



Deliverable No. D4.1

NAME OF THE DELIVERABLE:

**CHEMICAL AND REDOX BEHAVIOR OF THE INVESTIGATED RADIONUCLIDES
IN THE DIFFERENT SYSTEMS**

**REDOX PHENOMENA CONTROLLING SYSTEMS
ReCosy**

COLLABORATIVE PROJECT (CP)

Submitting organization: PSI
Due date of deliverable: 45 Project Months
Actual submission: 45 Project Months

Grant agreement N°.: FP7-212287

Start date of the project: 01 April 2008
Duration: 48 months

Project co-funded by the European Commission under the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities (2007 to 2011)		
Dissemination Level		
PU	Public	PU
RE	Restricted to a group specified by the partners of the project	
CO	Confidential, only for partners of the project	



This deliverable is also reported as the WP 4 summary in the Proceedings of the 4th Annual Workshop

The goal of the activities within work package 4 is to provide fundamental process understanding of the redox behaviour of radionuclides in solution and in solid matrices, including the question of equilibrium / disequilibrium with the system redox conditions. The objectives of this work package result from gaps in the knowledge identified from previous projects dealing with redox processes involving radionuclides.

The activities within D4.1 can broadly be divided in three main topics:

1. Interactions of radionuclides with pyrite
2. Interactions of radionuclides with far-field solids
3. Redox processes under hyperalkaline conditions

4.1.1. Interactions of pyrite with elemental iodine and iodide, iodate, selenite and selenate ions

During the fourth year of the project, the **CNRS/LCPME** activities consisted mainly in investigations performed in neutral and alkaline media. In this way, voltammetric measurements were performed using massive rotating pyrite electrodes and pyrite microparticles conditioned with soluble iodine and selenium species. After conditioning, the pyrite microparticles were characterized electrochemically and using XPS, Raman spectrometry. Moreover, the oxidation of pyrite by oxygen was monitored dielectrically.

1) Voltammetric measurements at massive rotating pyrite electrodes in the presence of elemental iodine as well as iodide, iodate, selenite and selenate ions

Measurements performed previously in acidic media were confirmed, and new voltammograms were recorded at pH 7 and 12 using pyrite electrodes immersed in 1 mM solutions of iodate, selenite and selenate ions as well as in a saturated solution of elemental iodine at pH 7. The measurement of corrosion currents brought information on the kinetics of oxidation of FeS₂ by the different oxidizers.

The experiments performed with I₂ neutral media (I₂ is not stable in alkaline media) showed the existence of important corrosion currents close to those recorded previously in acidic media. Because the iodate ions oxidizing properties decrease with the pH increasing, there are no corrosion currents at pH 7. On the other hand, the voltammograms indicate the presence of a corrosion process at pH 12 (probably because of the very high oxidizability of pyrite in alkaline media). No corrosion currents were observed with selenite ions. In neutral medium, the i-E curves are highly disturbed by the presence of a cathodic peak that is located very close to the rest potential (Fe₂(SeO₃)₃ precipitate?). The voltammograms recorded in alkaline medium are not exploitable. No corrosion currents were observed with selenate ions whatever the pH.

2) Chemical conditioning of pyrite microparticles with soluble iodine and selenium species at pH 7 and 12.

Sorption experiments were performed under argon atmosphere at room temperature by stirring the conditioning containers in the dark. The solution pH was adjusted to either

7.0 or 12 at the beginning of the experiment. The conditioning of pyrite suspensions has been performed using a 0.5% (w:w) solid/liquid ratio with $[I^-] = [IO_3^-] = [SeO_3^{2-}] = [SeO_4^{2-}] = 1$ mM. A saturated solution elemental iodide was used at pH 7 (solid I_2 was always present).

A good number of the solutions analysis data are still under processing. The most important and relevant results deriving from the analyses are the following: (i) when pyrite is treated with water adjusted at pH 12 it releases continuously sulphide ions (S^{2-}) in the solution. (ii) iodide ion is sorbed at the "pyrite" surface at pH 12; however, the amount adsorbed is extremely weak, and it is probably related to the presence of iron oxides on the FeS_2 surface. (iii) the reaction of iodate ions is slow at pH 12, (iv) as in acidic media, iodine quantitatively reacts with pyrite at pH 7.

3) Characterization of pyrite microparticles sampled after interaction with soluble iodine and selenium species by XPS, Raman and voltammetric measurements

The results of characterization of the pyrite microparticles, separated from the reaction media, rinsed and dried, by XPS and Raman microscopy, are rather disappointing. Some oxidized iron species but no selenium or iodine were detected with XPS. The samples appeared as well etched pyrite containing some silicate. Similar information was obtained from the Raman microscopy analyses and the electrochemical measurements using scan rates of 5 mV/s.

The results from the dielectric and electrochemical (under particular conditions) characterizations of pyrite microparticles sampled after reaction with iodine and selenium species were compared with the observations of Demoisson et al (2008). These authors investigated the oxidation processes of pyrite by dissolved oxygen and chromate using Raman spectroscopy. In particular, they have observed a drift of the vibration modes E_g and A_g of -3 and -6 cm^{-1} respectively. The present Raman measurements clearly demonstrate that the drift observed by Demoisson et al. was an artefact due to the heating of the samples by the laser beam.

Dielectric measurements further showed that (i) the resistance of the pyrite particles conditioned with deionised water, iodide or iodate, is about 1500 ohm (ii) the resistance of the pyrite particles conditioned with iodine is higher than 20,000 ohm and (iii) the resistance of the pyrite particles conditioned with selenite or selenate is even higher.

Voltammograms recorded using extremely slow scan rates (0.1 mV/s) allowed the electrochemical transformation of the complete electroactive matter immobilized at the working electrode. Therefore, after the electrooxidation of all the pyrite, species that have higher oxidation potentials can be detected. In this way it was found that: (i) after pyrite conditioning with deionised water, the voltammograms show only a main peak at about 0.95 V vs. SCE, (ii) after conditioning with iodine or iodate ions, this peak is followed by another at about 1.12 V vs. SCE, (iii) after conditioning with iodide, selenite or selenate ions, the main peak of pyrite is shifted to a lower potential by about 100 mV (0.85V).

XPS characterizations performed with extremely fine microparticles sampled after the reaction of FeS_2 with selenite or selenate ions in neutral and alkaline media revealed the presence of elemental selenium. The corresponding voltammograms show an additional voltammetric signal at about -0.7 V vs. SCE. Experiments are in progress in order to confirm the absence of any photochemical origin for the observed selenium.

4) Dielectric measurements with dry pyrite microparticles during their stepwise exposure to air or pure oxygen

This study was initiated after an attempt to use dielectric spectroscopy to monitor in-situ the interactions of pyrite with soluble selenium and iodide species (and was continued after the end of the 4th reporting period). We have remarked that once dry pyrite was exposed to air for a short time its impedance rose rapidly. However, along its stay in a hermetically closed dielectric cell, its impedance progressively decreased and finally became almost the same as that before the exposure to air. It was as if pyrite had “repaired” the damage induced by its exposure to air. We considered that the observed phenomenon was worth being explored further: (i) because of the importance of the pyrite oxidation during the mining works in relation the underground installations construction and (ii) for avoiding the misinterpretation of dielectric data obtained during the in-situ monitoring of the interactions in liquid phase of pyrite with soluble selenium and iodide species.

The work performed using pyrite microparticles put in a dielectric cell under alternative flows of dry argon and ambient air (or dry oxygen) confirmed the preceding observation. The observed changes in the dielectric spectra are probably due to extremely fine transformations on the pyrite surface that cannot be detected with usual spectroscopic techniques (Raman microscopy). If the ambient air is used as the oxidizing agent, the presence of moisture renders the phenomena more complex. Even if this work was quite long, it must be considered as a preliminary approach; its main objective was to check the reproducibility of the measurements and if no artefacts occurred. The systematic study of other parameters as the particles size, the temperature, moisture degree... as well as the use of a well-suited and complementary technique would bring essential information in order to understand the observed phenomena.

4.1.2. Interactions of radionuclides with far-field solids

The work performed within this topic is focused on obtaining fundamental process understanding of the interaction of redox sensitive radionuclides such as Tc, U, Np and Pu with various far-field minerals.

The contribution of **Chalmers University of Technology** to ReCosy WP4 consists of an investigation of the redox state of groundwaters relevant to a crystalline rock environment (Äspö, Sweden) with the help of selected redox sensitive radionuclides.

The investigations are basically divided into two parts:

1. Synthetic groundwater
2. Synthetic groundwater with added crushed minerals ("batch" experiments)

In both parts we intend to look into aspects of the E_n agreement in a synthetic groundwater system containing the redox couples Fe(II)/Fe(III) with added redox-tracer e.g. radioactive Tc(IV)/Tc(VII), U(IV)/U(VI), Np(IV)/Np(V), Pu(III)/Pu(IV). Our aim is to perform the studies under both oxic and anoxic conditions. Measurements with commercial redox electrodes as well as analysis and quantification of elemental oxidation states of redox tracer, using solvent-extraction, will be examined over time and discrepancies between these will be looked into.

Geological material and groundwater recipe are taken from the SKB Äspö LTDE-project (Long Term Diffusion Experiment), where results for in-situ adsorption of radionuclides onto rock surface and in-diffusion into the rock matrix is compared with laboratory results with crushed material.

During 2011 the experiments have continued with:

- 1) Production of An(IV) from An(V) or(VI) (An=U, Np) by catalytic reduction with H_2/Pt .
- 2) Spectroscopic measurement of redox state purity of 1mM solutions of An(IV) and its stability over time in inert atmosphere glove-box.
- 3) Separation of An(IV) from An(VI) by solvent extraction, using thenoyltrifluoroacetone (TTA), dibenzoylmethane (DBM) or 4-benzoyl-3methyl-1-phenyl-5-pyrazolinone (PMBP), for the purpose of quantification of ^{233}U and ^{237}Np in tracer concentrations ($<1 \mu M$).
- 4) Comparison of redox determination methods using synthetic groundwater of the LTDE type.

The reduction of 1mM solutions of U(VI) and Np(V) in 0.1M $HClO_4$ was followed with spectroscopy. 6 h of reduction was enough to convert U(VI) into U(IV), according to spectra. However, subsequent solvent extraction experiments were found to be more sensitive in the determination of redox state purity. Deviating results for extraction curves, where pH in aqueous phase was varied, was easily detected if traces of oxidized species was left after reduction. U(IV), U(VI) and Np(V) solutions were diluted to about 1-10 μM and solvent extraction in the pH range 0.6 - 7 with three different systems were made: 0.5M TTA in xylene, 0.5M DBM in chloroform and 0.05M PMBP in xylene. Although the disappearance of characteristic peaks in Np spectra indicated that Np(V) could be reduced with H_2/Pt , the peaks for Np(IV) were not correspondingly enhanced. Solvent extraction also gave typical Np(V) extraction results. It was therefore concluded that Np reduction would need a more forceful method, such as a potentiostat, to be fully reduced to Np(IV). It was therefore decided to proceed with U reduction only, for the subsequent redox determinations. From the results for solvent extraction pH=2 was chosen for optimum separation of U(IV) and U(VI), using 0.5M DBM in chloroform. This method was used for comparison with a Pt/Ag/AgCl combination electrode in determining redox in synthetic LTDE groundwater. This water was prepared in glove-box ($p(O_2)$ 1 ppm) to pH=7.0, $I=0.22M$ and with initial redox species $[Fe^{2+}]=12mM$, $[Mn^{2+}]=6.5mM$ and $[S^{2-}]=3.1mM$. Speciation calculations for this water gave a theoretical $E_h=-167mV$ and should then be saturated with pyrite and quartz. However, it was found that the prepared water had an $E_h=30mV$ when measured with a combined redox electrode. This is not surprising since the box atmosphere is not inert enough to maintain the initial conditions. A slow oxidation is therefore expected when reducing groundwaters are prepared and allowed to equilibrate with glove-box atmosphere. The prepared water was transferred to 100mL vessels, either with or without solid phase additions of crushed pyrite and/or granite. These samples were spiked with U(IV) tracer and then measured with electrode and with the U(IV)/U(VI) determination method. The results gave about 280-340mV for electrode measurements, while U speciation gave about 30-70mV. If this measured discrepancy between the two methods indicates either: a tendency for conservation of initial redox conditions due to slow response to changed redox (U measurement) and a *de facto* further oxidation of solution (redox



measurement) or: redox have actually not changed from what was as initially measured with electrode and the later electrode measurements were corrupted by some unknown disturbance, have not been established. A better control of initial redox is essential and some simple Fe(II)/Fe(III) strongly redox buffered systems may instead be used to establish: 1) whether the discrepancy between methods persist and 2) if possible, the cause for it. The inconclusive results were presented in the final workshop of ReCosy project. It is planned to publish more conclusive results in a full scientific paper, based on the S/T contribution (1) to the final ReCosy workshop.

The Center for Physical Sciences and Technology, Lithuania (FMTC) carried out batch sorption experiments with ^{243}Am from NaNO_3 solutions onto wustite/magnetite, hematite and soil. ^{243}Am sorption onto wustite/magnetite and soil in static batch-type experiments showed a negative linear relationship within pH values (pH 2.15; pH 4.00; pH 6.95; pH 9.01), while the adsorption of ^{243}Am ions onto hematite increased with increasing pH values (correlation coefficient $R=0.83$, $R=0.92$, $R=0.90$, respectively). ^{243}Am distribution in the geosorbent column vertical profile under different pH values and 0.5 ml/h flow rate of 0.1 mol/L NaNO_3 aqueous solution was determined. Experimental results suggest ^{243}Am accumulation in the upper 2 cm layer regardless of geosorbent origin and aqueous solution pH value.

University of Manchester is investigating the interactions between surfaces, humic acids and actinides in ternary systems, with the aim of developing a mathematical model to predict actinide chemistry and solid/solution partition.

During 2011, the partition of plutonium in oxidation states IV, V and VI between solid and solution phase has been studied in humic/quartz sand ternary systems as a function of time, both in the absence and presence of HA. The behaviour in the Pu(IV)/quartz sand ternary system appears simple, with the humic appearing to act largely as a competing solution phase ligand, and Pu sorption decreases with increasing HA concentration for all systems. The same type of behaviour was observed for the Pu(VI) system. For the Pu(V) system, the presence of humic at low concentrations enhances sorption, and so ternary complexes are very important. The Pu sorption in all systems is reversible to some extent, and in the Pu (IV) system, it seems fully reversible in the short-term. We have also augmented the database of humic-radionuclide binding constants for the WHAM speciation model.

Results:

Batch experiments with single oxidation states under controlled atmospheres the measured Pu concentration remaining in solution in ternary systems. To test reversibility, after equilibration, solid and solution were separated: fresh solid was added to the solution and fresh solution (Pu free) was added to the solid. These replacement experiments provide a more rigorous test of speciation models. They simulate processes that will take place as a Pu solution encounters fresh mineral surface as it migrates, as well as the ability of humic acid to re-mobilise Pu that has been sorbed to a mineral surface.

Figure 1 shows the data for the Pu(IV) system, which shows simple, 'classical' ternary system behaviour. As [HA] increases, the amount of Pu sorbed decreases. The main apparent effect of the humic is to act as a competing solution phase ligand, which holds Pu(IV) in solution. There is no significant difference between the 10 ppm and humic



free systems. The typical [HA] in the environment is < 10 ppm, and so the results suggest that for the quartz sand system, the presence of humic at realistic concentrations does not affect the solid/ solution partition. Further, the data show that this system is reversible, i.e., the data in Figure 1B may be predicted from that in Figure 1A. The Pu(V) system behaviour is much more complex, because low [HA] actually increases sorption. This can happen when the interaction with the humic is stronger than that with the mineral surface, which makes ternary complex formation (Quartz-HA-Pu) very significant. Hence, realistic [HA] may help prevent Pu(V) migration in quartz systems. Probably as a result of the these ternary complexes and the complex sorption behaviour, there is evidence for some irreversibility this time, and hence behaviour will be harder to predict for Pu(V). Pu(VI) is different to the Pu(V) in that the system appears largely reversible, which may be related to the fact that, like Pu(IV), the data show simple ternary behaviour (consistent increase in [Pu] with increasing [HA]). In the vicinity of a repository, the Eh may change. To test the effect, Pu(IV) was allowed to sorb before the experiment was exposed to oxygen (data not shown). Over a period of a few weeks, there was no significant effect. The data for the Pu (V/VI) systems are not shown here, but are available in the full S+T contribution.

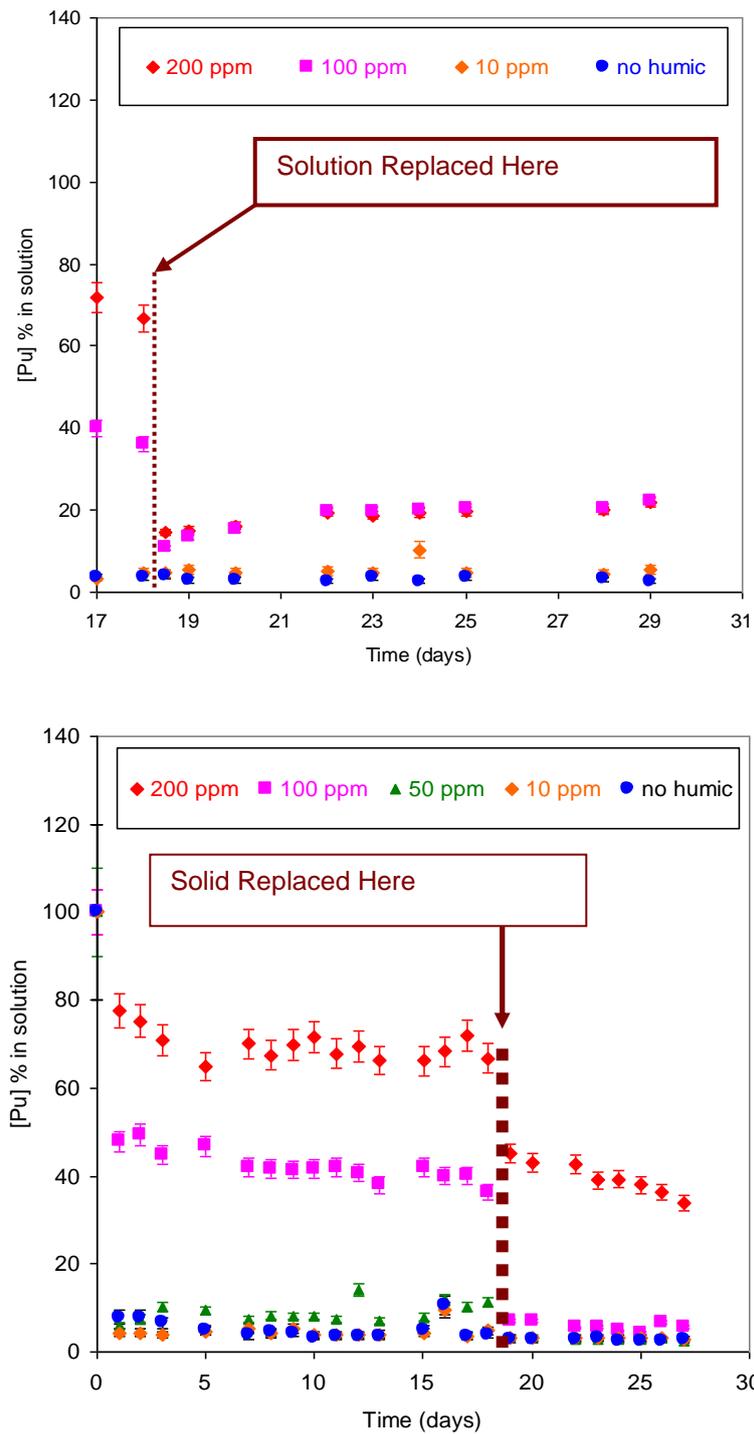


Figure 1: $^{239}\text{Pu}(\text{IV})$, 1.22 kBq ml^{-1} , $I = 0.1$, $\text{pH} = 6$. **A (upper figure):** Pu concentration following exposure to 2 successive samples of mineral. **B (lower figure):** Pu concentration before and after replacement of the solution for the same sample of mineral.

In addition to the ternary system work, we have used linear free energy relationships to estimate WHAM/Model VII binding constants for Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and

PuO_2^{2+} . The WHAM model has been widely applied to stable element speciation, but is lacking humic binding parameters for some radioisotopes. We have filled gaps in the binding constant database. When combined with the existing constants for inorganic species, this now allows the calculation of equilibrium distributions of important radionuclide species under a wide range of conditions. This has improved the applicability of the WHAM speciation model for radioactive isotope speciation and thus makes the model applicable to radiological performance assessment calculations. Full details of this work are available in Stockdale et al (2011).

It can be concluded that:

- HA/Quartz/Pu(IV)/(VI) systems show (short-term) reversible sorption;
- For quartz, realistic concentrations of HA have little effect on Pu(IV) solid:solution partition;
- Ternary complexes are very significant for Pu(V), and there is some irreversibility, making behaviour hard to predict;
- Exposure of a HA/Quartz/Pu(IV) system to oxygen does not seem to affect sorption in the short-term;
- We have extended the WHAM speciation model to include important radionuclides.

In the last ReCosy period, **KIT – INE** focussed its research towards the characterization of the Np, Pu, and Tc, which were sorbed on the clay surface after a long reaction time up to 8 months. The sorption and redox speciation of Np, Pu and Tc have been performed on crushed OPA and COx clay rocks with artificial pore water. The batch experiments were performed at the equilibrium pH 7.6 for OPA and pH 7.2 for COx under argon atmosphere (<1 ppm O₂) with 1% CO₂ conditions at room temperature. Four different solid to liquid ratios (S/L = 10, 20, 50, 200) have been regarded, at constant ionic strength (0.1 M NaCl). We have performed two series of sorption experiments, one at higher metal concentration of about 3.0×10^{-4} M and one at low metal concentration of 1.0×10^{-8} M. The higher concentration was necessary to get a chance for characterizing the metal by spectroscopic methods like X-ray absorption fine structure (XAFS), UV-Vis absorption, X-ray photoelectron spectroscopy (XPS).

We observed at low concentration that more than 80% of Np, more than 90% of Pu and only 20-50% of Tc is sorbed on the OPA as well as on the COx. The amount of the sorbed metal ion depends on the different S/L ratio; the higher the S/L ratios the higher the sorption. Liquid-liquid extraction of the aqueous solution after separating the clay by ultrafiltration (10 kD) showed reduction of Np(V), Pu(V), and Tc(VII) to the tetravalent oxidation state. About 50% of the remaining metal ions are in the tetravalent state whereas the rest of the metal ion is still in the higher oxidation state. These findings qualitatively match with the results of thermodynamic calculation based on measured E_h values of the solutions in contact with the clay. The E_h was measured after 8 months to be 10 – 40 mV for the Np/Clay system, (-180) – 40 mV for the Pu/Clay system, and (-100) – (-80) mV for the Tc/Clay system.

To remind the results at higher metal concentration, the Np and Tc ions were not sorbed in the lower oxidation state after a reaction time of 1 week. Only Pu has been found in the tetravalent oxidation state after 1 week. However, after a reaction time of 4 or 8 months neither Np nor Tc sorbed on the clay has been found in the tetravalent oxidation state by XANES. Even the presence of hydroquinone (10^{-3} M) and magnetite (0.6 g/L) did not change the speciation as well as the E_h value that still is the same as in the solution without them. From the EXAFS we could show with the help of the measured Pu-Pu interaction with a distance of 3.75 Å that the Pu(IV) must be precipitated as a Pu-polymer species on the surface. For the Np(V) we assume that with increasing reaction time the Np(V) surface complex changes from an outer sphere complex after 1 week to an inner sphere complex after 8 months. This is proven by a weak third shell signal coming from Si/Al neighbours at 3.75 Å, which was not observed in the spectra of samples after one week.

The lack of reduction at high metal concentrations might be due to limited number of reducing sites on the clay presumably pyrite sites. The concentration of pyrite sites is estimated to be around 10^{-8} mol/g (Descostes et al. (2010)).

However, the experiments showed that under reducing conditions, the elements Np, Pu, and Tc, whenever they are released in the pentavalent or heptavalent oxidation state, are sorbed in the tetravalent oxidation state when a sufficient amount of reducing sites are available on the clay for the reduction process.

4.1.3. Redox processes under hyperalkaline conditions

The work performed within this topic aims to provide an understanding of the redox behaviour of redox-sensitive radionuclides such as Tc, U, Np under hyperalkaline conditions.

The contribution of Loughborough University to the Reosy WP4 consists of an investigation of the effect of ISA and picolinic acid on the redox chemistry of technetium. The current UK option for the management of ILW is to store it in a deep geological disposal facility (GDF). This may then be backfilled with a cementitious material. The GDF will develop highly alkaline porewater for *ca.* 10^5 years. Corrosion of steel canisters will lead to reducing conditions, so the chemistry of Tc in the waste must be understood in the context of this chemistry. The aqueous chemistry of technetium is likely to be dominated by the highly mobile pertechnetate anion in aerobic waters, and by $TcO_2(am)$, in anaerobic.

Organic complexing agents will be present in ILW, including decontamination agents such as EDTA and picolinic acid, as well as polyhydroxylated carboxylic acids like α -isosaccharinic acid (ISA) and gluconic acid. Such ligands are often highly complexing and can cause significant increases in radionuclide solubility, especially at high pH. The GDF will not be homogenous so there will be areas of reducing and oxidising potential, which could mean both Tc(VII) and Tc(IV) are present. If TcO_4^- migrates into an area of reducing conditions, the organics may complex with Tc during reduction to form water-soluble species. Also of relevance, is the possibility of increased solubility when

organics are in contact with reduced Tc. In other words, does the presence of organics affect the reduction of Tc(VII) to Tc(IV)? Studies were undertaken in which TcO_4^- was reduced in the presence and absence of the four ligands, to determine whether there was an increase in Tc solubility when TcO_2 was contacted with the ligand.

Experiments were conducted in an N_2 glove box. Solutions were boiled, N_2 sparged and kept in presence of Fe filings to maintain reducing conditions. The ligands were added to $\text{NaOH}(\text{aq})$ in the form of solids at pH 13.3, to give concentrations between 0.4 and $0.001 \text{ mol dm}^{-3}$. NH_4TcO_7 was added and pH and Eh measured. Reduction was achieved by 3 methods, the addition of 0.7 g of SnCl_2 or FeCl_2 or electrochemically. Five replicates were used. Control experiments showed that reducing conditions were maintained for the requisite periods of time and that 14 days was sufficient for steady state to be established.

The red data points in figures 1 and 2 show the effect of ISA and picolinic acid concentration on Tc(IV) solubility. The slopes of close to unity for ISA and picolinate indicate that the increase in solubility of Tc is being controlled by the formation of a 1:1 Tc(IV)-ligand complex.

TcO₄⁻ reduction in presence of ligands

In the presence of ISA, a lowering of $[\text{Tc}](\text{aq})$ took place, showing that ISA did not prevent reduction taking place (Figure 2). If this reduction was to Tc(IV), then the final $[\text{Tc}](\text{aq})$ should be the same as that produced by the addition of ISA to Tc(IV) solution, i.e. the Tc(IV)-ISA complex would again be formed, but by 2 different routes at steady state. For ISA, this would seem to be the case. The presence of PA again inhibited the reduction of pertechnetate by all three reduction methods tried, (Figure 3).

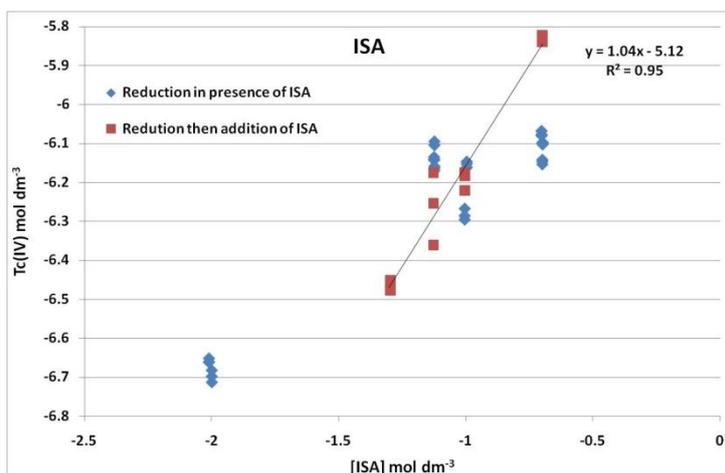


Figure 2: Comparison of final $[\text{Tc}]$ in presence of ISA at pH 13.3, starting from TcO_4^- and Tc(IV).

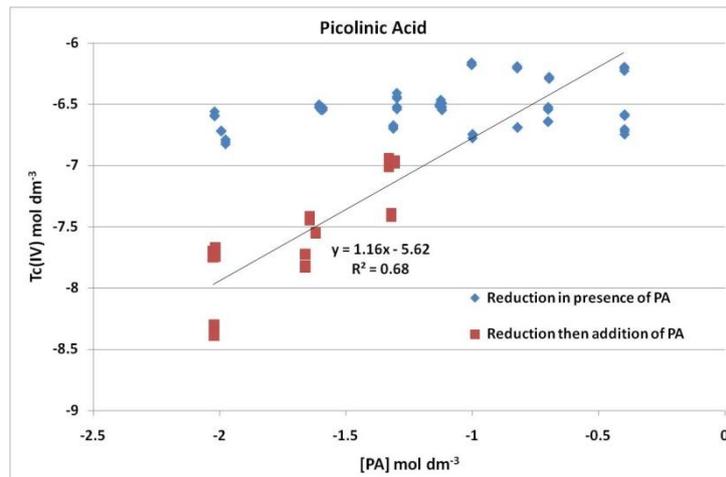


Figure 3: Comparison of final $[Tc]$ with of PA at pH 13.3, starting from TcO_4^- and $Tc(IV)$

AMPHOS has studied the solubility of uranium (IV) oxide in an alkaline environment (pH between 9-12) and using different anoxic / reducing conditions at 25° C in solutions without complexing ligands (carbonate, phosphate, silicate, etc.) where uranium oxides, oxyhydroxides or hydroxides are expected to be the solubility controlling solids (Riba et al. 2012). The proposed objectives of the project for the past year were to model solubility data of $UO_2(am)$ under alkaline pH and anoxic/reducing conditions under $H_2(g)$ atmosphere or by using dithionite as a reducing agent. Data used in the modelling exercise have been obtained during the previous years of the project and compared with data included in the literature. The objectives of the modelling exercise have been:

- To investigate the causes of the E_h - pH trend observed in the $UO_2(am)$ solubility experiments
- To study the mechanism determining the uranium concentration in solution.

The experiments performed under $H_2(g)$ atmosphere at pH = 9.4 and 11 and using $NaClO_4$ as electrolyte indicate that $H_2(g)$ behaves as an inert gas without reducing properties. The measured E_h is in agreement with the occurring uranium processes in the system. At low Na^+ concentration (0.01 M $NaClO_4$), the measured redox potential is in agreement with the oxidative dissolution process of $UO_2(am)$. However, at 0.1M $NaClO_4$ the measured redox potential responds to “redox-neutral” conditions (Neck et al., 2007) and measured uranium concentrations are in agreement with Na-uranate secondary phase ($Na_2U_2O_7 \cdot xH_2O$) controlling the solubility of U in solution (see Figure 4)

The experiments performed with Na-dithionite as a reducing agent (at pH = 10, 11 and 12, I = 0.1 M ($NaClO_4$)) and using two different dithionite concentrations (0.001 and 0.01 M) demonstrate the E_h measurements respond to different dithionite processes of oxidation and decomposition as a function of dithionite concentration, pH and reaction time. Despite the variability in the redox potential, the measured uranium concentrations

suggest that reducing conditions kept during the experiments are controlled by the formation of sulphide in solution, so that there is a limited oxidative dissolution process of $\text{UO}_2(\text{am})$. The low concentrations of U measured in solution are in agreement with the low solubility $\text{UO}_2(\text{am})$ under reducing conditions with an aqueous speciation scheme including U(IV) and U(VI) aqueous complexes but without any evidence of the formation of the anionic U(IV) species; $\text{U}(\text{OH})_5^-$ and $\text{U}(\text{OH})_6^{2-}$, proposed by Fujiwara et al (2005).

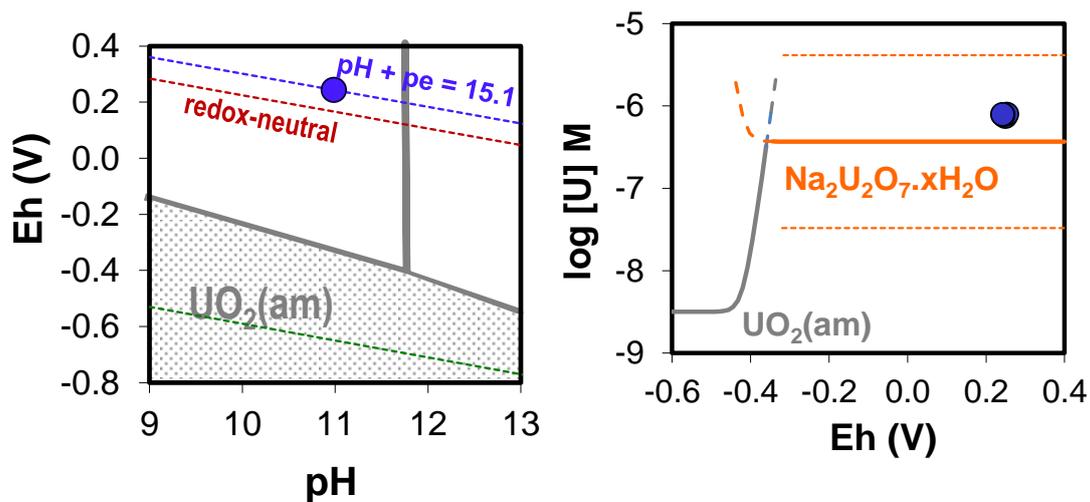


Figure 4: (Left). E_h/pH predominance diagram of uranium at uranium total concentration of $8 \cdot 10^{-7}$ M. The “redox neutral” conditions ($\text{pH} + \text{pe} = 13.8$) have been represented as a dashed red line and the experimental $\text{pH} + \text{pe} = 15.1$ is represented as a dashed blue line. The symbol represents the experimental data.

(Right) Solubility curve of $\text{UO}_2(\text{am})$ and $\text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ as a function of Eh at $\text{pH} = 11$ and $I = 0.1$ M. The dotted line represent the error associated to $\text{Na}_2\text{U}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ solubility. The symbols represent the experimental uranium concentration and measured Eh.

The contribution of PSI to WP4 focuses on the influence of redox conditions on the immobilization of Neptunium in highly alkaline cementitious environments.

Neptunium is commonly believed to exist in oxidation states +IV and +V in a cementitious environment under reducing, respectively oxidizing conditions. However, the possible formation of anionic Np(VI) species ($\text{NpO}_2(\text{OH})_3^-$ and $\text{NpO}_2(\text{OH})_4^{2-}$) under oxidizing hyperalkaline conditions, in analogy to U(VI), may significantly limit the stability field of Np(V) in favour of Np(VI) species. Whereas experimental data concerning the sorption of Np(V) by cementitious materials are scarce, sorption data concerning Np(IV) and Np(VI) are non-existing in the literature. In many sorption databases these gaps are filled by proposing estimates for the missing sorption data based upon chemical analogies (e.g. Th(IV) – Np(IV) or U(VI) – Np(VI)) or based upon the electrostatic interaction energy (expressed by the effective charge, Z_{eff}) implying

increasing sorption values in the series Np(V) ($Z_{\text{eff}}=2.2$) < Np(VI) ($Z_{\text{eff}}=3.0$) < Np(IV) ($Z_{\text{eff}}=4.0$) (e.g. Wieland & Van Loon, 2002). The PSI contribution to WP4 aims at validating these assumptions.

During the first 3 years of Reosy, emphasis was mainly put on the determination of the Neptunium redox speciation under hyperalkaline conditions and on the development of experimental procedures to control the redox conditions and measure the Np redox state during solubility and sorption experiments. Furthermore the sorption of Np(IV,V,VI) on CSH phases was investigated in detail. These latter studies showed that sorption distribution ratios (R_d values) measured for the Np(IV/V) sorption onto C-S-H phases are surprisingly high ($R_d=(6\pm 4) \cdot 10^5 \text{ L kg}^{-1}$) and independent of the C:S ratio and the pH. The sorption of Np(VI) on C-S-H phases was found to be strong at low C:S ratios but decreased with increasing C:S ratios (increasing pH).

The sorption behaviour of Np(IV,V,VI) on C-S-H phases is influenced by the properties of the C-S-H phases (varying composition, varying structure and high recrystallisation rates) and by the aqueous speciation of Np(IV,V,VI). To determine the effect of the aqueous speciation on the Np(IV,V,VI) uptake, sorption experiments were carried out on TiO_2 , a stable solid phase with a constant composition and structure, and low recrystallisation rates. Overall, with progressing hydrolysis of Np the formation of anionic species, appeared to adversely affect the sorption of this radionuclide. In the case of Np(IV), Np(OH)_4 is the sole species present in the pH range $10 \leq \text{pH} \leq 14$, resulting in constant sorption values for this tetravalent species (data not shown). In the case of pentavalent and hexavalent neptunium, the neptunyl moieties become progressively hydrolyzed with rising pH up to the formation of anionic hydroxy species ($\text{Np(V)O}_2(\text{OH})_2^-$, $\text{Np(VI)O}_2(\text{OH})_3^-$ and $\text{Np(VI)O}_2(\text{OH})_4^{2-}$) at the highest pH values. In parallel, the sorption of Np(V) and Np(VI) decreases significantly indicating a much weaker affinity of these anionic hydroxyl species for sorption sites of TiO_2 . The observed sorption reduction could be described in a satisfactory way assuming that the anionic species $\text{Np(V)O}_2(\text{OH})_2^-$ and $\text{Np(VI)O}_2(\text{OH})_4^{2-}$ are not sorbing and that the formation of these two anionic species in solution competes with the surface complexation reaction on the TiO_2 (Figure 5). Surprisingly, it has to be assumed that the $\text{NpO}_2(\text{OH})_3^-$ anionic species sorbs as strongly as the $\text{NpO}_2(\text{OH})_2$ species, to obtain a proper fit of the data.

For the modelling the following reduction factors were applied for Np(V) and Np(VI) respectively:

$$\text{Np(V):} \quad f = \frac{R_d}{R_d^0} = \frac{1}{1 + \frac{\beta_2^0}{\beta_1^0 \cdot [\text{H}^+]^{\gamma_- - \gamma_+}}} \quad (1)$$

$$\text{Np(VI):} \quad f = \frac{R_d}{R_d^0} = \frac{1}{1 + \frac{\beta_4^0}{\beta_3^0 \cdot [\text{H}^+]^{\gamma_2 - \gamma_+}}} \quad (2)$$

β_1^0 and β_2^0 are the stability constants for the formation of the hydroxy complexes $\text{NpO}_2(\text{OH})$ and $\text{NpO}_2(\text{OH})_2^-$, and β_3^0 and β_4^0 are the stability constants for the formation of the hydroxy complexes $\text{NpO}_2(\text{OH})_3^-$ and $\text{NpO}_2(\text{OH})_4^{2-}$. γ_- , γ_{2-} , and γ_+ are the activity coefficients for the monovalent and divalent anions, and for the monovalent cations in the SIT equation. SIT interaction parameters were taken from estimations presented by Hummel et al., (2009) assuming a NaCl matrix.

The values for these complexation constants were taken from the NEA thermodynamic database (Guillaumont et al., 2003) and from Gaona et al., 2011. The solid lines in Figure 5a and b are the model curves and the dotted lines are fitted curves with $\log \beta_2^0$ and $\log \beta_4^0$ taken as fitting parameters in equations 1 and 2 respectively. Figure 5a and b show that this model slightly overestimates the sorption values. However a comparison of the values for the thermodynamic complexation constants, $\log \beta_2^0$ and $\log \beta_4^0$, from the NEA TDB used in the models, with values obtained from a fit of the data (Figure ...a and b) show that the difference between the model and the fit actually is quite small. Hence, it is concluded that the sorption of Np(IV,V,VI) on TiO_2 under hyperalkaline conditions can be explained satisfactorily assuming that anionic hydroxyl species are not sorbing.

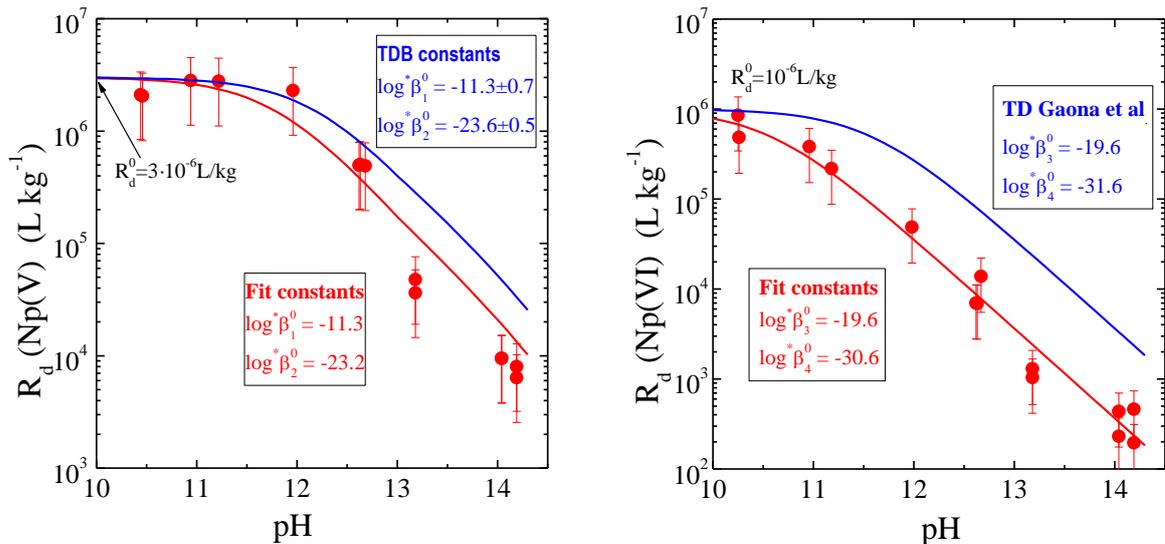


Figure 5: Effect of pH on the sorption of Np(V) (a) and Np(VI) (a) on TiO_2 . The S:L ratio = $2 \times 10^{-4} \text{ kg L}^{-1}$. $[^{239}\text{Np}] = 1.5 \times 10^{-10} \text{ M}$. $I = 1.0$.

The sorption behaviour of the tetravalent, pentavalent, and hexavalent actinides on C–S–H phases appears to be very similar to the sorption behaviour observed previously on TiO_2 up to a pH of 12.5 (Figure 4.9a) and can thus be explained by their speciation behaviour; i.e. with rising pH, negatively charged species increasingly dominate the aqueous speciation of the exavalent actinides, resulting in decreasing sorption. In the case of the tetravalent Np, the aqueous speciation is independent of pH in the pH range

studied, resulting in constant sorption values with rising pH for this redox state. In the case of Np(VI), anionic species dominate the aqueous speciation starting from pH = 11 resulting in a decrease of the measured R_d values. The constant sorption values observed in the case of Np(V) are explained by its weaker hydrolysis with anionic $\text{Np(V)O}_2(\text{OH})_2^-$ species appearing only above pH = 12.5. i.e. beyond the experimental pH range.

The similar sorption behaviour of the tetravalent, pentavalent and hexavalent neptunium on TiO_2 and C-S-H phases suggest that the variation in the C-S-H composition only has a marginal influence on actinide sorption.

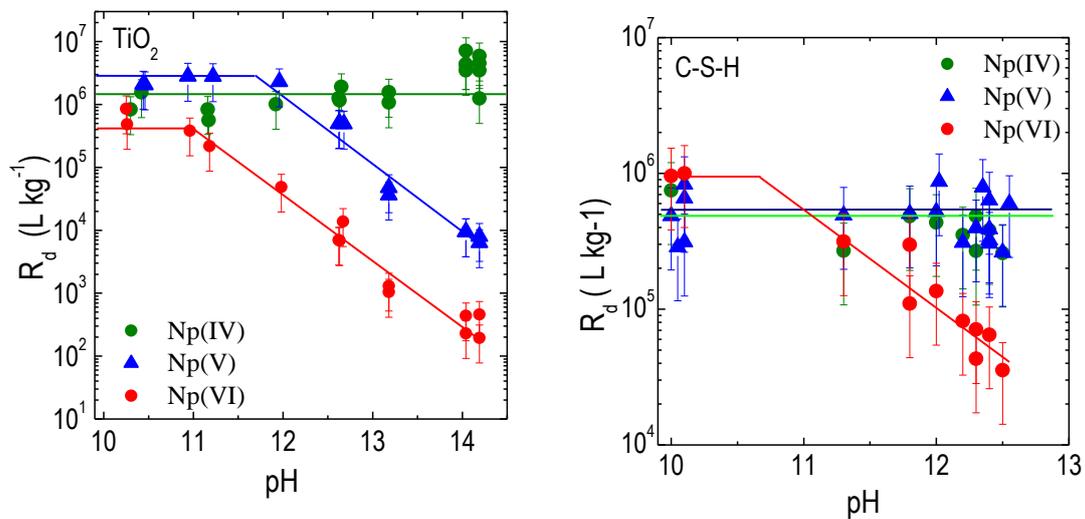


Figure 6: Effect of pH on the Np(IV,V,VI) sorption on TiO_2 (a) and on C-S-H phases (b). The S:L ratio = $2 \times 10^{-4} \text{ kg L}^{-1}$. $[\text{Np}] = 1.5 \times 10^{-10} \text{ M}$. I = 1.0.

References

- Carbol, P., Cobos-Sabaté, J., Glatz, J.-P., Ronchi, C., Rondinella, V., Wegen, D.H., Wiss, T., Loida, A., Metz, V., Kienzler, B., Spahiu, K., Grambow, B., Quiñones, J. and Martínez-Esparza, A. (2005). The effect of dissolved hydrogen on the dissolution of ^{233}U doped $\text{UO}_2(\text{s})$, high burn-up spent fuel and MOX fuel. SKB Technical Report TR-05-09.
- Demoisson, F., Mullet, M., Humbert, B. (2008). Pyrite oxidation in acidic medium: overall reaction pathway. *Surf. Interface Anal.* 40: 343–348.
- Descostes, M., Schlegel, M.L., Eglizaud, N., Descamps, F., Miserque, F., Simoni, E. 2010. Uptake of uranium and trace elements in pyrite (FeS_2) suspensions. *Geochim. Cosmochim. Acta* 74, 1551 (2010).
- Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K., Sasaki, T., Moriyama, H. (2005) Solubility of uranium(IV) hydrous oxide in high pH solution under reducing conditions. *Radiochim. Acta.*, 93, 347-350.



- Gaona, X., Dähn, R., Tits, J., Scheinost, A., and Wieland, E. (2011). Uptake of Np(IV) by C–S–H phases and cement: an EXAFS study. *Environ. Sci. Technol.*, Submitted.
- Gaona X., Tits, J., Dardenne, K., Liu, X., Rothe, J., Denecke, M.A., Wieland, E., Altmaier, M. (2012). Spectroscopic investigations of Np(V/VI) redox speciation in hyperalkaline TMA-OH solutions. *Radiochim. Acta*. Submitted.
- Holgersson, S.: On the use of actinides as redox tracer elements in groundwater samples. S/T contribution to 4th ReCosy workshop, Karlsruhe 23rd-26th March, 2012.
- Hummel, W. (2009). Ionic strength corrections and estimation of DIT ion interaction coefficients. PSI Technical Report, TM-44-09-01, Paul Scherrer Institut, Villigen, Switzerland.
- Neck V., Altmaier M., Fanghänel T. (2007) Solubility of plutonium hydroxides/hydrous oxides under reducing conditions and in the presence of oxygen. *C. R. Chimie*, 959-977.
- Ollila K. (2002) Uranium solubility. In: Nuclear Waste Managements in Finland. Finalreport of Public Sector's Research Programme, JYT 2001 (Ed. K. Rasilainen), Ministry of Trade and Industry, Helsinki, Finland, pp. 77-79.
- Rai, D., Felmy, A. R., Ryan, J. L. (1990) Uranium (IV) hydrolysis constants and solubility product of $UO_2 \cdot xH_2O(am)$. *Inorg. Chem.*, 29, 260-264
- Riba, O.; Montoya, V.; Grivé, M.; Duro, L. (2012). Uranium solubility under alkaline conditions using different reducing agents. Scientific and Technical Contribution, Recosy (in preparation).
- Ryan, J. L., Rai, D. (1983) The solubility of uranium(IV) hydrous oxide in sodium hydroxide solutions under reducing conditions. *Polyhedron*, 2, 947-952.
- Scholz, F., Meyer, B. (1998). Voltammetry of solid microparticles immobilized on electrode surfaces. In: *Electroanalytical Chemistry, A Series of Advances* (A.J. Bard, I. Rubinstein, ed.) Marcel Dekker, Vol. 20, pp. 1-86.
- Stockdale, A., Brian, N., Lofts, S. 2011. Estimation of model VII humic binding constants for Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and PuO_2^{2+} . *J. Environ. Monit.*, 2011, 13, 2946–2950.
- Torrero, M. E. (1995) Estudio de la disolución del UO_2 como análogo Químico de la matriz del combustible nuclear gastado. Influencia de los principales parámetros fisicoquímicos que definen los repositorios en medios salino y granítico. Universidad de Barcelona, Thesis, Barcelona, Spain.
- Wieland, E. and van Loon, L. R. (2002). Cementitious Near-Field Sorption Data base for performance Assessment of an ILW Repository in Opalinus Clay. PSI Report. Nr. 03-06, Paul Scherrer Institute, Villigen-PSI, Switzerland and Nagra Technical Report NTB 02-20, Nagra, Wetztingen, Switzerland
- Yajima, T., Kawamura, Y., Ueta, S. (1995) Uranium(IV) solubility and hydrolysis constants under reduced conditions. *Sci. Basis Nucl. Waste Management XVIII*, Symp. Proceedings, 353, 1137-1142



Acknowledgements

Manchester university would like to thank the United Kingdom Engineering and Physical Sciences (DIAMOND Universities Consortium) and Natural Environment (BIGRAD Consortium) Research Councils for funding this work.