentonite:					
	inorganic components	2×10^4	3×10^3	3×10^3	4×10^3	10^{-6}
	organic components	2×10^4	4×10^3	3×10^2	1×10^2	10^{-3} (10^{-6})
	trapped air	1	3×10^3	–	–	–
b	Groundwater					
	Annual input	5×10^{-3}	2×10^{-6}	1×10^{-6}	3×10^{-3}	–
	Integrated input over 10^6 years	5×10^3	2	1	3×10^3	–

Table 3
Key redox active species in the near field of a Swiss HLW repository (time periods are specified in years after repository closure)

Vitrified waste	Inventory (mol)	Time period (years)	Comments
Fe(III)	147	10^3–10^5	Oxidants made available by the slow corrosion of glass (10^{-5} year^{-1}) after canister failure (at 10^3 years after emplacement)
U(VI)	8	10^3–10^5	
Np(V)	2.4	10^3–10^5	
Canister			
Fe°	1.5×10^5	0 –10^4	Canister corrosion initially assumed to be Fe(O) → Fe(II); all Fe(O) consumed in 10^4 years and replaced by Fe(II)
Fe(II)	1.5×10^5	10^4 →	
Bentonite			
FeS_2	2.2×10^3	0 →	All trapped air assumed consumed within 10 years; siderite ($FeCO_3$) is present but is considered less likely to react with free oxidants than pyrite (FeS_2)
'CH_2O'	1.2×10^4	0 →	
trapped O_2	3.8×10^3	0 –10	
$FeCO_3$	5.4×10^3	0 →	
Groundwater			
HCO_3^-	$5\ \times10^3$	0 –10^6	Integrated supply over 10^6 years
SO_4^{2-}	$5\ \times10^3$	0 –10^6	
Radiolysis			
H_2O_2	3.8×10^2	10^3–10^6	Radiolysis only effective after canister failure; integrated production over 10^6 years
H_2	3.8×10^2	10^3–10^6	
Key redox pairs for particular time periods		Reductant	Oxidant
1–10 years		$FeS_2/Fe/Fe^{2+}$	O_2
10–10^3 years		$FeS_2/Fe/Fe^{2+}$	SO_4^{2-}/CO_3^{2-}
10^3–10^5 years		FeS_2/Fe^{2+}	H_2O_2/SO_4^{2-}/Fe(III)
10^5–10^6 years		FeS_2/Fe^{2+}	H_2O_2/SO_4^{2-}

correspond to about 1 litre year^{-1} past each waste package.

The key data required for the mass balance of C, N, S and P are listed in Table 2. In addition to the inventory of each element in materials, supply rates are given which are set by corrosion rates. These corrosion rates are measured in systems which are not sterile and hence include both inorganic and microbially catalysed components. It is clear from this data set that the near field is dominated by the bentonite which contains large quantities of these key elements. The rate at which elements become available is given by a simple linear corrosion (or degradation) rate – taken to be 1 part in 10^6 per year for the inorganic components of bentonite and 1 ‰ per year for organic carbon present. These corrosion rates give rise to steady state biomass production rates of 300 g (dry) year^{-1} for the first 10^3 years and ~0.4 g (dry) year^{-1} thereafter for each waste package (considered as a homogeneous system). In fact, the corrosion rate for the organics is probably extremely conservative as residual organic carbon in the purified backfill is likely to be very refractory. A more realistic corrosion rate of 10^{-6} year^{-1} would allow a continuous biomass production of ~0.7 g (dry) year^{-1} per package for the entire 10^6 year period of interest.

The repository near field, like the surrounding geological environment (the far field), is characterised by large inventories of potential reductants

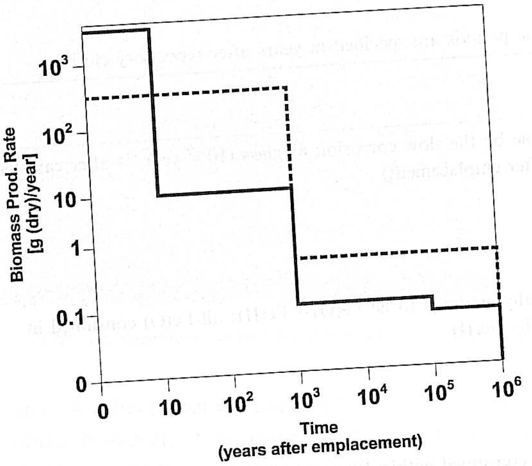

Fig. 3. Biomass production as a function of time: as set by energy constraints (solid line) and supply of key elements (broken line).

and hence the rates of redox reactions are set by the rate of supply of oxidants or their kinetics of reaction. The main 'electron donation half-reactions' involve Fe (from the steel canister), pyrite (from bentonite) and organic carbon (from both bentonite and groundwater). Obvious electron acceptors are O_2 (from an initial inventory of trapped air), CO_2/HCO_3^- (from trapped air, bentonite and groundwater) and SO_4^{2-} from groundwater. Unlike surface waters, concentrations of electron acceptors like Fe^{3+} and NO_3^- are negligible in most deep groundwaters.

In principle, water can also be considered to be an electron acceptor, because iron corrosion yielding both hydrogen and a range of iron oxyhydroxide solid phases is thermodynamically favourable. Direct microbial use of metallic iron as an electron acceptor has been demonstrated for methanogenesis with CO_2 as a source of C, but it appears that microbial coupling of Fe oxidation with the reduction of water is unlikely (cf. [22] and discussion in the following section).

As the vitrified waste is produced under oxidising conditions, it is also a source of oxidants (with inventories of Fe(III), U(VI) etc.). Radiolysis of water produces a mixture of oxidants and reductants which could also serve as a further source of microbially utilisable energy. The inventories and rates of supply of oxidants and reductants are summarised in Table 3. The optimisation of energy production for the given reactants can be evaluated by graphing the free energy of all potential oxidation/reduction half-reactions or by a linear programming optimisation method.

Maximum energy production from these reactants, converted into terms of resultant biomass, is plotted as a function of time in Fig. 3. Apart from the very short period in which trapped air is available, these calculated biomass production rates are much less than those evaluated on the basis of key element availability and hence, in this environment, populations are predicted to be constrained by energy availability.

As discussed in detail elsewhere (e.g., Refs. [4,10]), microbial populations could potentially affect several aspects of repository performance – by enhancing corrosion, producing gaseous or acidic by-products, taking up radionuclides, etc. Of most concern, in

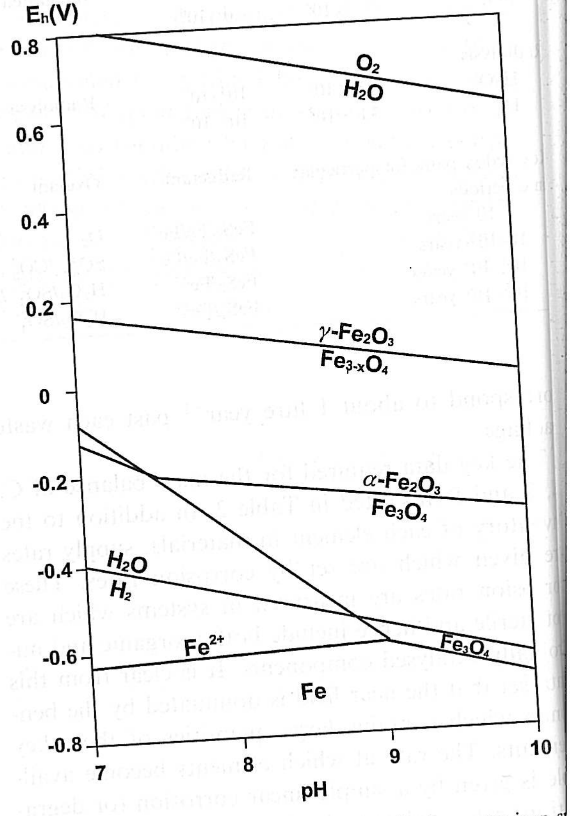

Fig. 4. E_h/pH plot ('Pourbaix diagram') indicating some iron species relevant to assessing HLW canister corrosion.

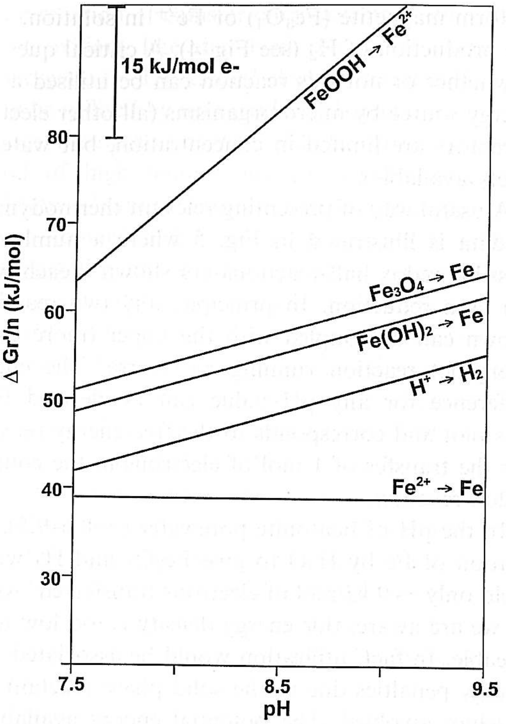

Fig. 5. Some relevant redox half-reactions for a Swiss HLW repository (in all cases calculated for reactions in the form of a reduction involving one electron).

terms of maximum detriment to barrier performance, is the production of soluble organic by-products which may complex radionuclides and enhance their solubility while also increasing their mobility (by decreasing the extent to which they are absorbed).

For steady state biomass production in the order of 10^{-2} g (dry) year^{-1} per waste package, the potential of this source of organic carbon is clearly large when compared to groundwater supply rates $\sim 10^{-5}$ g year^{-1} but small compared to the $\sim 10^5$ g of 'refractory organic carbon' contained in the bentonite. In order to assess the consequences of the production of such organic carbon, it is critical to assess the size distribution of the organics produced. As it has a microporous structure, and its plasticity/swelling pressure precludes persistence of open fractures or fabrication gaps, compacted bentonite will act as a very effective filter for species larger than a few nm in diameter [25–27] – equivalent to molecular masses in the order of a few hundreds or thousands of daltons. The complexing ability for radionuclides is observed to be generally higher for larger size organics of the humate type [28] which would be immobile in bentonite (MW $\sim 10^4$–10^7 Da).

As a worst possible case, it could be assumed that the steady state biomass production of 10^{-2} g year^{-1} is matched by an equivalent loss of 10^{-2} g of organics with an average MW of 10^3 Da – corresponding to a typical size for siderophores which are extremely strong, specific complexants for some radionuclides [28,29]. This production rate ($\sim 10^{-5}$ mol year^{-1}) is roughly equivalent to the integral, solubility-limited release rate of actinides from the waste glass and thus even the pessimistic assumption that all organics complexed only with actinides would only approximately double the maximum release rate. Such an increase is small relative to the large safety margins for this repository [25]. This worst case is, of course, likely to be over-pessimistic by orders of magnitude as:

1. the calculated standing biomass is a maximum value, assuming all available energy is used by micro-organisms
2. all biomass production is assumed balanced by organic carbon loss; in reality, carbon is expected to be efficiently recycled in such an oligotrophic environment
3. all organic carbon loss is assumed to be highly mobile; in reality, only a fraction of the by-products which are not recycled would have MW $< \sim 10^3$ Da and organics larger than this size would be immobile and could thus have a net positive effect in retarding elemental transport
4. mobile organic carbon is assumed to be highly complexing; very specific complexants such as siderophores are usually produced to sequester trace elements which are relatively unavailable – in particular Fe under oxic conditions. In this particular case, Fe is likely to be available in large quantities and production of such complexants is unlikely. Even though organic products such as citrate and gluconate form strong complexes with some important radionuclides, they are non-specific and their competition with inorganic species present at much higher concentrations (e.g., CO_3^{2-}) would be limited

5. all organic complexant is assumed to solubilise the most toxic components of the waste; in reality, there will be competition with other metals present in much larger concentrations (particularly Fe).

Taking all these points together, the net consequences of microbial activity in terms of complexant production can be safely taken to be negligible. This is in agreement with field observations in soil, where siderophore concentrations ~μM level are found only where very high microbial activities exist, ~nM concentrations are more reasonable for oligotrophic environments [29].

4. Redox fronts in the HLW repository near field

The analysis illustrated above involves the assumption that the near field is homogeneous and can be represented as a mixing tank. To examine likely microbial activity in a more realistic manner, interfaces between materials and gradients in chemistry need to be considered in more detail. The Swiss HLW case is relatively simple in that pH would be in the alkaline region (~7.5–9.5) throughout the engineered barriers. Redox conditions are harder to define rigorously – in low temperature systems Eh must be regarded as a convenient indication of some simple redox couples (e.g., Fe(II)/Fe(III)) and not a fundamental system parameter.

After repository closure, trapped air will be present in the repository, but oxygen will be quickly consumed by oxidation of the steel canister. This oxidation reaction will take place at the surface of the canister which will have a temperature of ~160°C and be effectively dry (no liquid water, but water vapour will be present). The likelihood that energy produced is directly useable by microbes is thus extremely low. At a later stage, any Fe(III) formed during this oxic phase may subsequently act as an oxidant but, as is clear from Fig. 1, the energy available will be very much lower.

Thereafter the near field will be generally reducing but the canister can be considered to be a geochemical anomaly as it is unstable with regard to oxidation by water. Although known to be kinetically slow, in the expected pH range iron should corrode to form magnetite (Fe_3O_4) or Fe^{2+} in solution, with the production of H_2 (see Fig. 4). A critical question is whether or not this reaction can be utilised as an energy source by micro-organisms (all other electron acceptors are limited in concentration, but water is freely available).

A useful way of presenting relevant thermodynamic data is illustrated in Fig. 5 where a number of possible redox half-reactions are shown – each written as a reduction. In principle, any two reactions shown can be coupled with the upper (more endoenergetic) reaction running in reverse. The energy difference for any pH value can be derived from this plot and corresponds to the free energy released for the transfer of 1 mol of electrons in the coupled redox reaction.

In the pH of bentonite porewater (~8.6–9.5), oxidation of Fe by H_2O to give Fe_3O_4 and H_2 would yield only ~9 kJ/mol of electrons transferred. As far as we are aware, this energy density is too low to be useable. In fact, utilisation would be associated with energy penalties due to the solid phase reactant and product involved. The potential energy available if methanogenesis is coupled to Fe oxidation is significantly larger (~18 kJ/mol) and that with sulfate as electron acceptor is larger still (~28 kJ/mol). Under these circumstances it seems reasonable to expect that methanogens and SRBs would be likely candidates for colonising the surface of the corroding canister [14,22]. In this case, an effective redox front exists at the canister surface and the rate of reaction is constrained by the diffusive supply rate of HCO_3^- and SO_4^{2-}. If necessary, such fluxes could be calculated but, in any case, they will be below the limiting values of supply assumed in the homogeneous model.

A more dramatic redox front develops when th canister eventually fails and water contacts the vitrified waste. The waste acts as a supply of oxidants a it dissolves (most contained radionuclides are in full oxidised form). In addition, radiolysis of water pr duces H_2 and equivalent quantities of 'oxidant' (us ally represented as H_2O_2 or dissolved oxygen). D to the kinetic hindrance of H_2 oxidation, the ar within the canister will become effectively oxidisi and a redox front will develop within the canist corrosion products as oxidants begin to diffuse o wards.

The reaction of canister corrosion products with a strong oxidant like dissolved oxygen is extremely exoenergetic (~150 kJ/mol electrons) and could certainly be utilised by iron oxidising bacteria as long as any aerobic organisms were able to survive the long period of high temperature (55–100°C) anaerobic conditions before canister failure. Indeed, even though somewhat less exoenergetic (~120 kJ/mol electrons) the microbially catalysed recombination of hydrogen and oxygen may well be expected – especially as hydrogen oxidising bacteria have been reported in deep sediments [30]. If oxidants are not consumed within the corroding canister, oxidation of pyrite and siderite in the bentonite could also occur.

It may be expected that the gross effect of microbial activity would be to catalyse the redox reactions which limit the rate of movement of the oxidising front. On a smaller scale, it is of particular interest to quantify the effects of such microbial growth on the mobility of radionuclides released from the waste as oxidised species (e.g., U as UO_2^{2+}, Np as NpO_2^{+}, Se as SeO_4^{2-}).

Using either Fe^{2+} or H_2 as a source of electrons, the reduction of these species would be exoenergetic, but their concentrations are so low that it is not expected that they would each show a distinct geomicrobiology. Rather they are more likely to follow the reactions of 'carrier' elements which are present in higher concentrations. The reduction of U(VI) by dissimilatory Fe(III) reducing micro-organisms is well established [31] and it is likely that Np(V) and other high-oxidation state actinides will follow U. Similarly, Se is known to follow S in biochemical cycles [32,33] and can be reduced by some SRBs. Other trace elements reductions are likely to be similarly catalysed. The reduction of such elements is generally associated with a considerable decrease in solubility and hence secondary phases may form. These are unlikely to be pure phases, but rather polymetallic mineralisations, as often seen associated with micro-organisms [34].

The overall picture emerging is that the worst case analysis of the homogeneous near field is likely to be extremely pessimistic. Not only are total microbial populations likely to be somewhat lower than estimated, but also such organisms will be closely associated with the source of chemical energy which is localised at a sharp redox front. Microbial catalysis of redox reaction will ensure that radionuclide mobility is generally low, microbes may directly participate in the immobilisation of radionuclides in secondary minerals formed at the redox front. The net role of micro-organisms in immobilising trace elements at redox fronts is, indeed, strongly supported by observations from natural analogues (such as Poços de Caldas [35], Redox halos [36]).

5. The high-pH fronts from a L/ILW repository

Repositories for L/ILW are inherently more complex than those for HLW due to the much greater heterogeneity of the waste and engineered barrier materials in the former. Nevertheless, the same basic mass-balance/thermodynamic approach can be applied to a homogenised mix of the main components to evaluate the global constraints on microbial growth. This has been documented elsewhere [37,38] and shows that potentially significant activity levels of microbes cannot be precluded. In order to develop a more realistic appraisal of this type of repository, therefore, it is again useful to consider the true heterogeneities in further detail. For the purpose of this paper, we focus on the 'far field' of host rock surrounding the engineered barriers. As indicated for the HLW case, detailed study of the materials interfaces within the engineered barriers may also be very instructive in this case.

A significant feature of repository designs for L/ILW is the large quantities of cement and concrete used in the engineered barriers. A consequence of this is that the near field will be characterised by hyperalkaline conditions, which will persist for thousands to hundreds of thousands of years. Radionuclides released from the repository will migrate in a 'high-pH plume'. Particular challenges for microbiologists are determining if microbial populations are to be expected within such a high-pH plume [39], whether such populations could significantly influence the structure or rate of movement of such a plume and if micro-organisms might affect radionuclide migration in this case.

Initially, the leachate from cement/concrete will have a pH ~12–13 due to the high concentration of Na/K hydroxides. This contrasts markedly with the surrounding groundwater which has pH values in the range of ~7.5–8.5. The hyperalkaline leachate is unstable in contact with the minerals of the host rock and will tend to be buffered by mineral alteration reactions (e.g., dissolution of rock-forming silicates and precipitation of C-S-H gels and, eventually, zeolites). Although exoenergetic, these reactions do not involve electron transfers and, to the best of our knowledge, cannot be utilised by lithotrophic micro-organisms as an energy source. Microbes can certainly use energy to establish pH gradients over membranes and biofilms, but it is impossible by chemiosmotic mechanisms to generate energy from a pH gradient when the surrounding pH is more alkaline than the intracellular pH and thus to obtain energy from a pH contrast between two groundwaters (R. Bachofen, personal communication). As this is a critical question in assessing the possible significance of microbial activity at such fronts, various mechanisms which could, indirectly, lead to redox reactions associated with the pH front have been considered.

Microbial cycling of Fe at redox fronts provides hints about how such an energy source may be utilised. Such cycling can be explained in terms of the differential solubility of the ferrous and ferric hydroxides. Although the thermodynamic data are rather uncertain for reducing hyperalkaline conditions, magnetite would be expected as the solubility-limiting phase for conditions at both sides of the high-pH front. This is based on a simple consideration of oxides and hydroxides only. Other important minerals in the natural system (e.g., siderite) might affect such conclusions. The solubility of Fe is, however, markedly different – calculated to be $\sim 10^{-4}$ M at pH 8 but 10^{-11} M at pH 12. This large concentration gradient would, for a slowly moving front, encourage diffusion of Fe^{2+} over the front. In this idealised front, magnetite (Fe_3O_4) could precipitate on the high-pH side with the half-reaction:

$$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^-$$

$$\Delta G_r \simeq -187.5 \text{ kJ/mol electrons at pH 12}$$

Microbial involvement in reactions involving magnetite formation are well known [40]. This half-reaction could be coupled to the $CO_3^{2-} \rightarrow CH_4$ reaction to give a net balance of ~131 kJ/mol electrons transferred – well above the minimum utilisable by methanogens. In fact even the utilisation of water as an electron acceptor with associated H_2 production would be energetically favourable in this situation ($\Delta G_r = 119$ kJ/mol electrons at pH 12).

This simple calculation assumes that a source of dissolved Fe^{2+} is available on the low pH side of the front – dissolution of ferrous minerals to supply such Fe^{2+} would be associated with a reduction of the net available energy. In fact, if the rate of front movement is slow relative to diffusion, direct mineral alterations may occur (e.g., siderite → magnetite) which may be microbially catalysed although it is difficult to assess how much of the free energy involved in such a solid phase transition would be accessible to the microbes.

The feasibility of such general reactions is supported by observations of the evolution of H_2 from natural hyperalkaline systems [41]. It is not clear whether microbial mediation occurs in this system, but this could certainly be explored in natural analogue systems by looking for evidence of microbial populations at sharp pH fronts associated with magnetite precipitation.

6. Conclusions and recommendations

This paper has illustrated a simple model which is used to evaluate the maximum consequences of microbial populations in a nuclear waste repository. Even for a simple homogenised representation of a HLW repository, such an approach indicates that such effects are negligible. Nevertheless, a better representation of the interfaces and heterogeneities involved gives a more realistic evaluation of possible microbial perturbations which indicates that the net effect of such populations may be positive, leading to decreased radionuclide releases. The critical assumption, however, is that microbes cannot utilise the very low energy density of the reaction between steel and water. However, they can use steel or the H_2 produced by inorganic corrosion in the presence of appropriate electron acceptors like sulfate or carbonate.

The situation with respect to L/ILW is more complex. This paper has focused on the high-pH front which may penetrate the rock surrounding such waste. The key question identified involves the extent to which microbes can utilise the chemical energy associated with such a front. A first evaluation of possible reactions which may be utilised by microorganisms under such conditions is presented but the approach is very simple and should be tested against observations from laboratory studies or natural hyperalkaline systems before further effort is invested in analysing consequences of such activity on repository performance.

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