## *The Mina Fe uranium deposit (Spain)*

***Description:*** Mina Fe is the most important uranium deposit in the Spanish Iberian Massif and it is located about 10 Km NW of Salamanca (Figure 1). It is hosted in highly fractured schistose rocks. The U mineralisation either fills open fractures or cements the fault breccia in the black slates of the Upper Proterozoic-Lower Cambrian Schist-Graywacke Complex, known as "Complejo Esquisto-Grauváquico (CGE). The U mineralisation has been intensively eroded and oxidised, as well as overlaid in places with sediments. Numerous secondary U minerals were also formed as a result of the weathering processes.

The analogies with key alteration processes that could be involved in repository evolution, suggested the study of this U deposit as a natural analogue. Thus, the uranium mineralisation at Mina Fe has been the subject of a research project (MATRIX project).

The main conclusions derived from the study of the "Mina Fe" U-deposit were:

Mineralogy and geochemistry of fracture fillings

The study of the primary and secondary fracture filling minerals have allowed us to establish the following vertical zoning in agreement with the pH/Eh conditions under which the minerals were formed: i) an upper oxidised zone, with the lower limit around 18 $\pm$ 2 m depth, ii) the transition redox zone, with a lower limit at 50 m depth, and iii) the reduced zone below about 50 m depth.

The oxidised zone shows a large abundance of Fe(III) and Mn-Fe oxyhydroxides, sometimes including Mn-Al-Ni and Mn-Pb oxides. The Fe(III) oxyhydroxides contain significant amounts of Ti, Cu, Zn, with lesser concentration of Cr, U and P. The Mn-Fe oxyhydroxides have variable amounts of Co, Ni and Ba. All these metals are at trace level. Other mineral phases that indicate acidic conditions are jarosite, a double sulphate of Fe(III) and K, allophane (amorphous $SiO_2.Al_2O_3.nH_2O$) and kaolinite. This zone also contains some secondary mineral phases formed at neutral pH, such as cerium oxides, Ce phosphates, La-Nd phosphates, autunite (Ca, and U(VI) phosphate) and rhodochrosite (Mn carbonate). Halloysite and/or metahalloysite and smectite are sometimes frequent in the oxidised zone.

The transition redox zone is characterised by a mineral mixture formed by the: i) primary phases, which originally filled the fractures; ii) mineral phases above described characteristic of the oxidised zone; and iii) secondary phases, which are the result either of the transition pH and Eh conditions, or the partial or total transformation of the primary minerals.

The primary minerals are: quartz, sulphides (molibdenite, pyrite, chalcopyrite, sphalerite and galena), lead selenides (clausthalite), carbonates (mainly ankerite, dolomite and calcite) and U(IV)/(VI)-oxides (pitchblende).

The secondary minerals formed as a result of changes in redox and alkalinity conditions are secondary Cu sulphides (covellite-chalcocite), undetermined Cu-Fe, Cu-Ag-Fe, Pb-Cu-Fe, and Fe-Sn sulphides, Fe-Cu sulphoselenides, and Ag-Pb-Fe selenides. These are clearly representative of the slightly reducing environment. Elemental Se or selenolite indicates slightly oxidising conditions, while uranium (VI) hydroxides coprecipitated with Fe(III) oxyhydroxides are more representative of oxidised and slightly acidic conditions (pH>4.2). Gypsum, barite, and clay minerals, such as smectite and corrensite, indicate neutral or slightly alkaline environment. Among the phases that are the result of the total or partial transformation of the primary minerals we find partially coffinitised pitchblende and pitchblende partially transformed to zippeite (poorly soluble uranyl sulphate). In addition, secondary siderite has been formed at expenses of ankerite at low temperature (T<25ºC) by ferrous metasomatism. Iron (III) and Zn oxyhydroxides are the result of the partial oxidation of sphalerite-marmatite and pyrite, and therefore closely related to these primary sulphides.

From the geochemical point of view, the transition zone is enriched in Fe, Cu, Ag, Ni, Zn, Se and U, as expected from the supergenic enrichment zones.

All these mineralogical and geochemical characteristics are consistent with neutral to slightly alkaline and intermediate redox conditions.

The reduced zone is characterised by the presence of the primary mineral association previously described. As a consequence, the physico-chemical conditions of this zone are reducing and slightly alkaline since pitchblende, sulphides and carbonates are stable.

The scavenger role of fracture fillings

In order to know the sinks of some elements, such as U, Ce, La and Ni, the results obtained from the application of an appropriate 7 step sequential leaching method to the fracture fillings can be summarised as follows: in the oxidised Fe-rich fracture fillings from "Mina D", U is mainly retained as U-minerals, mainly oxides, closely associated with crystalline Fe-oxyhydroxides. Though Ce and La also form independent minerals or "mineraloids" such as Ce oxides and La-Nd phosphates, they are mainly retained by amorphous Mn-oxyhydroxides. However, the crystalline Mn-oxyhydroxides are the main sink for Ni, and crystalline Fe-oxyhydroxides mainly retain phosphorous.

Time scale of the recent and recent-past up-takes and losses of U in the system

U-series disequilibrium of bulk samples of oxidised fracture fillings indicates that: i) about 50% of the bulk samples are almost in secular equilibrium for the upper part of the U-series, indicating that they have remained as closed systems in the last 1.6 Ma; ii) the remaining samples show activity ratios (ARs) that indicate water/rock interaction processes affecting the upper part of the U-series, such as recent or rapid U accumulation or losses ($<10^2$ ka), old $^{234}U$ accumulation ($<10^2$ ka) and recent or old $^{234}U+^{230}Th$ recoil gain; iii) the distribution of the AR values, as a function of depth, indicates that neither the closed isotopic systems nor the identified water/rock processes show any defined trend in relation to the location of fractures, even when considering samples from the redox transition zone of the system; iv) this apparently random distribution of processes seems to be the logical consequence of the different hydraulic behaviour of fractures in the system, which is mainly due to their varying degree of sealing, as a function of the amount and clayey nature of the fracture-infill materials.

Hydrogeology

Though the mining activities largely disturbed the original hydrogeological features of the system, the main conclusions obtained from the hydrogeological investigations are: i) the Boa fault is not a preferential flow path, but is part of a larger set of hydraulically active faults and fractures; ii) fractures associated with the Boa fault do not have a substantial influence on groundwater circulation, while other fractures without any relation to this fault have a similar or larger transmissivity; iii) the permeability distribution of fractures in the system is quite heterogeneous, showing fracture zones with low permeability, because of their size and/or fracture-infill materials, and others with higher permeability; and iv) the shallow groundwater flow is quite slow (0.01m/d) and directed towards the bottom of the Hole 01, while the deep groundwater flow is controlled by the regional flow system, which is conditioned by the Águeda River (Fig. 3).

Hydrochemistry of the system before site restoration

As the hydrogeology of the system, its original hydrochemical characteristics were also affected by the mining activities. Thus, some of the investigation boreholes were affected by proximity to the trough formed in Hole H-01, which is continuously flooded with high acidic $SO_4^{2-}$ waters (pH 2.9) and consequently with a large concentration of dissolved metal ions, including U.

Water samples taken before restoration of the system (1999) were classified as Ca-Mg-$SO_4^{2-}$, with some larger $HCO_3^-$ concentration in borehole SM-2. The conductivity increased in the waters from boreholes SM-2 to SM-4 (1220 μS/cm to 6060 μS/cm), while the alkalinity decreased, with pH values from 7.1 to 4.8. The reducing capacity of the waters decreased in the same sense, with Eh values from –300 mV (SM-2) to +8 mV (SM-4). This would indicate that there was an increasing portion of groundwater contamination from the Hole H-01 water as we moved from borehole SM-2 to SM-4. This would indicate that groundwaters from borehole SM-2 had the least influence from

the acid drainage waters of Hole H-01, since they have lower Eh, more alkaline pH values, less $SO_4^{2-}$ content together with a larger $HCO_3^-$ concentration. According to this, the metal ion content was in general lower, except for U with concentrations in the order of 272 μg/l, compared to 51.3 μg/l measured in SM-4 waters. In spite of the intensive oxic disturbance of the system, the large reducing capacity of the SM-2 waters indicated that there is a large redox buffer capacity in the aqueous system, such as Fe(II)/Fe(III), Mn(II)/Mn (IV) and $S^{2-}/SO_4^{2-}$ redox pairs and/or due to the presence of large amount of DOC in this water (29.6 mg/l). The large concentration of U measured in these apparently reducing waters from SM-2 is surprising, given that under these physico-chemical conditions all the U would be precipitated. Finally, the $^3H$ content of all the sampled waters indicate juvenile age (later than 1953).

Hydrogeochemical evolution of the system after site restoration in 2000

The evolutionary trend observed in groundwater samples from the Boa fault zone from 1999 to 2002 is mainly defined by an increase of its alkalinity, reducing capacity and a significant decrease of its electric conductivity. This evolution is generally shown by a tendency towards bicarbonate waters. Though the Fe behaviour is quite uneven, its general trend is to decrease, like Mn, Ni and Zn. On the contrary, the high U concentration observed in relation to the pH and Eh conditions of the groundwaters is relevant, since it should be almost totally precipitated. The filtration assays by 0.45 μm and 0.22 μm filters suggest that U in these groundwaters can occur either as soluble uranyl-carbonate complexes, which are stable under alkaline conditions, or as soluble U(IV)-organic complexes, because of the high amount of DOC in these groundwaters. The simultaneous presence of both types of complexes is not discarded.

Currently, these evolutionary trends, particularly in the water of borehole SM-3, are directly related to the restoration works performed in the site, for which the mine tailing materials were used as both sealing and buffer materials. In this way, the neutralisation of acid water from Hole H-01 and the obstruction of the connections between this Hole and borehole SM-3 were reached. As a result, SM-3 waters have evolved from a 56/44 mix ratio between rock formation groundwater and Hole H-01 water, as determined in 1999, to a groundwater almost in equilibrium with the rock formation and similar to that from SM-2. This process would be similar to the one that functioned in the uranium deposit since its formation until its exploitation, which was exposed to continuous and intensive downward weathering processes, the main chemical driving forces being the oxidation of sulphides, mainly pyrite. As a result, acid-sulphate groundwaters were originated with a large dissolution capacity for light and heavy metals, as waters from Hole H-01. The rock/water interaction processes, mainly those involving carbonate-filling materials, progressively buffered groundwaters in the deeper zones of the site, increasing their alkalinity and precipitating those pH-dependent metals. These processes originated groundwaters like those firstly sampled from borehole SM-2 and then from SM-3.

Concerning the redox potential, it is noticeable that groundwaters in the site restore their reducing conditions very fast and at a shallow level, regardless of fracture density in the site. This seems to indicate that the redox buffering capacity is mainly controlled by the abundant organic matter in the clayey walls of the Boa Fault, in addition to the redox capacity arising from the Fe(II), Mn(II) and U(IV) bearing minerals. The high concentration of DOC groundwaters suggest that it could mainly come from the carbonaceous clayey walls of the Boa fault, through the microbiologically mediated reduction of $SO_4^{2-}$ to $H_2S$ by organic matter.

Analogies

The most important analogue features are the following: i) the existence of large U concentrations as pitchblende ($UO_{2+x}$), which is analogous to the main component of spent nuclear fuel; ii) the behaviour of pitchblende as a result of interaction with groundwaters of varying chemical composition to be used as analogous of the spent fuel stability under severe alteration conditions; iii) some of the weathering products of pitchblende in the site are similar to those that have been identified during the experimental oxidative dissolution of $UO_2$, Simfuel ®, as well as natural uraninite and pitchblende; iv) the scavengers properties of the Fe(III)-oxyhydroxides in the oxidised zone of the deposit could be similar to those of the spent fuel steel container corrosion products that could be formed under redox transition conditions; and v) the behaviour of clays formed as a

result of the hydrothermal alteration and weathering of the schistose rocks is partially similar to that of the clays used in the engineering barriers of the repository, in relation to the radionuclide diffusion/retention processes.

Conceptual geochemical model

The most relevant geochemical processes in the system are related to the effect of the continuous oxidation of the site after the formation of the uranium-ore deposit, some 34 Ma ago, the main geochemical driving forces being the oxidation and supergenic enrichment processes that occur in sulphide-rich deposits under weathering. The differences concern to that the primary mineralisation in this case is a mixture of pyrite, carbonates and pitchblende.

In the oxidised zone, a set of reaction related to the supergenic oxidation of pyrite started the geochemical evolution of the system, generating strong acid conditions under which jarosite is formed. The presence of carbonates in the fracture fillings progressively buffered the aqueous system precipitating gypsum. Under more alkaline conditions, such as those from SM-3, Fe (III) hydroxide gels precipitate and age produces goethite.

Under acidic conditions, phosphates (apatite and monazite) inherited from the original host rock would partially dissolve releasing, in the case of monazite, Ce(III) in solution. The released phosphate would, at least partially, be sorbed onto Fe(III)-oxyhydroxides, as may be inferred form the relatively high correlation between $Fe_2O_3$ and $P_2O_5$ and the sequential leaching results. In the redox conditions under which both Fe(III) and Mn(IV) dominate, Ce(III) will be oxidised to Ce(IV), precipitating as $CeO_2$. Consequently, this explains the close textural relation observed among these three oxides in the fracture fillings from the oxidised zone.

The behaviour of U in this zone can be summarised as follows. Uranium, initially present as tetravalent in pitchblende, would be rapidly oxidised and dissolved as a result of the pyrite oxidation. The predominant speciation of U(VI) under this acid and $SO_4^{2-}$ rich conditions is $UO_2(SO_4)_{2\,(aq)}$. The released U would migrate away from the source or it would precipitate as uranopilite (hydrate uranyl sulphate), when the access of water would be low (dry periods).

When the pH of contacting solutions is increased, due to the carbonate dissolution away from the pyrite oxidation front, U(VI) is hydrolysed and the dominant aqueous complex is $UO_2(OH)_2(aq)$ in neutral media. The same applies for the dissolved Fe(III), which hydrolyses and precipitates under similar conditions. This would contribute to the co-precipitation of both cations under these conditions. However, the actual correlation between U and $Fe_2O_3$ is quite low. This could indicate that in the oxidised zone, the U mobilisation processes prevailed over the retardation ones. However, the results obtained from the sequential leaching suggest that U in this zone is mainly retained as U minerals closely mixed with Fe-oxyhydroxides.

Summarising, in the oxidised zone the conditions were dominantly acid and the water becomes abundant in $SO_4^{2-}$ until all the pyrite was consumed. As a consequence, U was mobilised, Fe(III) and Mn(IV) partially precipitated as oxyhydroxides and some significant amounts of trace metals (W, Cu, Ni, Co, Zn, Cu and even U) were retained.

In the transition redox zone, the presence of jarosite and secondary Fe(III) oxyhydroxides indicates that this zone is affected by oxidised, acid and sulphate containing waters. The presence of U(VI) co-precipitated with Fe(III) oxyhydroxides could be explained by the process previously discussed and/or alternatively by the reducing effect of the remaining Fe(II) in this zone on the U(VI) sulphate waters. The existence of Fe(II) is shown by the evidence of the transformation of the ankeritic carbonates into siderite.

The oxidative action of the Fe(III) coming from the upper oxidised zone is indicated by the partial oxidation of pyrite, which usually contains some sorbed uranium, and marmatite, closely associated to Zn and Fe oxides.

The presence of secondary metallic sulphides (Cu; Cu-Fe; Cu-Ag-Fe; Pb-Cu-Fe; Fe-Sn;), sulphoselenides (Cu and Fe) and elemental Se or $SeO_2$(s), all them products of the supergenic enrichment processes, indicates that the redox potential is transitional or slightly reducing. All these metallic cations, which come from the oxidation of sulphides and sulphoselenides, were transported from the oxidised zone as sulphates and selenates to the transitional zone where they precipitate, as the redox conditions became more reducing.

The most relevant processes affecting the U primary minerals are: i) the oxidation and partial transformation of pitchblende to zippeite, which is the result of the interaction between pitchblende and the sulphate containing waters, and ii) the coffinitisation of pitchblende due to the larger $H_4SiO_4$ content of the waters.

Finally, the scavenging of U by the slightly oxidised pyrite would indicate that U(VI) is reduced to U(IV) and subsequently precipitated.

Hence, this transitional redox zone results in the secondary formation and transformation of all the mineral phases and aqueous species that are redox-sensitive, once the pH and Eh conditions are restored.

The reduced zone is characterised by the stability of all primary minerals of the system. They are only weakly affected by the Fe(II)/Fe(III) content that has reached this depth as a function of the transmissivity of some fractures. This is the reason why the ore deposit has been commercially mined, in spite of the aggressive conditions prevailing in the upper zone.

Semiquantitative geochemical model

The semiquantitative model performed, which is unidimensional and includes kinetic and transport-reactive reactions, is in agreement with the conceptual model described above and includes the most relevant geochemical processes responsible for the mineralogical zoning observed at the Boa fault zone. The aim of this model has been to reproduce the effects caused by the interaction processes between oxidised and slightly acidic water and a lithological column with pyrite, pitchblende, calcite, dolomite and hydroxiapatite as essential minerals. Furthermore, it has been taken into account the kinetic dissolution of pyrite and pitchblende, the dissolution in equilibrium of carbonates and the precipitation in equilibrium of secondary minerals, such as goethite, schoepite and autunite.

The results indicate that, as the water penetrates down through the column, carbonates are dissolved, and pyrite and pitchblende are also oxidised, in agreement with the kinetic laws implemented in the calculation code used. Furthermore, as the redox potential of the system increases, autunite precipitates. Precipitation of schoepite occurs when the redox potential becomes clearly oxidising. Goethite precipitates as a result of pyrite oxidation. Thus, according to this chemical mechanism, the three mineralogical zones observed would be formed. In the upper or oxidised zone, with oxidising redox values and slightly acidic pH, schoepite and goethite would be present. In the transition zone, with more reducing redox values, pyrite and goethite as well as schoepite and pitchblende coexist. In the deeper or reducing zone, the primary minerals of the uranium mineralisation, pyrite, pitchblende and carbonates are stable and consequently persist.

Finally, the assumption of coffinite as secondary mineral in the system can not be correctly evaluated due to the lack of hydrochemical data from the reducing zone and valid thermodynamic and kinetic data for this U(IV) silicate. This evaluation can also be conditioned by the probable existence of U(IV)-organic mater complexes as well as uranyl carbonate complexes, which are thermodynamically stable under the alkaline and reducing conditions that prevail in the reducing zone of the system.

***Relevance:*** the study of the "Mina Fe" U deposit has supplied analogue information about processes that can occur in a radwaste repository after burial, under extremely adverse conditions. This analogue information concerns to the: i) composition, long-term stability and the alteration/dissolution of pitchblende as analogues to the spent fuel matrix stability; ii) role of the

redox processes and other geochemical discontinuities in the solubility, mobilisation and retention of natural radionuclides; iii) radionuclide retention processes in the ore alteration halo; iv) integration of these processes in conceptual and numerical models useful for the PA of a deep geological disposal and their comparison with the usual PA models; v) testing and validation of characterisation tools and methodologies.

***Position(s) in the matrix tables*:** the "Mina Fe" is of relevance to both the near-field (spent fuel stability and radionuclide migration under very adverse conditions) and far-field (role of the carbonates and organic C in the physicochemical discontinuities, mainly pH and Eh, and consequently in the migration/retention of U. Role of the precipitation and co-precipitation processes in the U retention).

***Limitations:*** the host rock of the U deposit of "Mina Fe" is unsuitable for a radwaste geological repository and the intense downwards oxic and acid alteration in the upper zone of the system is of no relevance in assessing repository behaviour. However, in the transition and particularly in the reduced zones, where the conditions of neutrality/alkalinity and reducing potential are restored, relevant processes for the PA occurs, such as co-precipitation of U(VI) and Fe (III), Ni and U(IV); precipitation of relevant trace elements that may occur as radionuclides in some long-lived radioactive wastes, such as Se and Ce; as well as the stability of pitchblende, which is partially analogous to the nuclear spent fuel. The fast and shallow restoration of the physicochemical conditions in the system, mainly due to the microbiologically mediated oxidation of the organic matter, gives support to the survival of the deposit since its formation 35 Ma ago.

***Quantitative information:*** the information derived from this study, particularly de geochemical modelling, is qualitative and quasi semi-quantitative.

***Uncertainties:*** they are mainly derived from the geological features of the site that is highly fractured al perturbed by the exploration and mining activities. These circumstances hampered the precise determination of the original hydrogeological and hydrogeochemical characteristics of the system. However, the evolution observed in the hydrogeochemical features after the restoration of the system allows us to have confidence in the physicochemical parameter measured in situ. Other uncertainties are related to lack of the hydrochemical data from the reduced or stabilisation zone of the deposit and of valid thermodynamic and kinetic data for coffinite that also hampered the correct modelling of the low-temperature coffinitisation of pitchblende, a process observed in fracture fillings of the site.

***Time-scale:*** U-series disequilibrium of bulk fracture filling samples shows that 50% of the samples remained as closed system for the upper part of this natural radioactive series in the last 1.6 Ma, while the remaining samples show activities ratios that indicate water/rock interaction processes, such as recent or rapid U accumulation or losses ($<10^2$ ka), old $^{234}U$ accumulation ($>10^2$ ka) and recent or old $^{234}U+^{230}Th$ recoil gain.

***PA/safety case applications:*** It shows the large stability of the $UO_2$ matrix in quite adverse geochemical conditions, provided there is the sufficient reducing capacity to withstand the disturbances. It gives clear indications of the alteration sequence of the spent fuel matrix under oxidising conditions.

The role of Fe(III) oxyhydroxide phases as radionuclide scavengers is duly supported. In addition, the occurrence of native Se in the redox transition zone is in accordance with the result of the solubility calculations performed for this element under repository conditions.

***Communication applications:*** In spite of the extreme adverse conditions under which the U deposit of "Mine Fe" has undergone since its formation 35 Ma ago, it is a good example to create a favourable public opinion about the geochemical stability of a radwaste repository provided that reducing conditions prevailed after burial.

***References:***

Both, R. A., Arribas, A., de Saint André, B., 1994. The origin of breccia-hosted uranium deposits in carbonaceous metasediments of the Iberian Peninsula: U-Pb geochronology and stable isotopes studies of the Fe deposit, Salamanca Province, Spain. *Econ. Geol.*, 89, 584-601.

Crespo, M.T., Pérez del Villar, L., Quejido, A. J., Sánchez, M, Cózar, J.S., Fernández-Díaz, M., 2003. U-series in Fe-U-rich fracture fillings from the oxidised cap of the "Mina Fe" uranium deposits (Spain): implications for processes in a radwaste repository. *Appl. Geochem.*, 18, 1251-1266.

Domènech, C., Arcos, D., Duro, L., Bruno, J. 2003.- Modelización geoquímica de la falla Boa. (Proyecto Matrix II) Informes ENVIROS, 51 pp.

Mangas, J., Arribas, A., 1984. Característstas físico-químicas de los fluidos asociados con las mineralizaciones de uranio de mina Fe (Salamanca). In: 7th Congreso Internacional de Minería y Metalurgia, Barcelona. Proc. Vol. 1, 435-451.

Pérez del Villar, L., Campos, R., Gómez, P., Cózar, J.S., Pardillo, J., Garralón, A., Turrero, M.J., Buil, B., Pelayo, M., Ruiz, B., Rivas, P., Arcos, D., Bruno, J., Grivé, M., Ruiz Sánchez-Porro, J., Marín, F., Izquierdo, A., Carretero, G., Ortuño, F., Floría, E., Suso, J., 2001. La pechblenda de mina Fe (Ciudad Rodrigo, Salamanca), como análogo natural del comportamiento del combustible gastado (Proyecto Matrix I). Publicación Ténica 05/2001, 175 pp. ENRESA (Madrid).

Pérez del Villar, L., Bruno, J., Campos, R., Gómez, P., Cózar, J.S., Garralón, A., Buil, B., Arcos, D., Carretero, G., Ruiz Sánchez-Porro, J., Hernán, P., 2002a. The uranium ore from Mina Fe (Salamanca, Spain) as a natural analogue of processes in a spent fuel repository. *Chem. Geol.,* 190, 395-415.

Pérez del Villar, L., Quejido, A.J., Crespo, M.T., Sánchez, M., Cózar, J.S., Galán, M.P., Fernández-Díaz, M., 2002b. Sequential leaching methods: review, previous experiences and proposed method for Fe(III)-U(VI)-rich fracture filling materials. *Trends in Geochem.* 2**,** 19-42.

Pérez del Villar, L., Campos, R., Garralón, A., Crespo, M.T., Quejido, J. A., Cózar, J.S., Pardillo, J., Buil, B., Pelayo, M., Gómez, P., Ruiz, B., Sánchez, M., Rivas, P., Arcos, D., Bruno, J., Grivé, Domènech, C., Duro, L., M., Ruiz Sánchez-Porro, J., Marín, F., Izquierdo, A., Carretero, G., Ortuño, F., Floría, E., Suso, J., Delgado, A., Reyes, E., 2004a. Análogos naturales de laliberación y migración del $UO_2$ y elementos metálicos asociados. (Proyecto Matrix, Fases I y II) (L. Pérez del Villar, D. Arcos y J. Bruno Eds.) CIEMAT/DIAE/54441/1/04. Vol I y II.

Pérez del Villar, L., Garralón, A., Delgado, A., Reyes, E., Cózar, J. S., Gómez, P., Núñez, R., Sánchez, L., Raya, J., 2004b. Hydrogeochemical evolution and C isotope study of groundwaters from "Mina Fe" U deposit (Salamanca, Spain): implications for processes in radwaste disposal. *Appl. Geochem.* (in press).

Quejido, A. J., Pérez del Villar, L., Cózar, J. S., Fernández-Díaz, M., Crespo, M.T., 2004. Distribution of trace elements in fracture fillings from the "Mina Fe" uranium deposit (Spain) by sequential leaching: implications for the retention processes. *Appl. Geochem.* (in press)

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