



State of the Art

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REDOX PHENOMENA CONTROLLING SYSTEMS ReCosy

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PU Public

RE Restricted to a group specified by the partners of the project

CO Confidential, only for partners of the project

X



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The objective of this deliverable is to document the state of the art of the research subjects within Recosy before the start of the project. This will facilitate the identification of the contribution that the Recosy work programme and outcome will make to the improvement of the knowledge in each one of the research issues included in the project.

The harmonization and documentation of the advance of the project is developed within WP1 and many of the activities within this WP are related with each other to ensure that the project is consistent from a documentation perspective.

One of the main activities during the first 10 months of the project was to prepare a questionnaire for the partners to inform about specific systems that will be studied under each one of the research activities planned. The questionnaire included questions such as type of redox couples to study, techniques used, expected outcome, etc... All partners gave their answers and a detailed work of analyses of the information was conducted, that permitted the classification and grouping of the different activities to be developed within each workpackage. The documentation of the answers from the questionnaire are included in deliverable D1.1. of the project.

Once the analyses of the questionnaire was finalized, and the activities grouped within each work package, the partners were asked to prepare a very short contribution that will constitute a reference document to set the state of the art of the knowledge in each one of the research subjects and to monitor the contribution of the research within Recosy to improve the knowledge in the areas identified.

The following different areas of research were obtained from the analyses of the questionnaires treated in D1.1:

WP2. Development of redox determination methods

1. Quantification of the redox potential for the reduction of Np(V) to colloidal Np(IV) in non-complexing aqueous solutions at pH 5 – 10
2. Redox state determination in hyperalkaline solutions by speciation of Selenium
3. Redox measurements in specific electrodes (clay pastes or pyrite) particularly when exposed to redox perturbations
4. Determination of oxygen concentration and redox potential in biofilms
5. Measurement of redox potential in brines
6. Optical sensing – expectations, hopes, and limitations
7. Use of amperometry on the determination of redox states. State of the art

WP3. Redox response of defined and near-natural system

1. Response of crystalline environment to redox perturbation
2. Response of clay environment to redox perturbation
3. Role of Fe/S system(s) in buffering the redox state in natural systems
4. Role of microbes in redox processes
5. Incorporation of reducing capacity concept in reactive transport simulations

WP4. Redox reactions of radionuclides.

1. Interactions of soluble species of selenium, iodine, and uranium with pyrite



2. Redox Speciation of Tc, Np, and Pu
3. Determination of redox state of investigated system and redox sensitive elements with relevance to a crystalline rock environment
4. The Prediction of Radionuclide-Humic Acid Speciation and its Effect upon Transport
5. Tc and Anthropogenic Organic Ligands
6. Redox behaviour of Uranium under hyperalkaline conditions
7. State of art - Pu oxidation-reduction
8. Uptake of Np(IV) and Np(V) by cementitious materials under controlled redox conditions
9. Determination of redox processes of radionuclides in biofilms

WP5. Redox processes in radionuclide transport

1. Determination of diffusion parameters of redox sensitive radionuclides through clay formations)
2. Redox processes affecting the migration of radionuclides
3. Relevance of redox condition for phosphogypsum wastes

WP6. Redox reactions affecting the spent fuel source-term.

1. Corrosion of spent fuel in presence of corroding Fe
2. Influence of redox sensitive metals in the fuel
3. Corrosion of spent fuel in presence of H₂
4. The effect of iron corrosion on spent fuel dissolution – the state of the art
5. Reductive Trapping of Actinides in Container Corrosion Products during Spent Fuel Corrosion

The detailed texts on the state of the art of each research subject are presented in the following sections.



WP2. Development of redox determination methods

State of the art

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Quantification of the redox potential for the reduction of Np(V) to colloidal Np(IV) in non-complexing aqueous solutions at pH 5 – 10

FZK-INE

In geochemical systems of nuclear waste repositories, the migration behaviour of neptunium depends primarily on its oxidation state, either +V or +IV. Under most conditions Np(V) is highly soluble and mobile whereas Np(IV) is very immobile because of its high tendency towards sorption and the low solubility of $10^{-(9\pm 1)}$ M in the near-neutral pH range [1, 2]. The reduction of Np(V) has been investigated in numerous studies, for instance in site-specific groundwater systems containing the reducing sediments [3], humic substances [4, 5] or dissolved iron and iron minerals [6, 7]. However, the experimental observations are usually described phenomenologically. The goal of the present study is to explore whether there is a well-defined redox potential for the reduction of Np(V) in aqueous solution and to quantify the redox process. For this purpose we performed a systematic study on the reduction of $3.5 \cdot 10^{-5}$ M Np(V) solutions in the pH range 5 - 10 in non-complexing 0.1 M NaCl solutions under Ar atmosphere. To cover a wide range of chemically different reducing systems, the redox behaviour of Np(V) was studied in numerous homogeneous solutions and heterogeneous suspensions containing 1 - 2 mM additions of $\text{Na}_2\text{S}_2\text{O}_4$, Fe(II)/Fe(III) buffers (10:1), metallic iron powder, magnetite $\text{Fe}_3\text{O}_4(\text{cr})$, hydroquinone and sodium anthraquinone / anthrahydroquinone disulfonate (AQDS/AH₂QDS) redox buffers.

In more than 20 solutions and suspensions the reduction process was monitored as a function of time (up to 100 - 300 days) by the decrease of the aqueous Np(V) concentration determined after removal of colloidal Np(IV) particles by 10 kD ultrafiltration. The values of $\text{pH} = -\log a_{\text{H}^+}$ (activity scale) were determined with combination pH electrodes (type ROSS, Orion) calibrated against standard pH buffers. Redox potentials were measured with a combined Pt and Ag/AgCl reference electrode (Metrohm) calibrated against commercial redox-buffers. The measured potential is converted into E_{h} vs. SHE by correction for the potential of the Ag/AgCl reference electrode. The apparent electron activity ($\text{pe} = -\log a_{\text{e}^-}$) is calculated from $E_{\text{h}} = -(RT/F) \ln a_{\text{e}^-}$ according to the relation: $\text{pe} = 16.9 \cdot E_{\text{h}}(\text{V})$ at 25 °C.

The experimental results indicate that the redox potential of $E_{\text{h}} = 0.01 \pm 0.02$ V ($\text{pe} = 0.15 \pm 0.35$) is a general border for the reduction of $\text{NpO}_2^+(\text{aq})$. Regardless of the reducing agent and whether the system is homogeneous or heterogeneous, Np(V) is found to be stable at $E_{\text{h}} \geq 0.03$ V ($\text{pe} \geq 0.5$) and reduced to Np(IV) at $E_{\text{h}} \leq -0.01$ V ($\text{pe} \leq -0.2$). The more negative the redox potential the faster is the reduction.

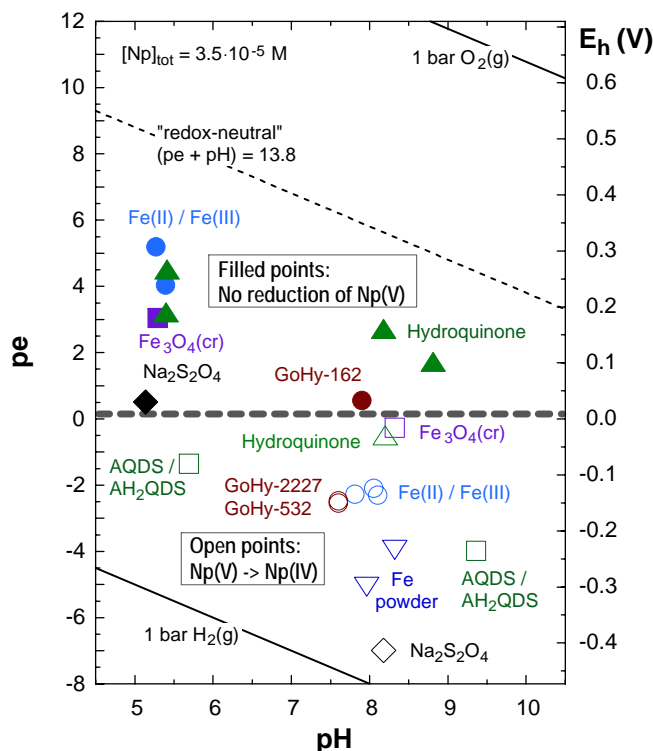
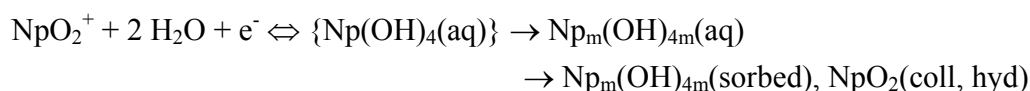


Fig. 1. Experimental studies on the reduction of Np(V) in 0.1 M NaCl (p.w.) and in dilute Gorleben groundwaters (GoHy) [4, 5]. In the systems shown as open symbols Np(V) is reduced to colloidal Np(IV), in the systems shown as filled symbols Np(V) is not reduced within the time of investigation (≥ 100 days).

The observed borderline for the reduction of Np(V) is about 0.35 V (6 pe-units) lower than the Np(V) / Np(IV) borderline usually calculated in a Pourbaix (E_h -pH) diagram for $[Np]_{tot} = 3.5 \cdot 10^{-5}$ M from the redox couple $NpO_2^+(aq) / NpO_2(am, hyd)$. The experimental border does not refer to the reaction $NpO_2^+ + e^- \rightleftharpoons NpO_2(am, hyd)$ but rather to an initial reduction step from $NpO_2^+(aq)$ to $Np(OH)_4(aq)$ or small polymers $Np_m(OH)_{4m}(aq)$. However these polymers undergo further agglomeration to colloidal $NpO_2(coll, hyd)$ particles and are sorbed on the container walls or solid phases present in heterogeneous systems. The reduction of Np(V) is probably a complex process including consecutive and/or parallel reactions:



Therefore, the observation that Np(V) is reduced in the presence of corroding iron powder or Fe(II)-bearing solid phases does not necessarily mean that the reduction process is a surface



reaction as concluded previously [6, 7]. Under the same redox conditions (p_e and pH) in homogeneous solutions, $Np(V)$ is reduced as well. Vice versa, above the borderline of $p_e = 0.15 \pm 0.35$, $Np(V)$ is neither reduced by $10^{-3} M Fe^{2+}$ in solution nor in an investigated $Fe_3O_4(cr)$ suspension at $pH \approx 5$.

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Redox state determination in hyperalkaline solutions by speciation of Selenium

ARMINES

Selenium is a redox sensitive element existing in aqueous solutions in the redox states –II (organic and inorganic), IV and VI and in the solid state as well as Se(0). It is of large radiological concern, due to the relative high mobility of both Se(IV) and Se(VI) in natural water environments. Laboratory experiments show that even at high Se concentrations over a wide range of pH the Pt electrode is completely insensitive to the relative abundance of dissolved Se(VI) and Se(IV) (Runnells and Lindberg 1990). Hence, Se speciation cannot be deduced directly from Eh measurements with Pt electrodes and geochemical equilibrium calculations. This indicates that under certain conditions the Pt electrode measured Eh does not correspond to a “master variable” of the redox system. It is for example often observed that dissolved oxygen and organic carbon are together present in a groundwater system even though they are not in mutual thermodynamic equilibrium (Washington, Endale et al. 2004). This clearly points to the need of direct measurement of solution speciation to assess the redox state relevant for Se speciation.

A full review of the chemical thermodynamics of selenium in aqueous/solid systems has recently been presented by the NEA-TDB project (Olin, Noläng et al. 2005). However, no thermodynamic data were proposed for ion pairs of the form $X(\text{SeO}_3)$ where X could be Ca or Mg. Thermodynamic data were proposed by (Liu and N. 1994) . For CaSeO_3 a formation constant of $\log K=3.17$ was proposed. It recently has been observed that the effect of Ca concentrations on the sorption behaviour of Se(IV) on bentonite could only be explained by the assuming the presence of a neutral CaSeO_3 complex (Alhajji 2007). A formation constant of $\log K = 4$ provided a good representation of the experimental data. Similarly, in hyperalkaline solutions in contact with cement pastes, adsorption behaviour of Se(IV) could only be explained by assuming presence of a CaSeO_3 complex (Macé 2006). However, a detailed study of the formation constant of the CaSeO_3 complex is still missing.

Solution speciation and redox state formation from speciation in hyperalkaline solution will further be complicated by the formation of polyselenide species such as $\text{Se}^{-2} \text{Se}^{-2}$, Se^{-2} with important stability in the pH range $>\text{pH } 8$. These ions have formal oxidation states between 0 and –II.



Polymer species will strongly reduce the stability field for Se(0, triclinic). Essentially, in the interesting hyperalkaline pH range between pH 11 and 13, no Se(0, triclinic) will be formed. Even further reduced is the probability to form monoclinic Se(0).

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Redox measurements in specific electrodes (clay pastes or pyrite) particularly when exposed to redox perturbations

BRGM

Redox is one of the main factors affecting the migration of redox-sensitive radionuclides. The mobility of critical chemical species differs greatly depending on their redox state (e.g. TcO_2 vs. TcO_4^- , I^- vs. IO_3^-). It is thus of great interest to investigate the redox reactivity of the formation, particularly when exposed to redox perturbations such as plumes of redox-influencing substances (i.e. nitrates) or O_2 diffusion in the claystone formation following the construction and ventilation of tunnels and galleries. The formation is known to be an anoxic and reducing system containing pyrite, iron carbonate, iron(II)-bearing clay minerals, and organic matter. These four components account almost entirely for the total reduced capacity (TRC) of the rock (1-2). Using a thermodynamic equilibrium approach, one can consider that the totality of these components could oxidise in response to a redox perturbation. However, redox reactions are complex phenomena that are dominated by kinetics rather than thermodynamics. As an example, pyrite can exist as a metastable mineral due to a surface coating of oxidation products such as iron oxy-hydroxides. Redox systems thus have to be considered both in terms of redox potential (thermodynamics) and redox reactivity (kinetics).

The redox reactivity (kinetics and thermodynamic redox potential) of the Callovian-Oxfordian rock (COX) samples are already under study by BRGM using microscopic, spectrometric and wet analysis techniques. In order to cross and overcome certain limits by improvement in the knowledge, in the frame of RECOSY, BRGM propose to complete the description of the COX formation by investigating the redox (potential and reactivity) of its various mineral components. This must be taken into account, e.g. in order to obtain reliable models of the porewater's chemical composition.

The main objective is to retrieve the electrochemical kinetics of the COX system in contact with different plausible redox perturbations by using:

- i) specific electrodes built out of COX rock samples and individual redox reactive minerals that constitute the COX, and
- ii) diverse electrochemical techniques.

These specific electrodes will be devoted to the deepening of the electrochemical behaviour of the COX system in different situations. As a consequence to the methods for predicting the evolution of redox conditions in the host rock of the deep repository, we aim to design and



experience sensors based on reliable and robust concepts able to observe evolutions in the underground environment during a part of its planned secular duration.

The BRGM has long experience in the field of the materials behaviour, which they are metal (3-10) or minerals (11). It also acquired a good knowledge in the field of the chemical sensors and biosensors (12-15). Phenomenology, chemical and geochemical modelling are also some of the domains where the BRGM built its reputation (16-17). The study of the many deep environments and more particularly, that of the Dogger of the Paris Basin (18-19) and Callovian-Oxfordian of the Bure site (1-2), enabled him to acquire a lot of experience.

Historically, the redox state is the ratio of the (interconvertible) oxidized and reduced form of a specific redox couple. Nowadays, the redox state of a redox couple is defined by the half-cell reduction potential and the reducing capacity of that couple. This new definition of redox state better represents concentration-dependent redox couples. Thus, the term redox state should be reserved to reference specific redox couples and is best expressed through the use of the Nernst equation. Nowadays, it is inappropriate to use the term redox state with systems that have many linked redox couples, the use of redox environment for these systems is more suitable. The redox environment of a linked set of redox couples (as found in the COX system) is the summation of the products of the reduction potential and reducing capacity of the linked redox couples present.

Many tens of articles present the manufacture of electrodes in clay paste, pyrite etc. in order to determine the electrochemical behaviour of these electrodes in the medium where they are immersed. The theory of the conduction of different metals, oxides, hydroxides, sulfides, as well as the electrode performance and the interfacial electrochemistry in solid electrodes is reported, among others, in five books (20-24). As a rule, when measuring the redox potential of a given solution, the indicating electrode must satisfy a vital condition: it must be inert and unattackable. Whereas Pt or Au electrodes meet this requirement, the same cannot be said a priori of a pyrite or of a clay paste electrode. The central idea is that, after having confirmed the proper behaviour of the new constructed electrodes (pyrite or clay paste electrodes), their use in the actual COX system will be considered, implicitly assuming that their behaviour, despite their larger exposed area, would be identical and hence representative of, or at least similar to that of each of the grains consisting of the COX material. Concerning the prediction of the COX and of the hidden material's behaviour in contact with different plausible redox perturbations, electrochemical techniques are suitable in the condition of having specific electrodes even in a case where the system is not electrochemically reversible. Electrochemistry, with its established formalisms and



its more or less sophisticated techniques (Open circuit potential, cyclic voltammetry, Electrochemical Impedance Spectroscopy,..) offers a lot of potential for rapid and controlled tests and allows us to access to the electrochemical kinetics of a system.

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Determination of oxygen concentration and redox potential in biofilms

FZD

In recent years, a range of microsensors studies were carried out to measure in situ microbial activities and microbial metabolic processes in biofilms. But investigations of the influence of toxic heavy metals on the metabolic activity of biofilms using microelectrodes are sparse. Notwithstanding their importance as essential micronutrients, heavy metals are toxic to microorganisms at higher concentration because of their adversary binding to enzymes and DNA (Schmidt et al., 2005). Despite the importance of microbial responses to toxic heavy metals in environmentally relevant concentrations, there is little information on this issue. A study of the impact of Zn and Ni on microbial benthic communities was conducted by Viret et al. (2006) estimating the oxygen consumption on the basis of microsensor profiles. In a recent study by Krawczyk-Bärsch et al. (2008) the metabolic response of stable multispecies biofilms on the stress factor uranium, was studied for the first time by electrochemical oxygen microsensors. The studied biofilms were grown in the laboratory biofilm reactors at the air/liquid interface and exposed to uranium in ecologically relevant concentrations (1×10^{-5} and 1×10^{-6} M), e.g., in seepage water of Schlemma/Saxony, Germany. The microsensor profile measurements in the stable multispecies biofilms exposed to uranium showed that the oxygen concentration decreased faster with increasing biofilm depth compared to the uranium free biofilms. The fast decrease in the oxygen concentrations in the biofilm profiles showed that the bacteria in the top region of the biofilms, i.e., the metabolically most active biofilm zone, battle the toxic effects of aqueous uranium with an increased respiratory activity. This increased respiratory activity results in oxygen depleted zones closer to the biofilm/air interface which may trigger uranium redox processes, since suitable redox partners, e.g., extracellular polymeric substance (EPS) and other organics (e.g., metabolites), are sufficiently available in the biofilm porewaters. Such redox reactions may lead to precipitation of uranium (IV) solids and consequently to a removal of uranium from the aqueous phase.

Within the framework of ReCosy first comparative investigations of electrochemical and fiber-optic sensors were performed in collaboration with the University Potsdam (UP). Fiber-optic sensor measurements in biofilms have some advantages compared to those made by electrochemical microelectrodes. As described in Beyenal et al. (2000) fiber-optic sensors are immune to environmental changes in pH, salinity, and ionic strength and immune to interference from moisture, carbon dioxide, methane, and other substances. A range of fiber-optic sensor studies



were carried out to measure in situ geochemical gradients in biofilms (e.g. Ganesh, A.B. et al., 2008; Klimant, I. et al., 1997; Gruber, W.R. et al., 1993, Kohls, O., 2000). To our knowledge optical sensors applied to biofilm samples exposed to heavy metals are so far not reported in the literature. In our first collaboration with the UP we compared the oxygen concentration profiles obtained by electrochemical and optical microsensors, respectively. Oxygen concentration profiles were measured in the biofilms by electrochemical microsensors of the Clark design (Unisense, Denmark). These Clark-type oxygen microsensors are generally used for microbial ecology studies and contain a guard electrode (Revsbech, 1989, 2005). They have a tip diameter of 10 μm , a stirring sensitivity of <1–2%, and a response time of <1 s. The used multispecies biofilms (microbial diversity described in Krawczyk-Bärsch et al., 2008) were cultivated in the laboratory under non-sterile conditions in different biofilm reactors. One biofilm reactor was adjusted to a uranium concentration of (1×10^{-5} M), which is typical for uranium contaminated sites. The data achieved from both sensor methods are directly comparable. Fiber-optic sensor measurements showed high concentrations of oxygen over the total thickness of the biofilms, which were not in contact with uranium. In contrast, biofilms exposed to uranium revealed a much lower oxygen concentration in the bottom parts of the biofilm as described before in Krawczyk-Bärsch et al. (2008). Already at a depth of approximately 400 μm no oxygen was detectable. The comparative studies revealed that depending on the existing environmental conditions during the measurements a decision for the appropriate method is possible. However, further developments, e.g. miniaturization of the sensor equipments, are needed and aimed for within ReCosy.

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Measurement of redox potential in brines

GRS

Redox potentials in aqueous media are most commonly measured by determining the electric potential between a platinum metal electrode and a reference electrode (e.g. Ag|AgCl). In natural systems there are generally more than one redox couple present and most of them are in disequilibrium. It follows that an aqueous system has not only one redox potential but several potentials specific for each redox couple present. Unfortunately a redox electrode can measure only one potential that consequently must be regarded as a somehow mixed product of the individual redox couple potentials. But how do the redox couple potentials contribute to the apparent electrode potential? Measurements in natural media showed that the apparent electrode potential is more closely to the Fe²⁺/Fe³⁺ redox couple potential than to any other. This is probably due to the relatively fast electron exchange between the two species. Other researchers found that the platinum electrode acts as an iron specific electrode after Fe²⁺ has been oxidized to Fe³⁺ and subsequently precipitated as Fe(OH)₃ on the platinum surface (Doyle , 1968; Lindberg and Runnels, 1984; Runnels und Lindberg 1990)

There is no information if and how the measured potential of the platinum electrode and the reference electrode is altered by the presence of high concentration of inorganic salts. In principle both electrodes could be affected.

The reference electrode by changing liquid junction potentials at the interface between reference solution (e.g. 3 M KCl) and the measuring solution as it is been observed in pH measurements

The platinum electrode by influencing or even inhibiting the electrochemical surface reactions

Another method for accessing element specific redox potentials is by species analysis. A large number of different analytical approaches exist (Cornelis, 2005), but in our study we concentrate on spectrophotometric methods with UV-VIS complexing active agents like phenantroline, ferrozine or thiocyanate. Phenanthroline and ferrozine are both used for determining the Fe²⁺ concentration and, by adding a reducing agent, the total amount of iron. According to Anastácio et al. (2007) the phenanthroline method is more reliable. Ferrozine also forms a complex with Fe³⁺ which can be photochemically reduced to the Fe²⁺-complex. This often leads to an overestimation of the Fe²⁺ concentration. Thiocyanate is used for the quantitative analysis of Fe³⁺. Methods like these have been in use in water analysis since a long time but there has been no application to brines with trace iron concentrations.



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Optical sensing – expectations, hopes, and limitations

UPPC

The use of light (photons) in science, technology, and society is playing a major role in the 21st century. Photonics and optics as the major constituents of optical sciences encompass fundamental and applied research on the interaction between light and matter. Comparable with electronics as a key technology of the 20th century, photonics is now widely recognized as the dominating driver of the 21st century. This has been already recognized in national as well as European programs (such as Photonics21). Fundamental research in this area is paramount and forms the basis for future innovations in life science, medicine, geological and environmental monitoring, material sciences, process control, remote sensing, chemistry, and many others.

Optical fiber-based sensing applications for environmental monitoring are in particular interesting, when prerequisites for the measurements are i) remote and in-situ capabilities, ii) on-line monitoring, and iii) measurement under extremely harsh conditions are key parameters for a successful analysis.

The fiber-based detection of physical parameters like temperature, moisture, and tension is already on-hand. The fundamental sensing principles are based i) on changes in length of the fiber due to temperature or tension influence, ii) back scatter of light in optical time-domain reflectometry (OTDR) applications, or iii) on alterations of the evanescent field (e.g., due to variations in water content of the fiber-surrounding medium). Variations in length or bending of the fiber can be detected with outstanding sensitivity. In combination with Fiber-Bragg gratings (FBG) alterations in the sub-ppm range can be monitored – over distance of several kilometres. FBG are periodic structures imprinted in special optical fibers. Depending on the intrinsic structure certain wavelength are reflected. In case of length variations of the fiber (due to tension or temperature change) the reflected wavelength is changed. OTDR is based on the fact that part of the light travelling inside a fiber-optical device is scattered (e.g., due to the presence of tiny amounts of impurities or defects in the fibers). The scattered light contains contributions from Rayleigh, Stokes, and Anti-Stokes scatter. Based on the intensity ratio of Stokes and Anti-Stokes scatter (Raman effect!) the temperature at the origin of the scatter event can be calculated. In combination with a time-resolved detection scheme, high-resolution temperature profiles over tens of kilometres can be measured. Upon removing the cladding of an optical fiber part of the light can penetrate into the surrounding medium (tunnel effect) depending on parameters like the



refractive index of the surroundings the light inside the fiber is altered, e.g., attenuated. The degree of attenuation can subsequently be used to monitor variations in physical parameters such as moisture.

The application of fiber-based sensing of physical parameters is already at an advanced level and is applied in many areas of everyday life. Optical fibers are implemented and used in such diverse areas as monitoring of cracks in concrete (e.g., buildings, bridges), in aircrafts, for the detection of extreme temperatures (such as combustion processes or in accelerators) or in the exploitation of oilfields.

On the other side the optical fiber-based monitoring of chemical parameters (fiber-based optical chemical sensing, FOCS) is much more heterogeneous with respect to its application level. In combination with specific probes, such as fluorescence tracers, so-called optodes are created and in combination with multi-channel detection, optical fiber-based sensing of chemical parameters can be developed. Key parameters such as oxygen concentration and pH value can be measured in-situ and in-line prerequisites for innovative environmental monitoring and process control (e.g., along the food chain in order to improve food safety and traceability).

While the detection of oxygen in biological systems even down to the cellular level is commercially available, FOCS based applications for monitoring of other chemical parameters such as cations or Eh are at its infancy. The outstanding potential for miniaturisation of FOCS based applications is demonstrated by in-vivo sensing of chemical parameters in cells and has been proven a powerful alternative to electrochemical-based techniques. In case of oxygen detection standard electrochemical techniques are based on a Clark-type electrode design, which inherently consumes part of the analyte during the measurement. In contrast, FOCS are based on luminescence measurements and are free of analyte consumption, which can be an advantage especially for oxygen sensing in very small compartments like cells. The detection scheme is based on the luminescence quenching of a Pt-complex by molecular oxygen. Using dual-phase modulation (or dual lifetime referencing) the often encountered problems arising from strong unwanted background signals (e.g., in biological matrices often chlorophyll is present in the sample) are effectively circumvented. Compared to electrochemical approaches FOCS may have further advantages with respect to miniaturization potential, durability of the sensors, response time, and costs.

Although suitable chemical probes for the detection of a wealth of chemical parameters are



commercially available, their integration in FOCS schemes is just beginning. The difficulties to overcome in the future are i) the integration of the particular chemical probe into a suitable polymer matrix (such as it is permeable for the analyte molecules, but at the same time sufficiently retarding the probe molecules), ii) the attachment of the polymer sensor to the optical fiber with efficient signal transduction, iii) reduction of cross-sensitivity for other compounds present in the sample, and iv) the further adaptation of detection electronics (e.g., MHz to GHz modulation frequencies). Due to the outstanding potential for miniaturization, multiparameter detection, and distributed sensing tailor-made FOCS solutions for specific needs of systems investigated can be envisaged. In combination with the development of new fiber materials such as hollow core fibers or other metamaterials the potential for innovative sensing schemes can only be anticipated.



Use of amperometry on the determination of redox states. State of the art

CNRS, LCPME

Our objective in this work is to develop an amperometric method of determining redox potentials by means of Ultramicroelectrodes (UMEs). In this report we will consider successively: i) the state of the art in the direct determination redox potentials using potentiometry, ii) the particular properties of UMEs, their advantages and disadvantages and iii) as to our knowledge an amperometric method for the determination of redox potentials has never been reported, we will present the way of our scientific reasoning.

Potentiometric measurement of redox potentials

The book "Redox: Fundamentals, Processes and Applications" Schüring et al. (1999) constitutes an excellent collection of review articles which provide a complete state of the art on the determination of the redox potential in general and more especially sediments and natural waters. The two first chapters, written respectively by L. Sigg and H. Galster, are a mine of information on several aspects, theoretical and practical, on the redox potential measurement.

In this way we have to keep in mind the following points:

- The redox potential is based on the concepts of equilibrium thermodynamics and it can only be measured at equilibrium.
- A potentiometric electrode is neither allowed to react with parts of the solution nor to have any catalytic effect on an equilibrium in the solution.
- To ensure an adequate potential measurement, the exchange current has to be different from zero. (the electrochemical kinetics of the redox system has to be fast): Fe(II)/(III) in acidic solution or Fe(CN)₆⁴⁻/3⁻).
- The measurement of a redox couple which has the greater exchange current is less influenced by other systems having a smaller exchange current. An irreversible system causes only small exchange currents by itself, therefore it can influence the measurements only when it is catalysed by the electrode.
- Several reversible redox systems might react simultaneously in the same solution and contribute to an equilibrium with defined potential.
- O₂/H₂O, NO₃⁻/N₂, NO₃⁻/NH₃⁺, SO₄²⁻/HS⁻ and CO₂/CH₄, are very slow reactions. The corresponding exchange currents are insufficient to establish a stable potential.



- Monovalent electron transfers are faster than multivalent transfers.
- Electron transfers between complexated molecules or ions run faster, because their configuration remains unchanged. Organic redox couples are reversible, when the transfer is followed only by a negligible change of structure: quinone/hydroquinone and ascorbic acid/hydroascorbic acid.
- Among the redox couples in natural waters, Fe(II)/(III) is the most important one that exchanges electrons at an electrode at sufficient rates, especially at low pH.
- A reliable redox potential measurement requires that equilibrium is established not only at the electrode surface, but also among the various redox couples in solution. Furthermore, this condition is often not fulfilled in natural waters, because most redox reactions have slow kinetics.
- Examination of measured redox potentials shows that the measured values are most often in discrepancy to the calculated redox potentials on the basis of chemical analysis.
- More reliable electrochemical Eh measurements in natural waters may be obtained under conditions where the Fe(II)/(III) system is predominant: $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + \text{e}^- \leftrightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$
- In most cases detailed chemical analysis of natural waters with respect to several redox species therefore give a more reliable description of the redox conditions.
- Pt-oxides are capable of conducting electrons and they do not directly influence the adjustment of redox potential, but they do increase the equilibration time with the solution is reached.
- Measurements of the redox potential of dissolved oxygen are always incorrect. This follows from the simultaneous electrode reactions: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$ and $\text{PtO} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{Pt} + \text{H}_2\text{O}$.
- Pt-oxides must be removed. The redox potentials in groundwaters being smaller than that of all Pt-oxides.
- Some authors recommend to reduce the oxides on the electrode using chemical agents, e.g. sodium sulfite, sodium hydrogensulfite, or ascorbic acid, but every reduction turns platinum into a fine powder. Repeated applications can enlarge the catalytic activity of platinum. The same is true for cathodic reduction by applying a voltage. It is better to reduce only to the level of the probable measuring potential.
- In-situ measurements are even better, if possible, one should measure in a flow-through mode.

Ultramicroelectrodes (UMEs)

The information contained in this rubric comes from the review 'Voltammetry at Ultramicroelectrodes', by R.M. Wightman and D.O. Wipf (1989); the book 'Microelectrodes: Theory and Applications' Montenegro et al., (1991), and from our own experience.

Usually UMEs are prepared by sealing in glass fine metallic wires as Pt, Au, glassy carbon.



Typical wire diameters are in the range of 0.1 to 50 μm . The active area of the UME is the cross section of the metallic wire. When the dimensions of an electrode are decreased from the millimetre to the micrometre scale, many changes occur in their voltammetric behaviour and use.

✓ The currents measured are very small (in the nA to pA range). However, CNRS/LCPME has already used UMEs for in-situ amperometric measurements with remote control in various media just as well in the laboratory as in nuclear plants (collaboration with EDF) and particle accelerators. In this last case, UMEs were used for both amperometric and potentiometric measurements.

✓ The steady state diffusion is spherical (convergent diffusion) and therefore:

- i) the current density is very high, the smaller the electrode the higher the density, (factor 100 between a 1 μm UME and a classic rotating disc electrode) and the sensitivity is quite better
- ii) UMEs tend to be immune to convection (flow-rate independent)
- iii) the effects of catalytic reaction are less apparent.

✓ Ohmic drop is dramatically reduced and voltammetric curves are not distorted even if the electrolyte level is very low. Moreover, experiments can be performed in pure deionised water without electrolyte addition. In this way, electrochemistry becomes a non-invasive technique like spectrometry.

✓ The UMEs capacitance is reduced and therefore:

- i) improvement in the faradaic/charging current ratio in steady state conditions that allows the shortening of the duration of voltammetric experiments by increasing the scan rate
- ii) pulsed techniques are more successful

✓ Because of their small size (submicrometric tips can be prepared) UMEs are useful tools for determinations in low volumes of samples (fluid inclusions included).

✗ There is a risk of complete passivation of the UMEs by deposition of solid microparticles on the active surface area. However, this kind of passivation happens rarely.

✗ UMEs of very small size are very fragile.

Amperometric determination of redox potential using ultramicroelectrodes.

The quantitative determination of the two components of a redox couple, or the estimation of their ratio, is likely to provide in-situ measurement of the solution potential. The couple can be selected in the system or added as an indicator. This determination can be performed not only spectrometrically but also electrochemically using voltammetric techniques.

The voltammetric techniques have over the potentiometric ones some advantages:

- The amperometric response of an electrode varies linearly with the concentration (as the spectrometric one) whereas the potentiometric response varies logarithmically.
- A possible small instability or drift of the reference electrode has virtually no influence on current determinations, whereas they could be disastrous for direct potentiometric measurements.
- Voltammetric determinations can be performed successfully even if the electrochemical



kinetics is not rapid.

- Voltammetric electrodes may be polarized for cleaning purposes or for avoiding the biofilm development.
- The record of a complete voltammogram is likely to give in situ information about the electrode “health”

Moreover, if UMEs are used:

- The signal/noise-ratio is excellent because of the high current density.
- The measurements can be performed, whatever the ionic strength (even in pure deionised water).

Therefore, the ultramicrochemical characterization of a solution or suspension may provide rapid information on the redox systems contained: number of species, estimation of the concentrations, electrochemical kinetics. More detailed measurements in the region near the zero current potential measurements are likely to bring details on the existence of a redox couple that can be used as an internal redox indicator. If it is the case, the potential conditions for optimum amperometric detection can be defined. If such a couple does not exist, an external indicator must be added in the medium. It will be chosen by considering the voltammetric curves.

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WP3. Redox response of defined and near-natural system State of the art

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State of the art of the knowledge on redox-controlling processes in crystalline rock environments and contributions from the Swedish Site Characterisation Program

UNIZAR

Despite the efforts made in different characterisation projects, our knowledge about the temporal and spatial distribution and evolution of the redox processes in deep groundwaters from crystalline rock systems remains considerably poorer than for other more accessible natural systems, like soils, sediments or shallow aquifers. In this context, both the main concepts and the methodological approaches derived from the study of those relatively well-known systems have been usually extrapolated to crystalline systems.

This extrapolation is especially clear for the more accessible data, like the dissolved redox-sensitive, metabolic-related species (e.g. O₂, Mn(II), NO₃⁻, Fe(II), SO₄²⁻, S(-II), CH₄, etc) used to identify the dominant redox processes. The behaviour of these species has been frequently interpreted in terms of the classification of redox environments proposed by Berner (1981) for the classical sequence of redox zones in marine sediments (e.g. Champ et al., 1979; Berner, 1981; Thorstenson et al., 1979; Stumm and Morgan, 1996; Langmuir, 1997, Kehew, 2001; Appelo and Postma, 2005). In this sequence of redox zones, organic matter reactivity is considered the ultimate engine that drives most redox reactions in aquatic systems (Appelo and Postma, 2005) and, therefore, the microbial metabolisms (and the competition between metabolically distinct groups of microorganisms for metabolic intermediates; Lovley and Goodwin, 1988) are at the base of these sequential successions of redox environments. In standard geochemical conditions (e.g. Stumm and Morgan, 1996), the sequence of TEA's (or of metabolic groups) is assumed to be O₂ (aerobic bacteria) > NO₃⁻ (nitrate reducing bacteria, NRB) > Mn(IV)-oxides (manganese reducing bacteria, MRB) > Fe(III)-oxides (iron reducing bacteria, IRB) > SO₄²⁻ (sulphate reducing bacteria, SRB) > CO₂ (methanogenic microorganisms). However, this approach has important limitations, some of them common to most aquifer systems and others more specific to the characters of the crystalline systems under study.

One of the main limitations is related to the need for a high spatial resolution in the sampling network. Short screens and small sample volumes are crucial in order to avoid mixing of groundwater from different redox zones and to define the dominant redox processes or the assignment of redox zones (Christensen et al., 2000). This need is especially critical in systems where horizontal and vertical variations may be significant, like the fractured crystalline systems studied in the Swedish Site Characterisation Program. Their complex paleohydrological history favours the existence of hydrogeochemical systems with local heterogeneities containing probably different redox environments. This situation difficults the use of the changes in concentration of redox-sensitive species along clear flow paths for the estimation of the dominant electron acceptor processes. Furthermore, the concentrations of dissolved species may change during drilling and sampling operations owing to the possible input of atmospheric oxygen and to mixing of pristine groundwaters with drilling waters or with waters from different depths as a consequence of pumping in the boreholes.

Other important limitations of the use of redox-sensitive species to infer the redox-controlling processes at different depths in crystalline systems are related to the influence of inorganic reactions in the dissolved contents of these species. Many biological and inorganic reactions occur in close proximity and even with mutually exclusive effects (e.g. elimination of dissolved sulphide by FeS precipitation). Moreover, many dissolved redox indicators may have an inorganic origin derived from "deep sources" (e.g. H₂, CH₄), from mineral dissolution (e.g. Fe(II), Mn(II), S(-II)) or even from inorganic reduction (e.g. Mn(II) derived from Mn(IV)-reduction by Fe(II) or H₂S). This situation makes very difficult the discrimination between



the organic and inorganic reactions taking place and the identification of the effects of each type of reaction in the bulk chemical analysis (Canfield et al., 1993). Furthermore, it critically affects the usual relationship established between the presence of dissolved indicators (e.g. Mn(II), Fe(II) or CH₄) and the existence of the corresponding microbiological processes (e.g. Mn(IV), Fe(III) reduction and methanogenesis, respectively; Thornton et al., 2001 and references therein).

Therefore, the evaluation of redox conditions based on measurements of dissolved redox-sensitive species should only be taken as merely indicative, especially if the spatial scale of groundwater sampling is small compared with the whole studied system. Estimations based only in groundwater composition may be erroneous or, at least, incomplete. On the other hand, the sequential scheme of redox or biogeochemical zonation is not always observed to hold. There is substantial evidence from field studies suggesting that, under anoxic conditions, some TEAPs can be used simultaneously by distinct microorganisms, promoting different types of overlaps or the inexistence of a clear segregation between different redox zones (e.g. Postma and Jakobsen, 1996; Jakobsen and Postma, 1999; Thornton et al., 2001; Park et al., 2006; Jakobsen and Cold, 2007).

Only an integrated analysis, combining the hydrochemical information with other data and criteria, can provide some restrictions to this complex situation. In this sense, microbiological analyses and mineralogical data can be used as extremely valuable sources of additional information, as already proposed by Christensen et al. (2000).

Microbial data from different boreholes and at different depths can contribute to ascertain the possible distribution of the redox zones in the studied crystalline systems and to know whether they are segregated and dominated by mutually exclusive respirative functional groups of microbes or not. On the other hand, diagnostic redox-related mineralogy can be used to identify the present (or past) redox processes (e.g. the presence of manganese and iron oxyhydroxides is necessary to support the metabolic activity of manganese and iron reducing bacteria, respectively).

The huge amount of hydrochemical, microbiological and mineralogical information obtained throughout the Swedish Site Characterisation Program offers a unique opportunity to fill the existing knowledge gap about the processes buffering the redox evolution of crystalline rock environments and the interactions between them. The identification of these processes is a crucial step for the understanding of the temporal and spacial variations in the redox conditions of this type of systems.

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The effect from microorganisms on the redox state of laboratory and natural systems

MICANS

Summary

Until summer 2008, Micans have worked in the laboratory with pilot tests of how microbial cultures of sulphate reducing bacteria influence the redox potential in the culture media. Site investigation data on the relation of microbial numbers and redox have been evaluated. Field experiments in the Äspö tunnel have generated data on the relation between sulphide, ferrous iron and microbes. It remains to correlate these observations to the evolution of redox potential. Pressure resistant *in situ* microelectrodes for pH and redox have been developed for up-coming field work in the Äspö hard rock laboratory tunnel environment.

Laboratory experiments up to summer 2008

Redox measurements were done in the laboratory under sterile controls and in growth tubes with sulphate reducing bacteria, growing on lactate or hydrogen with acetate. The oxygen-reduction potential (ORP) was measured with an ORP electrode Blue line 31 Rx from Schott Instruments. From these experiments we will be able to establish the effect from microbial processes on the redox state under *in vitro* conditions. Concentrations of hydrogen and sulphide both correlated with the redox. Consequently, microbial processes will influence several redox controlling species simultaneously. Their consumption of hydrogen will increase redox, while their production of sulphide counteracts this increase. The design of coming experiments will aim at separating these effects for modelling purposes.

Field observations and experiments up to summer 2008

Site investigation results from Forsmark and Laxemar

Micro-organisms are included in the hydrogeochemical modelling efforts in the ongoing Swedish programme to characterize potential sites for the geological disposal of spent nuclear fuel. During the site investigations for a nuclear waste repository in Forsmark and Laxemar, significant correlations have been found between the measured redox with the Chemmac redox electrodes and the number of sulphate reducing bacteria (See figure 1 below). The correlation is very clear for Laxemar, and obvious for Forsmark. The data was generated by two independent site organizations, so the data sets are independently representing two deep groundwater sites that differ in many aspects. One significant difference is that in Forsmark, opposite to Laxemar, iron and manganese reducing bacteria are numerous at redox values above 200 mV. Sulphate reducing bacteria appears to be an important component for the measured redox state in the studied deep groundwater.

Underground work in the Äspö hard rock laboratory at 450 m depth

Enumeration and cultivation methods for microorganisms were tested and evaluated on groundwater from boreholes at 450 m depth in the Äspö laboratory. A methodology that analysed microbial process rates was developed and tested under open and closed controlled *in situ* conditions in a circulation system situated 447 m underground in the MICROBE laboratory in the Äspö tunnel. The maximum sulphide and acetate production rates were determined to be 0.08 and 0.14 mg L⁻¹ day⁻¹, respectively (See Figure 2 below). The numbers of sulphide- and acetate-producing micro-organisms increased concomitantly in the analysed circulating groundwater. Flushing the sampled circulation aquifer created an artefact, as it lowered the sulphide concentration. Microbial and inorganic processes involved in sulphur

transformations are summarized in a conceptual model, based on the observations and results presented here. The model outlines how dissolved sulphide may react with ferric and ferrous iron to form solid phases of iron sulphide and pyrite. Sulphide will, consequently, continuously be removed from the aqueous phase via these reactions, at a rate approximately equalling the rate of production by microbial sulphate reduction. The following model will serve as a base for the Reosy research. The effect from these microbial processes on the redox potential in laboratory and natural systems will be investigated.

- $H_2 + CO_2 +$ acetogenic bacteria \rightarrow acetate
- $SO_4 +$ acetate $+ H_2 +$ sulphate-reducing bacteria $\rightarrow H_2S$
- $Fe^{3+} +$ acetate $+ iron-reducing bacteria \rightarrow Fe^{2+}$
- $DOC + SO_4 +$ sulphate-reducing bacteria $\rightarrow H_2S$
- $CH_4 + SO_4 +$ sulphate-reducing bacteria $\rightarrow H_2S$

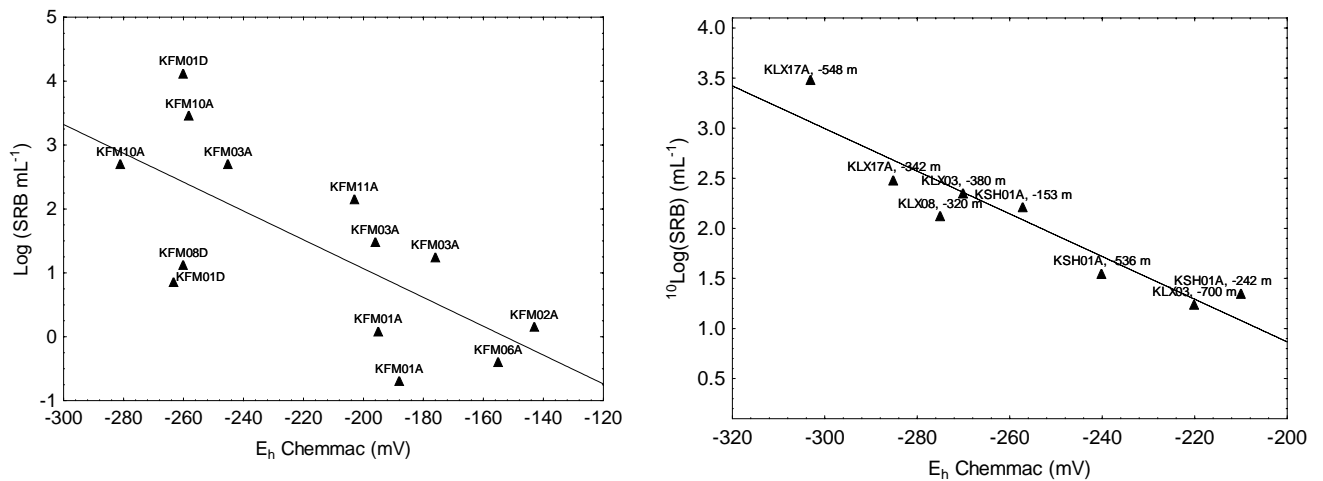


Figure 1. The relation between the number of sulphate reducing bacteria and the E_h analysed with the Chemmac system in the site investigation in Forsmark (left figure) and Laxemar (right figure).

Forsmark: $^{10}\text{Log}(\text{SRB}) = -3.44 - 0.023 \times E_{h_i}$, $r = -0.69$, significant at $p = 0.0087$, $n = 13$.

Laxemar: $^{10}\text{Log}(\text{SRB}) = -3.39 - 0.021 \times E_{h_i}$, $r = -0.94$, significant at $p = 0.0006$, $n = 8$.

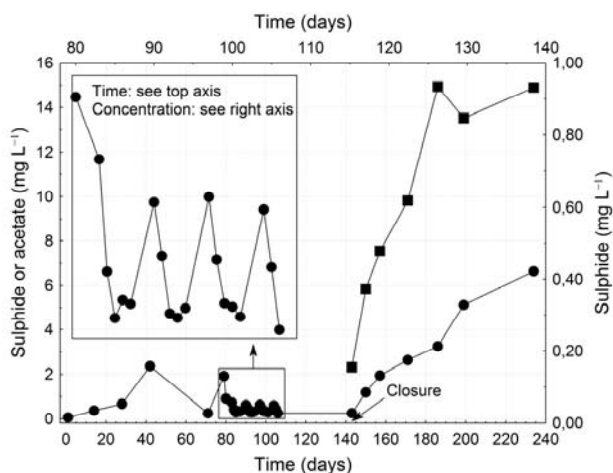


Figure 2. The concentrations of sulphide and acetate over an open (0–140 days) and a closed (140–230) period in a circulation system under in situ pressure (0.3 MPa) and chemistry conditions at 450 m in the Äspö Hard Rock Laboratory. (●) Sulphide, (■) Acetate. It is obvious that sampling disturbed the concentration of sulphide and possibly also the redox potential

Incorporation of Reducing Capacity Concept in reactive transport simulations

Amphos 21

In the context of the stability of the waste radioactive repositories, the study of the redox state of the system is one of the most fundamental aspects. The spent nuclear fuel is mainly composed by UO_2 , and its corrosion increases with the redox potential (U(VI) species are mobile in contrast with the U(IV) species, which are preferentially retained into solid phases). To typical depths of repositories, groundwater shows reducing conditions. But certain geochemical and hydrological processes can generate oxidizing species (flow through open fractures, dissolution of Mn-carbonates, among others). For this reason, in the repository designs, it is essential to characterize the redox buffer capacities of the host-rock. In this way, some geological environments and mineral paragenesis have been studied related to its redox buffer capacity.

The redox state of the system will be given by the ratio between the main electron donors and acceptors. In this way, different authors (Scott and Morgan, 1990; among others) have proposed the concepts of OxiDising and ReDucing Capacities (OXC and RDC), due to the difficulty to obtain redox potentials from field data. The RDC is defined as the amount of electrons available for reduction over a defined reference state. The RDC of a system gives an estimation of its capacity to accept oxidants, and it is formally defined as:

$$RDC = \sum_i n_i \times [Red] - \sum_j n_j \times [Ox]$$

where $[Red]$ and $[Ox]$ are the concentration of reducing and oxidising species present in the system, respectively, and n_i and n_j are the number of electrons involved in the redox reactions. The RDC concept has been previously developed for a hypothetical HNLW repository system, where the UO_2 was the main contributor to the RDC (Bruno et al., 1996). This concept was been also applied by Bruno and Duro (1996) to a hypothetical natural system, with the Fe(II) as the main contributor to the RDC of the system.

The main determinants of OXC and RDC in bedrocks are Fe-oxides, Fe-sulfides and Fe-bearing silicates. In spite of in specific scenarios some redox equilibriums as U(IV)-U(VI) or Mn(II)-Mn(IV) can reach the control over the redox state of the solutions (Ahonen et al., 1994; Salas and Ayora, 2004; Duro et al., 2008), in most deep groundwaters the redox state is governed by electron transfer between Fe(II) and Fe(III) species. Therefore, the largest reductive capacity of such systems will be given by their content in Fe(II). Particularly pyrite, siderite, biotite and chlorite dissolution have been traditionally considered to be the main source of electron donors. The mechanisms of these reactions are strongly dependent of pH and O_2 concentrations (Thomas et al., 2000).

The most realistic approach to reproduce oxidation of Fe-bearing minerals is considering kinetic assumptions. The kinetic rates of dissolution depend on pH,

temperature, and reactive surface areas of solid phases. Recent studies have also shown that the presence of microbes enhances the capacity of the system to buffer redox (Nordstrom and Southam, 1997).

Analytical experiments have been carried out in order to determine the dissolution reactions and the kinetic rates of the most common Fe-bearing minerals, as olivine (Duro et al., 2005; Giménez et al., 2006; Malmström et al., 1995), pyrite, siderite, chlorite and biotite. The kinetic expressions have been reproduced by simplistic numerical models, in order to describe the evolution of the redox state as the corrosion reactions advance.

Kinetic studies of water-rock interaction found in the literature mainly address mineral weathering processes. Applications can be found in fields such as the geochemical evolution of sediments and the influence of the mineral weathering extent on the chemistry of soils and groundwaters. The experimental analysis with respect to kinetic dissolution of different solid phases will provide information on the chemical composition and, consequently, on the redox conditions of the groundwater flowing through these buffer materials. In this way, it will be possible to predict porosity changes induced by precipitation and/or dissolution of minerals.

Minerals as pyrrhotite (found in massive sulfide deposits associated with pyrite), magnetite, hematite and goethite (as accessory minerals in igneous and metamorphic rocks and iron deposits) are not traditionally included in this type of study. The kinetic laws of this type of Fe-sulfides and oxides have not been extensively studied, and are not commonly included in the most of the kinetic databases. To simulate the presence of one of these minerals, it is frequent that numerical models include the kinetic laws of an alternative mineral phase (pyrite, $\text{Fe}(\text{OH})_3$, e.g.), or consider them under equilibrium assumptions. In this way, the main task of Amphos21 within WP3 will be focused on the role of Fe/S system ($\text{FeOOH}/\text{Fe}(\text{II})$, $\text{Fe-S}/\text{S}(\text{VI})$, and $\text{Fe}(\text{II})\text{-clay}/\text{FeOOH}$) in buffering the redox state in natural systems, evaluating the results of the work performed by CTM, and the available data in the literature. These mechanisms will be incorporated in reactive transport models, in order to reproduce hydrogeochemical scenarios leading to modification of the chemical composition of groundwaters. In each scenario, we will consider the geochemical long-term evolution of the system.

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WP4. Redox reactions of radionuclides

State of the art

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Interactions of soluble species of selenium, iodine, and uranium with pyrite

CNRS/LCPME/CEA

During the bibliographic investigations, a great attention has been paid in order to find articles relative to previous studies performed using electrochemical techniques, which will be used preferentially by our laboratory during the project, but surprisingly, there are virtually no data in the electrochemical literature.

Reactivity of pyrite with selenium species

Yllera de Llano et al.¹ measured adsorption percentages of Se(VI) on FeS and FeS₂ for various pH values. For pyrrhotite, the adsorption is 100% effective whatever the pH, and for pyrite it is about 10% and increases slightly with increasing pH. Synchrotron-based X-ray absorption spectroscopy measurements demonstrated that partial reduction of Se(VI) to Se(II) and Se(IV) occurred at the pyrrhotite surface.

Yakovleva et al.² showed the existence of a limited solid-solution series between pyrite and dzharkenite (FeSe₂) and provided a Pourbaix diagram for the Fe-S-Se-H₂O system.

A. Maes et al.³ performed experiments on the reactivity of selenate and selenite towards pyrite in conditions which mimic the reducing environment in Boom Clay (O-depleted glove box, 99.6% N₂, 0.4% CO₂). With selenate there is no considerable sorption or reduction over a period of 60 days. With selenite a steady decrease in time (60 days) of SeO₃²⁻ concentrations was observed, until a final concentration in solution of approximately 3×10⁻⁹ M. The SeO₃²⁻ reduction occurs through sorption onto FeS₂ and a Se⁰ precipitate is formed on the pyrite surface. When similar experiments are performed in the presence of a Boom clay extract the total selenium concentrations decreased in time with the same rate as if no organic matter were present.

Ryser et al.⁴ reported X-ray Absorption Near Edge Structure (XANES) data on various selenium compounds as FeSe₂ (synthetic ferroselite), NiSe₂ (Penroseite), CuSe₂ (Krutaitite) SeS₂...

In a recent paper Breynaert et al.⁵ investigated by XANES-EXAFS the reactivity of selenite towards pyrite and troilite (FeS) in a 95/5% N₂/H₂ atmosphere. In both systems elemental Se is formed either as intermediate (troilite) or final (pyrite) product. In the case of pyrite, the final product, Se⁰, does not contain elements of the reducing surface (Fe or S) which rules out the possibility of surface precipitation. In the case of troilite,

¹A. Yllera de Llano, G. Bidoglio, A. Avogadro, P.N. Gibson, P. Rivas Romero, 'Redox reactions and transport of selenium through fractured granite', *J. Contm. Hydrology*, 21 (1996) 129

²V. A. Yakovleva, E. V. Belogub, K. A. Novoselov, 'Supergene iron sulpho-selenides from the Zapadno-Ozernoe copper-zinc massive sulphide deposit, South Urals, Russia: a new solid-solution series between pyrite and dzharkenite', *Mineralogical Magazine*, 67 (2003) 355

³ a) A. Maes, C. Bruggeman, J. Vancluysen, 'Reduction and Solubility Behaviour of Selenium under Boom Clay Conditions', *Euradwaste'04*

b) C. Bruggeman, J. Vancluysen, A. Maes, 'New selenium solution speciation method by ion chromatography + gamma counting and its application to FeS₂-controlled reducing conditions', *Radiochim. Acta*, 90 (2002) 629

⁴A. L. Ryser, D. G. Strawn, M. A. Marcus, J. L. Johnson-Maynard, M. E. Gunter, G. Möller 'Micro-spectroscopic investigation of selenium-bearing minerals from the Western US Phosphate Resource Area', *Geochem. Trans.*, 6 (2005) 1

⁵E. Breynaert, C. Bruggeman, A. Maes, 'XANES-EXAFS Analysis of Se Solid-Phase Reaction Products Formed upon Contacting Se(IV) with FeS₂ and FeS', *Environ. Sci. Technol.*, 42 (2008) 3595

Se⁰ is formed in solution by reduction with sulphide, immediately after addition of selenite to the system. During the further reduction of Se⁰ to FeSe_x, a (surface) precipitate is formed.

Scheinost et al.⁶ have also studied the reactivity of selenite towards FeS (mackinawite) and other Fe(II)-bearing minerals: siderite (FeCO₃) and magnetite (Fe₃O₄) under strictly anoxic conditions (<1 ppmv O₂). Selenite is rapidly reduced within one day by nanoparticulate mackinawite. According to the pH value selenite is reduced into FeSe (pH 4.3) or into red elemental selenium (pH 3.3).

Organic matter can influence the Se content of sulphides⁷ by sequestering Se from the pool labile Se in coal swamps or by creating a more reducing environment. As selenium is more readily reduced than sulphur a decrease in redox potential would increase the ratio of Se to S incorporated into diagenetic pyrite.

In a US patent⁸, it is reported an exchange reaction of selenous acid with pyrite giving FeSSe: H₂SeO₃ + FeS₂ → H₂SO₃ + FeSSe. Belzile et al.⁹ reported also that dissolved Se species can be removed from interstitial waters through the formation of ferroselite (FeSe₂) or through the incorporation of Se into sulphide minerals such as amorphous Fe sulphide, FeS, FeSeS or pyrite.

Liu et al.¹⁰ studied the reaction of Se(-II) with pyrite in NaCl medium under potentiostatic control in order to minimise the FeS₂ surface evolution, and to ensure the stabilization of Se(-II). The reaction mechanism was investigated by several spectroscopic techniques (XRD, in-situ XANES, XPS). The authors proposed the surface redox reaction: ≡FeS₂ + HSe⁻ → ≡FeS + Se⁰ + HS⁻.

2. Reactivity of pyrite with iodine species

Fuhrmann et al.¹¹ published in 1998 a very interesting and complete study on the sorption of iodine on pyrite and other minerals performed by XANES and ¹²⁵I tracer sorption experiments. According to this work pyrite does not sorbs iodide and the reaction of this mineral with iodate can be written as: 4FeS₂ + 12IO₃⁻ + 4H₂O → 4FeOOH_(s) + 6I₂ + 8SO₄²⁻, I₂ being sorbed on the pyrite surface. However, some results could be questioned because, pyrite was crushed, sieved and stored in air, and the authors presume that its surface was partially oxidized and, moreover, during ¹²⁵I⁻ tracer sorption experiments iodide was apparently oxidized into iodate.

Most of the electrochemical studies dealing with pyrite and iodine species are related to photoelectrochemical investigations. The quantum efficiency is higher when at the FeS₂/electrolyte interfaces are present negatively charged redox species, such as iodide or tri-iodide in contrast to species like Fe²⁺. The photoconversion performance of natural FeS₂ electrodes can be enhanced by formation of the FeS₂/□-Fe₂O₃ heterostructure upon thermal treatments in air. Moreover, it is reported that the iodide adsorption preferably occurs at the edges and defects of the crystal structure.

⁶A. C. Scheinost, L. Charlet, 'Selenite Reduction by Mackinawite, Magnetite and Siderite: XAS Characterization of Nanosized Redox Products', *Environ. Sci. Technol.*, 42 (2008) 1984

⁷C. Lussier, V. Veiga, S. Baldwin, 'The geochemistry of selenium associated with coal waste in the Elk River Valley, Canada', *Environmental Geology*, 44 (2003) 905

⁸S.E. Khalafalla, 'Method for accelerating recovery of selenium from aqueous streams', US4910010 (A), 1990-03-20

⁹N. Belzile, Y.-W. Chen, R. Xu, 'Early diagenetic behaviour of selenium in freshwater sediments', *Appl. Geochem.*, 15 (2000) 1439

¹⁰X.Liu, M. Fattahi, G. Montavon, B. Grambow, 'Selenide retention onto pyrite under reducing conditions', *Radiochim. Acta*, 96 (2008) 473

¹¹M. Fuhrmann, S. Bajt, M. A. A. Schoonen, 'Sorption of iodine on minerals investigated by X-ray absorption near edge structure (XANES) and ¹²⁵I tracer sorption experiments', *Applied Geochemistry*, 13 (1998) 127

Chongvang et al.¹² reported that when a polished pyrite electrode is placed in contact with the redox electrolyte I_3^-/I^- the FeS_2 surface is not affected by corrosion and only a very poor (photo)current-voltage performance is observed. On the other hand, a temporary cycling of FeS_2 , in presence of chloride in the electrolyte leads to a considerable improvement of the photoelectrochemical properties of the $FeS_2/I_3^-/I^-$ interface.

Salvador et al.¹³ give evidence for strong interaction of I^- and I_n^- with the FeS_2 surface via complex formation with Fe^{3+} lattice ions generated by hole capture during anodic polarization. The rest potential of pyrite in 0.2 M and 2.0 M KI (pH 4) is very the standard I_2/I^- redox potential.

Quite a few authors have envisaged the use of the reducing properties of pyrite for the removal of iodine, iodide and iodate from wastewater, radioactive or not. All the iodine species are transformed into iodide that is removed with an ion exchange resin. Apparently, in a first step, iodate would be transformed into iodine that is reduced in a second step when the whole of IO_3^- are reduced.

Finally, some articles and patents are concerned with the gold leaching in auriferous pyritic concentrates: I_2 or I_2/I^- mixtures are used in replacement of toxic cyanide. According to the authors, both Au and FeS_2 are oxidized into gold iodo-complexes $Fe(II)$ and sulphate.

3. Reactivity of pyrite with U(IV)

Several authors have been interested in the reactivity of uranyl ions towards pyrite under anoxic conditions.

In 1994, Wersin et al.¹⁴ showed that U(VI) uptake is strongly dependent on pH (>98% when $4.8 < pH < 5.5$) and, using spectroscopic methods (AES, XPS, FTIR), demonstrated that the distribution of uranium was patchy on the FeS_2 surface and associated with oxidized species of sulphur and iron. The authors demonstrated the partial reduction of uranyl and suggested the formation of a U_3O_8 -type compound on the sulphide surface.

In 2006, Aubriet et al.¹⁵ characterized by micro-Raman spectrometry, voltammetry, SEM and high resolution XPS pyrite particles previously conditioned with U(VI) at pH 6. They demonstrated that the reaction first occurred via a redox process leading to the formation of U_3O_8 , sulphate and iron oxides and oxyhydroxides at the FeS_2 surface; then, if an excess of U(VI) remains in solution it is sorbed as UO_3 and shoebite.

Eglizaud et al.¹⁶ investigated the reaction by solution chemistry and XPS and confirmed the redox process. XPS results are consistent with: the coexistence of a uranium(VI) species and of uranium in a reduced form and the presence of iron(III) oxide or (oxy)hydroxide. No sulphur oxidation products were observed.

Finally, in 2007, Scott et al.¹⁷ reported that freshly polished pyrite surfaces are efficient scavengers of uranium from solution, while weathered surfaces exhibit only limited

¹²Liu Chongyang, C. Petienkofer, H. Tributsch, 'Enhancement of photoactivity in pyrite interfaces by photoelectrochemical processes', *Surface Science* 204 (1988) 537

¹³P. Salvador, D. Tafalla, H. Tributsch, H. Wetzel, 'Reaction mechanisms at the n- FeS_2/I interface: an electrolyte electroreflectance study' *J. Electrochem. Soc.*, 138 (1991) 11

¹⁴P. Wersin, M. F. Hochella, P. Persson, G. Redden, J. O. Leckie, D. W. Harris, 'Interaction between aqueous uranium (VI) and sulfide minerals: spectroscopic evidence for sorption and reduction' *Geochim. Cosmochim. Acta*, 58 (1994) 2829

¹⁵H. Aubriet, B. Humbert, M. Perdicakis, 'Interaction of U(VI) with pyrite, galena and their mixtures: a theoretical and multitechnique approach', *Radiochim. Acta*, 94 (2006) 657

¹⁶N. Eglizaud, F. Miserque, E. Simoni, M. Schlegel, M. Descostes, 'Uranium(VI) interaction with pyrite (FeS_2): chemical and spectroscopic studies', *Radiochim. Acta*, 94 (2006) 651

¹⁷T.B. Scott, O. Riba Tort, G.C. Allen, 'Aqueous uptake of uranium onto pyrite surfaces; reactivity of fresh versus weathered material', *Geochim. Cosmochim. Acta* 71 (2007) 5044



uptake. Results also indicate partial reduction of uranium at the pyrite surfaces, with a heterogeneous distribution of U(IV) and U(VI) species.

Redox Speciation of Tc, Np, and Pu

FZK-INE

In crystalline and clay environments potential reduction of Tc(VII), Np(V) or U(VI) might occur through Fe(II) containing mineral phases. These mineral phases occur as accessory minerals (pyrite, siderite, magnetite) or main components (biotite-annite, chlorite). Previous studies on pyrite, biotite or magnetite indicated that Fe(II) in all of the three minerals can reduce U(VI) to U(IV)^{18,19,20,21} but none of these studies considered the influence of bicarbonate on the reduction. Up to date, there are only few studies on the potential reduction of U(VI) by Fe(II) in the presence of (bi)carbonate in the scientific literature²². The main goal of our study is to find out if U(VI) can be reduced by structural bond Fe(II) and to what extent HCO₃⁻ affects this process in the natural mineral assemblage and for synthetic magnetite.

The Tc redox reaction product found in Fe(II) systems seems to depend on the initial Tc concentration used, whereas Zachara et al.²³ found a single Tc(IV)₂O₁₀ octahedral dimer linked in edge-shearing mode to a single Fe(III)-O octahedral site in ferrihydrite to be the best-fit model for their Tc- EXAFS (1.1·10⁻⁵ mol/L), Maes and coworkers²⁴ found that a model of extended Tc(IV)O₂·nH₂O octahedral chains described best their Tc(IV) products starting with Tc(VII) concentrations of 2.2·10⁻³mol/L in presence of pyrite, magnetite and humic substances. The work of Zachara et al. furthermore indicated the formation of Fe(II/III)/Tc solids with ferromagnetic character indicating at least some formation/conversion to magnetite or maghemite which could not be resolved with the methods applied. Oxidation rates of the products found by Zachara et al. and significantly higher oxidation rates detected for Tc(IV)O₂·nH₂O formed through reaction of Tc(VII) with biogenic Fe(II)²⁵ clearly show that the molecular environments of Tc(IV) will trigger the mobility of Tc during redox disturbances.

Concerning the activities with hydroquinone it was demonstrated earlier that HA may reduce Tc(VII) to Tc(IV)²⁶. This was also demonstrated for Pu(VI) and Pu(V)^{27,28} but rather controversial data were reported concerning Np(V) reduction. The HA separated from Gorleben groundwater induces slow reduction of Np(V) to Np(IV)²⁹, while no reduction took place in case of Aldrich HA as demonstrated by Sachs and coauthors³⁰. The contrasting results on redox behavior of humic substances could stem from structural variations inherent to HS isolated from different natural environments. The redox properties of humic materials are known to result from the presence of quinonoid

¹⁸ Wersin, P., et al. (1994) *Geochim. Cosmochim. Acta*, 58(13), 2829-2843.

¹⁹ Ilton, E.S., et al. (2004) *Geochim. Cosmochim. Acta*, 68(11), 2417-2435.

²⁰ Ilton, E.S., et al. (2006) *Environ. Sci. & Technol.*, 40(16), 5003-5009.

²¹ Scott, T. B. et al. (2005) *Geochim. Cosmochim. Acta*, 69 (24), 5639-5646.

²² Behrends, T., Van Cappellen, P., (2005) *Chemical Geology*, 220(3-4), 315-327.

²³ Zachara, J.M. et al. (2007) *Geochim Cosmochim Acta*, 71, 2137.

²⁴ Maes, A. et al. (2004) *Environ. Sci. Technol.* 38, 2044.

²⁵ Burke I.T. et al. (2006) *Environ. Sci. Technol.* 40, 3529.

²⁶ Maes, A., et al. (2003) *Environ. Sci. Technol.* 37, 747.

²⁷ Marquardt, C.M., et al. (2004) *Radiochim. Acta* 92, 617.

²⁸ Andre, C., Choppin, G.R. (2000) *Radiochim. Acta* 88, 613

²⁹ Artinger, R. et al. (2000) *Radiochim. Acta* 88, 609.

³⁰ Sachs, S., Bernhard, G., (2005) *Radiochim. Acta* 93, 141.



moieties in their structure, which undergo reversible redox transformations^{31,32}. In this way, the use of quinonoid-enriched derivatives of HS or hydroquinone/anthraquinone offers a potential for investigating the fundamental processes controlling the radionuclide redox state in natural systems.

³¹ Nurmi, J.T.; Tratnyek, P.G. (2002) *Environ. Sci. Technol.* 36, 617.

³² Österberg, R., Shirshova, L. (1997) *Geochim. Cosmochim. Acta* 61, 4599.

Determination of redox state of investigated system and redox sensitive elements with relevance to a crystalline rock environment

CTH

The equilibrium indicated in the measurement of Eh is presumed to occur at the electrode surface. A true redox potential occurs when the chemical potential due to differences in concentration of reduced and oxidized species is equal to the potential difference between the reference and platinum electrodes and there is no net flow of electrons – the system is at equilibrium as stated by the Nernst equation.

It is of importance to realize that the investigated deep geological waste disposal sites systems may not be at perfect, or near perfect equilibrium. This is naturally true during the time of construction of the facilities as well as a time period thereafter. A possible failure of the repository will represent another scenario when the system changes and is not at equilibrium. Further, chemical reactions occur at different rates and the equipment used to register Eh and pH has built in errors and biases. This implies careful considerations as to whether or not we have equilibrium, relevant reactions to be considered, instrument calibrations that will be valid for the system of calibration as well as the system to be investigated (Mudroch et al., Whitfield (1974), Whitfield (1969)). In a more complex system with several redox participants, a perceived equilibrium with a net zero current, may in fact be a summation of potentials that results in a pseudo-equilibrium.

Platinum electrodes can yield unstable readings when investigating systems that contain species that are stronger reducing agents than hydrogen or platinum. Such a system is e.g. the uranium(IV) system (Nordstrom et al.).

Iron is Omni-present in the underground rock matrix and waters, and the redox couple Fe(II)/Fe(III) plays an important role. Studies of amorphous PuO₂ in a 0.001 M FeO₂ solution have indicated that the solubility of PuO₂(am) is many fold higher than predicted from thermodynamic data, and that Pu(III) is the dominant Pu oxidation state of this system (Rai et al.). Pertechnetate, Tc(VII), has been shown to be reduced to Tc(IV) by aqueous Fe(II) under anaerobic conditions at 6 < pH < 8 (Zachara et al.). There are also several studies indicating that the presence of solids or minerals in solutions affects the redox behavior of certain species. U(VI) → U(IV) and Fe(II) → Fe(III) in the presence of hematite (Liger et al.); Np(V) → Np(IV) and Fe(II) → Fe(III) in the presence of magnetite under both aerobic and anaerobic conditions (Nakata et al.). Transition metals in aqueous solutions have also been shown to be reduced on surfaces of Fe(II)-containing oxides (White et al.).

All in all, given the aforementioned characteristics of redox-potential measurements, a more thorough investigation and evaluation of Eh-measurements are warranted. Eh coupled with other means of oxidation state verification, e.g. solvent extraction, ICP-MS and radioanalytical techniques, is relevant for further investigations of systems under conditions similar to those of the proposed underground repository in a granitic



host rock matrix.

Goal of project

The purpose of the planned investigations here at Chalmers, is to give a clearer picture of the agreement and disagreement between measured Eh and actual quantification of the various oxidation states of the elements at hand in the system. The composition of the system will be varied, from actual ground water from the Äspö Hard Rock Laboratory to synthetic ground water with varying ionic media. Investigations with Äspö minerals are performed as to assess the impact the presence of minerals and surface to possibly facilitate changes of redox states. Similar investigations using potentiostat, are also intended to focus on discrepancies between Eh and actual quantification. In short: are we working in the system we believe we are, and if not so, how does it differ from the actual state of the system?

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The Prediction of Radionuclide-Humic Acid Speciation and its Effect upon Transport

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Prediction of Metal Ion/ Radionuclide Speciation at Equilibrium

Over the last twenty years predictive models of metal ion/humic substance (HS) speciation have been developed, but the great majority of interest has been in the behaviour of stable element systems, such as Al or the 'heavy' metals. Two complex models have been more successful and widely applied more than others: MODEL VI of Tipping (Tipping 1998) that simulates the chemical heterogeneity with a finite number of discrete binding sites; The NICA model of van Riemsdijk et al (Kinniburgh et al 1999) that uses a continuous distribution approach. These codes can simulate metal ion speciation in complex systems containing HA/FA. For example, NICA has been used to calculate the speciation of metals in groundwaters (Fest et al 2007) soils (Lumsdon 2004) and soil solutions (Weng et al 2002), and WHAM/MODEL VI has been applied to lake and river waters (Cory et al 2007; Guthrie et al 2005) and soils (Almas et al 2007). In Radiological Performance Assessment (RPA), it is necessary to predict radionuclide speciation, but the chemical models must be simple. Hence, these complex models cannot be used. Fortunately, it has been found that under certain conditions metal ion binding can be described much more simply. Buckau (2004, 2005) has proposed the Effective Humate Ligand Concentration (EHLIC) approach, which treats the humic as a mixture of simple ligands that all have the same stability constant. This approach has been successfully applied to a number of metal ions (Pashilidis and Buckau 2007; Kolokassidou and Pashilidis 2007, Reiller et al 2007, Ivanov et al 2008).

Ternary Systems

Much current work in this area has focussed upon the behaviour of metal ions in ternary systems (metal ions, humic substances and mineral phases together). In these systems, there are a number of binary interactions: metal ion/humic; metal ion/mineral; humic/mineral. Ternary complexes (Surface-HS-M or Surface-M-HS) are crucial to understanding these systems, since they can significantly affect metal ion solid/solution partition. In the *Linear Additive Approach*, the behaviour of the full ternary system is simulated just with the separate binary models: this is not always successful, since the presence of all three components may perturb the binary interactions (Evans et al 2007). It has been shown that the success of the linear additive approach is a function of the metal ion/humic stability constant: as it increases, the humic dominates the chemistry and the performance of the linear additive approach improves (Evans et al 2007). For predicting humic and metal ion speciation in ternary systems at equilibrium, the Ligand Charge Distribution (LCD) model has been developed by van Riemsdijk et al (Weng et al 2005, 2006 2007A, 2007B). It includes: the CD-MUSIC model to describe the binding of radionuclides to mineral surfaces; the NICA model for the interaction of metal ions with humics; The ADAPT model to calculate the sorption of humics to mineral surfaces. The LCD calculates the free energy change associated with humic and

humic-metal complexes binding to surfaces (ternary complex formation), and uses the fact that at equilibrium the chemical potential of sorbed species must be the same as those in solution. The LCD is a self-consistent and rigorous description of the thermodynamics of polyelectrolyte species in ternary systems. It is the most successful approach currently available. For example, it can even predict ternary system behaviour where the Linear Additive Approach does not work (e.g., Weng et al 2005). It is able to explain the difference in sorption behaviour between fulvic acids and larger humics (Weng et al 2007B) and even the increase in sorption with increasing ionic strength, regardless of the polarity of the charge on the surface, by taking into account the contraction in the humic structure as ionic strength increases.

Kinetics and Predicting Radionuclide Transport

Over the last decade, studies have shown that humic substances bind metal ions in two different modes (King et al 2001). Initial uptake is to an 'exchangeable' fraction, where the metal ion is bound strongly, but may be removed instantaneously if a stronger competing sink is encountered. Over time, the metal may transfer to the 'non-exchangeable'. Here, it may not dissociate instantaneously, and the (first order) rate at which it dissociates from the humic is fixed and independent of the concentration or strength of any competing sink. While it is effectively 'trapped' within the non-exchangeable, it takes on the characteristics of its host humic. Further, the interaction of humic and humic-metal complexes can also be slow (Bryan et al 2005). The importance of kinetics was first shown experimentally during a series of batch and column experiments (Artinger et al 1998): The amount of metal-humate complex that broke through reduced with decreasing flow rate and breakthrough increased with Am/humic pre-equilibration time. A speciation model of the binary M/HS binary system, KICAM, was developed to predict the changing speciation with time (Schuessler et al 2000, 2001, Artinger et al 2002). Early versions had only 2 humic bound components, one fast dissociating (the exchangeable) and another slower (the non-exchangeable). Later, a third intermediate fraction was added. In common with the approach of Warwick et al (2000) and Bryan et al (2005), initial uptake is to the exchangeable or fastest fraction, and subsequent transfer between humic fractions is first order in both directions. The speciation in the full ternary system is complicated by the fact that the sorption of humics, and hence ternary complex formation, can also be slow. Hence there are two types of kinetic effect that must be considered to predict radionuclide speciation in ternary systems. A kinetic model has been developed to predict their behaviour (Abrahamsen et al 2007, 2008; Bryan et al 2006; Farrelly et al 2007), which effectively includes the 2 site version of KICAM. It has been found that there is more than one humic sorption reaction. For simplicity, the model uses two reactions (fast and slow) to simulate the behaviour. Two versions of the model are required for different mineral phases, the first uses a single humic species and two binding sites (e.g. sand and quartz), whilst the other has two humic types and one binding site (e.g. hematite, montmorillonite).

Attempts to simulate radionuclide transport in the presence of HS using equilibrium only models have failed, even using the complex approaches, such as MODEL VI (Warwick et al 2000). Column modelling has shown that in order to simulate transport, it is necessary to include the non-exchangeable effect. Most approaches consider only

two humic bound components, the exchangeable and the slowest non-exchangeable fraction, i.e., the KICAM approach (Warwick et al 2000, Schuessler et al 2000, 2001, Bryan et al 2005). Only one study Artinger et al (2002) has used an intermediate fraction. In most cases, the intermediate fractions effectively behave as if they were exchangeable. Many authors have found that even for the exchangeable fraction, there is a wide spectrum of binding strengths. However, it seems that this too need not be included in order to simulate transport in lab column experiments. In other words, the EHLC approach seems a sufficient description of the exchangeable interaction. In column experiments where the sorption of humic-metal complexes is significant, the studies have shown that kinetics are required to produce an adequate prediction (Bryan et al 2005, 2007), using 2 chemical reactions to simulate ternary complex formation, i.e., an identical approach to the ternary speciation model of Abrahamsen et al (e.g. 2007, 2008) described above. The combined kinetic effects are able to explain the transport of radionuclides in column experiments and at a real site (Bryan et al 2007). Of course, the division between equilibrium and kinetic descriptions of reactions depends upon the timescale of the observation or prediction, and kinetic calculations are computationally more expensive. Therefore, a set of rules have been developed, based upon the residence time of material in transport problems, that determine when an equilibrium or kinetic approach is the required for the metal-humic and humic-surface interactions (Bryan et al 2007).

The Next Step

Over the last few years, there have been significant improvements in the understanding of humic binary and ternary interactions, and we are now able to predict the results of at least some transport experiments. However, all of the systems described above concern either radionuclide ions that show no redox change at all or experiments with conditions such that oxidation states will not change during the experiment. Redox reactions are not currently included at all in these models. For example, EHLC type equilibrium constants may be defined for individual oxidation states of the actinides, but the transformation from one oxidation state to another or the conditions when that would happen in humic ternary systems cannot be predicted. Hence, the next step in this field is to introduce redox chemistry to the speciation and transport models.

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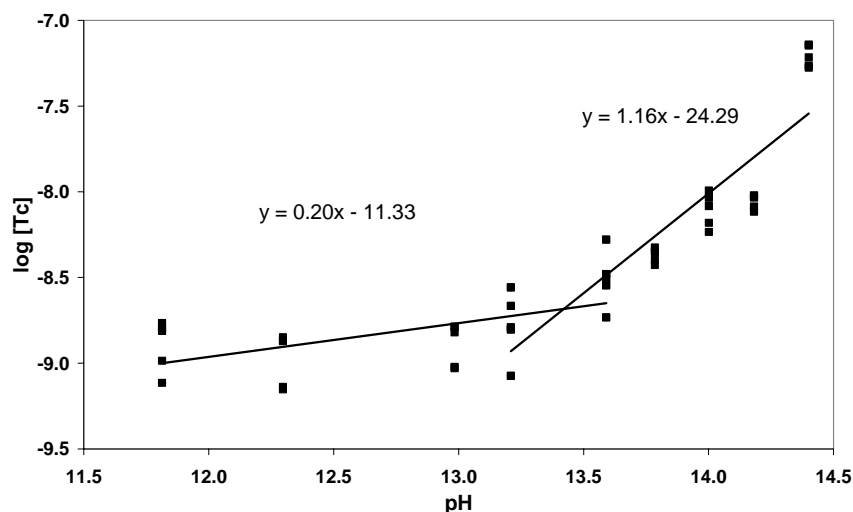
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Tc and Anthropogenic Organic Ligands

unilough

The aqueous chemistry of Tc in a cementitious radioactive waste repository is likely to be dominated by the highly mobile pertechnetate anion (TcO_4^-) in aerobic waters, and by Tc(IV), as TcO_2 (am) solid, in anaerobic. Under reducing conditions, TcO_4^- in non-complexing aqueous solutions initially undergoes a one-electron reduction to the unstable TcVIO_4^{2-} species [1-3]. Subsequent 2- or 3-electron reductions to Tc(V) or Tc(IV) species then readily occur. However, the Tc(V) and Tc(VI) species are unstable and disproportionate into more stable Tc(IV) and Tc(VII) species. A study by Warwick et al. [4] showed that, from pH 11 to 13.5, the aqueous Tc concentration appeared to be independent of pH. However, at pH values greater than 13.5, the aqueous concentration of technetium increased with increasing pH (see figure below). The increase in solubility can be explained by the equilibrium in eqn. 1. Log K for the species $\text{TcO}(\text{OH})_3^-$ was determined to be $\log K_2 = -14.2$ [4], but this anionic Tc(IV) species is only likely to be formed in significant quantities above the highest pH likely to be found in a cementitious repository, and hence should be of little interest to performance assessment.



It has been suggested that anthropogenic ligands may affect the redox chemistry of Tc at high pH, by stabilising intermediate oxidation states. This idea is well known in the formation of $^{99\text{m}}\text{Tc}$ radiopharmaceuticals [5]. Tc(V) chemistry is governed by oxotechnetium species, TcO_3^+ . The coordination character of TcO_3^+ with multidentate oxygen donor ligands is controlled by the square pyramidal geometry of TcO_3^+ complexes. Complexes of TcO_3^+ with polyhydric alcohols and 2-hydroxy carboxylates are stable in aqueous solution due to chelating effects [6]. It is known that polyhydric complexes of Tc(V) can be formed by the reduction of pertechnetate in aqueous solution of the excess O-donor ligand [7], although in pharmaceuticals this is not carried out at pH 13.3. Apart from a few cases, the complexes have not been structurally

characterised, because of the difficulty of obtaining pure compounds in crystalline form. The Tc-glycolato complex [8] has been identified as $[\text{TcO}(\text{OCH}_2\text{CH}_2\text{O})_2]^-$. The anion shows the square-pyramidal arrangement typical of five-coordinated oxotechnetium(V) complexes with the short Tc-O(oxo) bond and longer Tc-O bonds between the metal and the diol oxygen atoms. Hence, it can be assumed that a Tc(V)-ISA complex, such as that shown in figure 5, may have been formed, causing the difference in final solubilities for ISA and gluconic acid.

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Redox behaviour of Uranium under hyperalkaline conditions

Amphos 21

Redox reactions of radionuclides

The solubility of actinides under reducing and alkali conditions is of major relevance in order to assess the repository environments under cementitious conditions. Figure 1 shows the pH-Eh diagram for the uranium system calculated by using the NEA database [03GUI/FAN] in the pH range 10 to 14. The Pourbaix diagram indicates $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ are the predominant U(VI) complexes under alkaline and hyperalkaline conditions, respectively, and $\text{U}(\text{OH})_4(\text{aq})$ is the only U(IV) hydrolysis complex under highly reducing conditions ($E_h < -0.3\text{V}$)

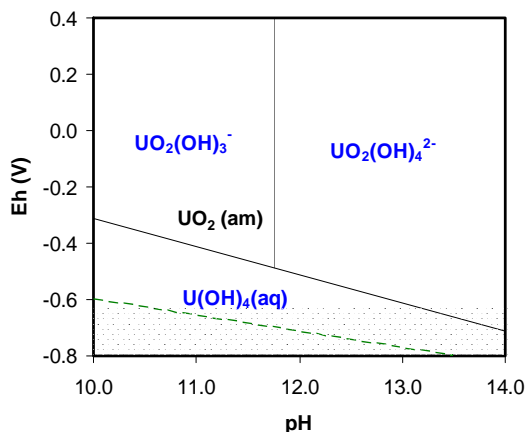


Figure 1. Pourbaix diagram of the uranium hydrolysis system using NEA database. Black-shaded area corresponds to the precipitation of $\text{UO}_2(\text{am})$. $[\text{U}]_{\text{TOT}} = 1 \cdot 10^{-7} \text{ M}$, $I = 0$.

Despite the $\text{U}(\text{OH})_4(\text{aq})$ complex is currently the only U(IV) hydrolysis species accepted by NEA, discussion on U(IV) speciation under this critical conditions has been ongoing for decades ([57GAY/LEI], [61GAL/STE], [81TRE/CHE], [83RYA/RAI], [87BRU/CAS], [89CAS], [90RAI/FEL], [95TOR], [95YAJ/KAW], and [05FUJ/YAM]). Published experimental data on the aqueous concentration of uranium in equilibrium with a UO_2 solid phase has been collected and plotted in Figure 2. In Table 1 we indicate the experimental conditions reported for each solubility experiment.

Despite the wide range of experimental conditions used by the authors, the data show the common trend of increasing UO_2 solubility with pH. There are currently two explanations for this solubility increase observed under hyperalkaline conditions:

- Partial oxidation of the uranium U(IV) to U(VI).
- Formation of anionic species of uranium U(IV) such as $\text{U}(\text{OH})_5^-$ and/or $\text{U}(\text{OH})_6^{2-}$

The reviewed experimental data has been modelled in the current document considering both approaches. In Figure 2a is indicated the modelled uranium solubility considering different Eh and, therefore, different degrees of oxidation. The uranium speciation associated with this approach is the one represented in Figure 1. The modelling results plotted in Figure 2b performed at different Eh values have included the U(OH)₅⁻ and U(OH)₆²⁻ hydrolysis constants determined by [05FUJ/YAM]. As indicated by its corresponding speciation diagram (Figure 2c), the contribution of U(OH)₅⁻ and U(OH)₆²⁻ would be insignificant at Eh > -0.5 V compared to the U(VI) complexes.

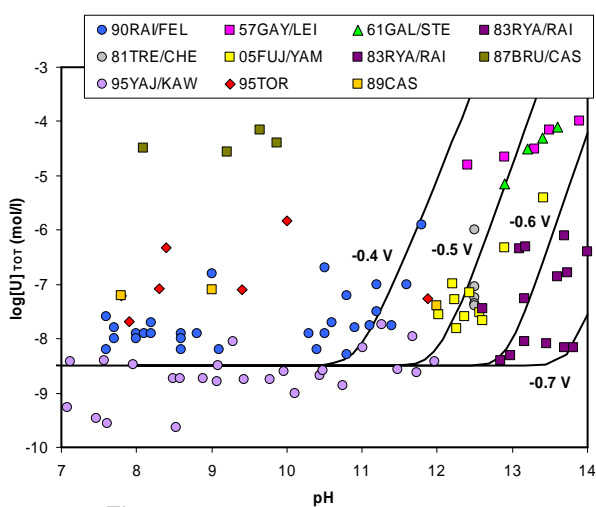


Figure 2a

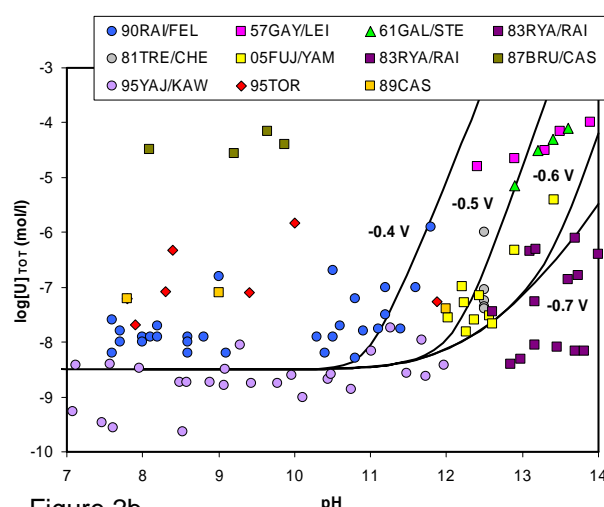


Figure 2b

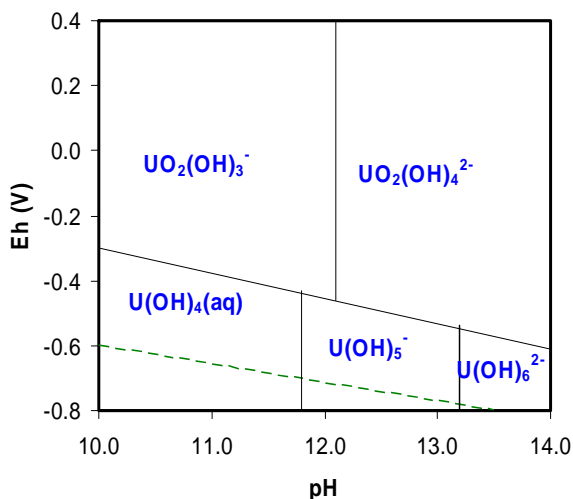


Figure 2c

Figure 2. Symbols in Figure 2a-b: Solubility data described in the literature under alkaline and hyperalkaline conditions for uranium oxide (UO₂). **2a** Lines: Calculated solubility at different Eh values taking into account NEA database selection [03GUI/FAN], I = 0. **2b** Lines: Calculated solubility at different Eh values taking into account the ionic species described in [05FUJ/YAM], I = 0 **2c.** Predominant species Eh – pH diagram corresponding to model shown in Figure 2b, [U]_{TOT} = 1·10⁻⁷ M, I = 0.

Table 1. Summary of the reported experimental conditions of the experimental solubility data plotted in Figure 2a-b.

Reference	pH range	Experiments	Solid Characterization *	Equilibration time	Reducing agent	Atm.
57GAY/LEY	13 -14	undersat.	No specified	10 days	No	N ₂
61GAL/STE	> 13.5	undersat.	No specified	6 days	No	Ar
81TRE/CHE	12 - 13	flow-through	XRD, XPS	several hours	H ₂	Ar
83RYA/RAI	> 12.5	oversat.	No specified	16 days	Zn(s) and/or NaS ₂ O ₄	Ar
87BRU/CAS	2 - 10	Oversat. & undersat	XRD	14 days	H ₂ , Pd (catalyst)	N ₂
89CAS	3 - 12	Oversat. & undersat.	XRD	14 days	H ₂ , Pd (catalyst)	N ₂
90RAI/FEL	2 - 12	oversat. & undersat.	XRD	days	Fe(s) or EuCl ₂	N ₂
95TOR	1.5-12	undersat.	XRD, SEM, EDS, XPS	No specified	H ₂ , Pd (catalyst)	N ₂
95YAJ/KAW	2 - 12	oversat. & undersat.	XRD	7, 14 & 28 days	NaS ₂ O ₄	
05FUJ/YAM	12 - 14	oversat.	XRD	4 weeks	NaS ₂ O ₄	Ar

XRD = X-ray diffraction XPS= X-ray photoelectron spectroscopy, SEM = scanning electron microscope, EDS = Energy Dispersive X-ray

The two different dissolution mechanisms considered in the modelling calculations show that the experimental data can be described considering both approaches. Therefore, performing the solubility experiments under well controlled experimental conditions is essential to understand the dissolution mechanism of UO₂. Several difficulties have been outlined in the literature to explain the large scattering of data [07OPE/WEI]

- Presence of oxidized U(VI) surface layers on UO₂ prior to solubility experiments.
- Difficulties in using suitable techniques and reducing agents that effectively control/maintain uranium in the tetravalent state for a wide range of pH
- If insufficient methods of phase separation are applied, colloids can be misattributed to the liquid phase resulting higher solubilities,
- It is worth to highlight that crystallinity of UO₂ will not effect the dissolution process as the amorphous fractions, always present at alkaline conditions because of the rapid hydrolysis of the uranium oxide surface, control the UO₂ solubility [03GUI/FAN].

Amphos will perform a combination of UO₂ solubility experiments under well controlled redox conditions. An attempt to continuously monitor the reducing conditions will be made by connecting the bath reactor to the Time-resolved Laser-induced Fluorescence Spectrometer (TRLFS), which would analyse the concentration of U(VI) species [98MOU/LAS] In order to elucidate the dissolution mechanism, not only

the aqueous phase but the solid phase will also be characterized at different stages with spectroscopy techniques (e.g. XANES and XPS).

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State of art - Pu oxidation-reduction

IPL

Under environmental conditions plutonium is able to exist in five different oxidation states as the oxy/hydroxy ions Pu(III)^{3+} , Pu(IV)^{4+} , $\text{Pu(V)}\text{O}_2^{2+}$, $\text{Pu(VI)}\text{O}_2^{2+}$, and $\text{Pu(VII)}\text{O}_4^{-1}$ [1]. PuO_4^- is not considered a stable species in the natural environment. At near neutral pH levels or oxic groundwater, Pu(III) is rapidly oxidized to Pu(IV) [2,3]. In strong acid systems, the redox potential between III, IV, V and VI states is almost identical [2]. The trivalent state is much less likely to be present when pH increases to neutral and basic conditions because reduction potential of Pu(III) becomes negative, making Pu(III) unstable in neutral and basic solutions [3,4]. The dominant oxidation states in oxic waters are Pu (IV), Pu (V) and Pu (VI) whereas in anoxic waters Pu(III) is present and may become the dominant soluble species [4].

Pu has a high affinity for solid phases such as iron oxides, manganese oxides, and other naturally occurring solids, however, data on association of plutonium with geological material is rather contradictory. McDonald et al. found that plutonium is predominantly associated with Fe, Mn oxyhydroxides (43.9 %) and organic complexes (43.5%) in the Irish Sea sediments, whereas McCubbin et al. reported 37 % of Pu as upper limits for the fraction associated with magnetic + nonmagnetic Fe minerals in samples collected at close area of the Cumbarian coast [5,6]. Data was obtained using different methods: sequential extraction and magnetic extraction technique. Using selective extraction procedures was shown that Pu was associated predominantly with Mn oxides. The dominant association with the Mn oxides occurred despite the fact that the Fe oxides were present at concentrations higher by factor from 2 to 30 in comparison with the Mn oxides [7].

X-ray absorption spectroscopy, in combination with microautoradiography, electron microprobe, and petrographic microscopy techniques were used to detect the spatial distribution of sorbed Pu on the zeolitic Topopah Spring Tuff sampled at Yucca Mountain [8,9]. Large concentrations of sorbed Pu were associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. In a similar experiment in which Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes. These zones contained Fe-rich amorphous materials [10]. It was shown that Pu(V) and Pu(IV) sorption on γ -alumina and goethite generally increases as a function of pH. Pu(IV) sorption on goethite occurs at pH values between 2 and 6, whereas Pu(V) sorption on goethite occurs at pH values between 4 and 8. Pu(V) sorption on γ -alumina also occurs at pH values between 6 and 10 [11]. Pu sorption on amorphous silica or on quartz is expected to occur at much lower pH values because of the much lower pH ZPC (the pH point of zero charge), at about 2, in contrast to that of the iron and aluminium hydroxides, which generally occurs between 7 and 9. Studies performed in natural systems indicated that Pu associated with suspended matter and sediments was Pu(IV) whereas in aqueous phase was predominantly Pu(V). The transformation of Pu oxidation state through interactions with solid surfaces of minerals was found in many previous studies. The reduction of Pu (V) adsorbed to goethite surfaces, the simultaneous oxidation and reduction of Pu(V) after the adsorption to goethite was observed [12]. Kinetics of Pu(IV) oxidation by manganese dioxide was studied by

Morgenstern and Choppin [13]. The low oxidized plutonium fraction found in the neutral pH range than under acidic conditions was due to the strong hydrolysis and stabilization of the tetravalent state. The aqueous-phase Pu(IV) concentrations are controlled by formation of hydroxide solid phase and in solutions with high Eh and pH values Pu(V) and Pu(VI) dominate e.g. in sea water and diluted salt solutions [14]. Pu oxidation state transformation by Mn(IV)-bearing minerals was observed in many studies and it was found that initial oxidation step was followed by reduction to Pu(IV), which became the predominant solid-phase Pu species [15]. Reduction of Pu(V)O_2^+ by synthetic magnetite, goethite, hematite was studied by Powel et al. In pH range 5 to 8 adsorption by magnetite was a rate-limiting step and reduction was mediated by the solid phase, at pH 3 reduction occurred in the aqueous phase. The reduction mechanisms by goethite, hematite was not proposed, the unclear redox transformation was addressed to the semiconductor properties of the materials [16,17]. The important redox role of natural organic substances in the transformation of the Pu oxidation state was shown in recent publications. Reduction of Pu (V) by humic acids was observed by Andre and Choppin [18], Pu(III) and Pu(IV) were mainly found in humic substances containing groundwater. In experimental study Pu(V) was reduced to Pu(IV) within 20 days whereas Pu (III) was not observed [19].

Data obtained from reductive dissolution of $\text{PuO}_2(\text{am})$ as a function of time, for pH from 0.5 to 11 showed that reduction reactions involving Fe(II) and hydroquinone are relatively rapid may play an important role in controlling Pu behavior under reducing environmental conditions. Pu(III) was the dominant aqueous oxidation state. The experimental pH, pe, and Pu(III) concentrations from both the Fe(II) and hydroquinone systems provided a $\log K^0$ value of 15.5 ± 0.7 for $[\text{PuO}_2(\text{am}) + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Pu}^{3+} + 2\text{H}_2\text{O}]$ [20]. Although reduction mediated by biogenic Fe^{2+} well known the first observation of steady-state (Pu(III) in association with natural sediments exposed to air was published in 2007 by Kaplan et al. On the basis of lysimetric experiments with well-defined solid sources of Pu(III) (PuCl_3), Pu(IV) ($\text{Pu}(\text{NO}_3)_4$ and $\text{Pu}(\text{C}_2\text{O}_4)_2$), and Pu(VI) ($\text{PuO}_2(\text{NO}_3)_2$) it was concluded that Pu(III) may have a wide natural occurrence especially in acidic environments [21]. Sorption of Pu(IV) was not affected by the mildly reducing conditions achieved in the laboratory batch sorption experiments performed in order to investigate variations in the retardation behavior of redox-sensitive radionuclides [22].

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Uptake of Np(IV) and Np(V) by cementitious materials under controlled redox conditions

PSI

In most current concepts for repositories for intermediate level nuclear waste (ILW), cementitious materials will be applied for solidification of the waste, as backfill and as construction material. The uptake of redox-sensitive actinides such as Neptunium, by cementitious materials under repository conditions is poorly known (e.g. WIELAND and VAN LOON, 2002). In many sorption databases used in performance assessment studies for nuclear waste repositories, it is assumed that the sorption behaviour of Np(IV) is similar to Th(IV) whereas the sorption behavior of Np(V) is expected to be similar to bi- or trivalent metal cations based on its effective charge of 2.3 (CHOPPIN, 1983). To verify these assumptions a study on the uptake of Np(IV) and Np(V) by calcium silicate hydrates and hardened cement paste was started within the framework of Reosy.

Redox conditions expected in a cementitious near field of a nuclear waste repository

It is generally assumed that after closure, the available oxygen in an ILW repository will be depleted rapidly (within 100 years) and conditions will become reducing (WERSIN et al., 2003). The redox potential will mainly be controlled by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple due to the corrosion of steel resulting in the formation of magnetite as the major corrosion product (BERNER, 2003; WERSIN et al., 2003). Based on this assumption, WERSIN et al (2003) estimated the redox potential in the cementitious near-field of the planned Swiss ILW repository to be between -750mV and -230 mV (SHE) .

Neptunium speciation under alkaline conditions

The chemistry of Neptunium in acidic solutions is rather well investigated whereas the information on the Neptunium behavior in alkaline media is rather poor.

Under alkaline conditions mainly three oxidation states of Np are important: IV, V, and VI (GELIS et al., 2001), whereas Np(III) and Np(VII) are unstable under these conditions. The standard potentials (E_H^0) derived from the thermodynamic data selected by HUMMEL et al. (2002) for the different redox couples are presented in Table 1: The resulting Np redox speciation under alkaline conditions in the absence of CO_2 is presented in Figure 1. Taking into account the redox conditions expected in a cementitious repository, discussed above, Np(IV) and Np(V) are expected to be the prevailing oxidation states.

Table 1. Standard potentials (E_H^0) for the Np(VI)/Np(V) and Np(V)/Np(IV) redox couples

	E_H^0 (V)
$\text{NpO}_2^{2+} + \text{e}^- = \text{NpO}_2^+$	1.17
$\text{NpO}_2^+ + 4\text{H}^+ + \text{e}^- = \text{Np}^{4+} + 2\text{H}_2\text{O}$	0.604

Though considerable fundamental information is available on the chemical thermodynamics of Np(V), significantly less is known about Np(IV) mainly because measurements of this less-stable oxidation state are very difficult.

The existence of oxidation state analogies and systematic trends in the chemical properties of the actinides may help to compare or estimate stability constants of aqueous complexes and solubility products of isostructural solids. Actinide complexation constants are known to correlate with the electrostatic interaction energy between the metal cation and the ligand, expressed by z/d (z is the effective charge of the metal cation; d is the distance between the metal and the ligand) (CHOPPIN and RIZKALLA, 1994). The effective charge of Np(V) in NpO_2^+ was estimated to be 2.3 (CHOPPIN, 1983), which is markedly lower than indicated from the oxidation state of the metal centre. Taking into account this effective charge, it is to be expected that the stability of Np(V) aqueous complexes is lower than the stability of Np(IV) complexes (effective charge = 4).

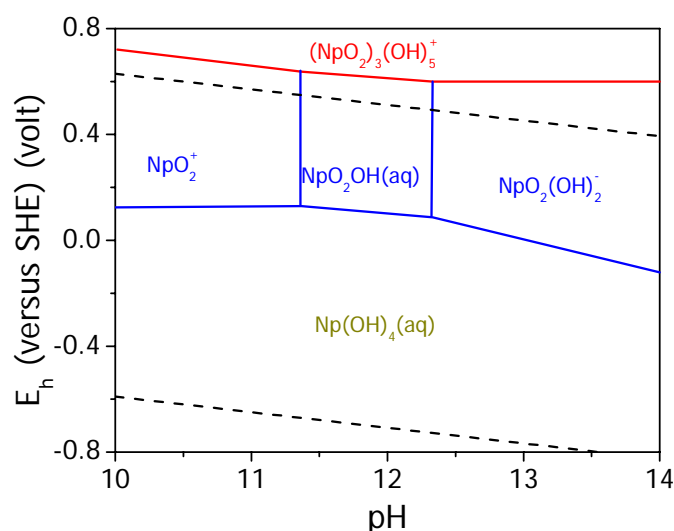


Figure 1. E_h /pH predominance diagram for Np aqueous species.

Actinides having the same oxidation state tend to form (hydr)oxide and carbonate solids with similar stoichiometries and crystal structures. Within the series of the tetravalent actinides, solubilities of e.g. the amorphous oxides and hydroxides vary considerably in correlation with the metal to ligand distance in the lattice (FANGHÄNEL and NECK, 2002); i.e.; $K_s^0(\text{Th}(\text{OH})_4(\text{am})) > K_s^0(\text{U}(\text{OH})_4(\text{am})) > K_s^0(\text{Np}(\text{OH})_4(\text{am})) > K_s^0(\text{Pu}(\text{OH})_4(\text{am}))$.

Sorption of Np(V) and Np(IV) onto cementitious materials under controlled redox conditions

Whereas data concerning the sorption of Np(V) by cementitious materials are scarce, literature sorption data on Np(IV) are non-existing (WIELAND and VAN LOON, 2002). Furthermore the oxidation state of Neptunium is uncertain in most of the published

sorption studies because the redox conditions were not controlled and measurements of the Np redox state are lacking.

Sorption reactions onto solid surfaces mainly involve interactions with surface ligands (e.g. surface hydroxyl groups), and thus similar correlations as in the complexation chemistry are expected to be valid. As mentioned above, the effective charge of NpO_2^+ is 2.3. Therefore, in some current sorption databases (e.g. WIELAND and VAN LOON, 2002), sorption distribution ratios (R_d 's) for Np(V) are assumed to be similar in value to those of the bivalent metal cations (i.e. between $0.1 \text{ m}^3 \text{ kg}^{-1}$ and $0.5 \text{ m}^3 \text{ kg}^{-1}$).

Following the same reasoning, the sorption behavior of Np(IV) onto cementitious materials is generally assumed to be similar to the sorption behavior of Th(IV), which is characterized by extremely high R_d values up to $100 \text{ m}^3 \text{ kg}^{-1}$ -(TITS et al., 2002; TITS et al., 2000).

On the atomic level the existing information of uptake of Np by cementitious materials is very poor as well. To the best of our knowledge, the work by ZHAO et al. (2000) is the only XAFS study with Np(IV/V) on cementitious materials. The authors determined the oxidation state of Np in untreated and hydro-thermally treated hardened cement paste (HCP). Np(V) was found to be reduced to Np(IV), which increased the fraction of Np(IV) bound in HCP over time. Nevertheless, a structural model of Np(IV/V) coordination in HCP could not be deduced.

Goal of project

The investigations planned by PSI in the framework of Recosy aim at obtaining a better understanding of the Np(IV/V) behavior in a cementitious environment under well-controlled redox conditions, whilst assessing the validity of the analogies in sorption behavior discussed above. To achieve this goal, batch solubility and sorption studies with both Np(V) and Np(IV) will be carried out on different cementitious materials under carefully controlled redox conditions with emphasis on the identification of the oxidation state of Np in these experiments. In parallel EXAFS studies will be performed on some of the samples resulting from the batch sorption studies to obtain information about the coordination environment of the sorbed Np species.

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Determination of redox processes of radionuclides in biofilms

FZD

Biofilms show a complex architecture of heterogeneously distributed sessile bacteria embedded in extracellular polymeric substances (EPS), made of polysaccharides, proteins, lipoproteins and glycoproteins (Flemming, 1991). They are interspersed by open water channels, through which nutrients and possibly toxic heavy metals from the surrounding bulk solution effectively infuse into the biofilms to the microorganisms and metabolites (Stoodley et al., 1994). The retention of radionuclides by biofilms is probably different from the interactions with single cell suspensions of only one type of bacterial species. In recent years, a range of microsensor studies were carried out to measure in situ microbial activities and microbial metabolic processes in biofilms (e.g., Revsbech and Jorgensen, 1986; de Beer et al., 1997; Bishop and Yu, 1999; de Beer, 2000; Yu and Bishop, 2001; Flemming et al., 2004; Kühl, 2005). However, investigations of the influence of toxic heavy metals on the metabolic activity of biofilms using electrochemical microelectrodes are sparse. Notwithstanding their importance as essential micronutrients, heavy metals are toxic to microorganisms at higher concentration because of their adversary binding to enzymes and DNA (Schmidt et al., 2005). Despite the importance of microbial responses to toxic heavy metals in environmentally relevant concentrations, there is little information on this issue. A study of the impact of Zn and Ni on microbial benthic communities was conducted by Viret et al. (2006) estimating the oxygen consumption on the basis of microsensor profiles. In a recent study of the Krawczyk-Bärsch et al. (2008), the metabolic response of stable multispecies biofilms, grown in the laboratory, on the stress factor uranium was studied for the first time by electro-chemical oxygen microsensors. The gradient of the oxygen concentration within the studied multispecies biofilms was seriously affected by the presence as well as by the concentration of uranium in the bulk solution. The addition of uranium (VI) in ecologically relevant concentrations (1×10^{-5} and 1×10^{-6} M) to stable multispecies biofilms induced a fast decrease of the oxygen concentration with increasing biofilm depth. It showed that the bacteria in the top region of the biofilms, i.e., the metabolically most active biofilm zone, battle the toxic effects of aqueous uranium with an increased respiratory activity, resulting to increased oxygen depleted zones. Such oxygen depleted zones may induce redox reactions which may lead to precipitation of uranium (IV) solids and consequently to a removal of uranium from the aqueous phase.

Within the framework of ReCosy redox processes in biofilms, grown in-situ in radionuclide contaminated environments, will be studied by oxygen and redox potential microsensors. First measurement activities have already taken place in a former uranium mine in Saxony (Germany). For remediation the biggest part of the former underground mining is in the process of being flooded. Huge biofilms with a thickness of more than 10 centimeters are currently growing in drainage channels (so far not flooded) under acid conditions and in the presence of uranium concentrations of approximately 1×10^{-4} M. Concentration profiles of oxygen were measured in these biofilms in-situ by means of electrochemical microsensors of the Clark design (Unisense, Denmark). These Clark-type oxygen microsensors are generally used for microbial ecology studies and contain

a guard electrode (Revsbech, 1989, 2005). They have a tip diameter of 10 μm , a stirring sensitivity of <1–2%, and a response time of <1 s. The sensors were connected to a picoammeter and fixed in a holder on a motor-driven micromanipulator stage, connected with a motor controller, for a precise small-scale positioning and for automated measurements in 20 or 50 μm steps in Z-axis. The motor controller communicated with a PC via the RS-232 serial port, which was controlled from the PC with the program PROFIX (Unisense, Denmark). Due to the heterogeneities of the biofilm, numerous microprofiles were measured at different points of the biofilm. The results revealed a fast decrease of the oxygen concentration in the biofilm profiles. Already at a depth of approximately 2 mm no oxygen was detectable. It can be assumed that the microorganisms of the biofilm battle the toxic effects of aqueous uranium in a similar way as the biofilms described in Krawczyk-Bärsch et al. (2008). The increased metabolic activity of the microorganisms, as a result of an activation of heavy metal resistance mechanisms, will lead to larger anoxic zones within the biofilms, which may induce redox processes. In these zones uranium (VI) can be reduced to highly insoluble uranium (IV) through abiotic processes.

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WP5. Redox processes in radionuclide transport

State of the art

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Diffusion of redox sensitive radionuclides through clay formations

CEA

Due to extreme hydraulic and retention properties, indurate clay rocks are considered worldwide as potential host rocks for radioactive waste disposal. Numerous studies have shown that migration of radionuclides in argillaceous rocks is mainly controlled by molecular diffusion. This is the case for the Callovo-Oxfordian argillite (COx). Diffusive parameters of different radionuclides through the COx have been already determined. One can distinguish three different families according to their mobility. Hence, HTO is often taken as an inert tracer since this radiotracer offers the possibility to access to the total porosity^[1-4]. Second, cationic species which are known to be sorbed onto clayey materials, exhibit however high D_e compared to neutral species^[1-2;5-6]. This behaviour, called “surface diffusion mechanism”, is attributed the migration of cations within the electrical double layer, next to mineral surfaces. Last, the anionic species migration, such as Cl^- , I^- and SeO_3^{2-} , is characterized by a systematic delay with respect to HTO^[4;7-8]. This is due to anionic exclusion, as anions are repelled by the permanent negative charge of the surface of clay minerals. However, anions are less subject to sorption onto clayey minerals. This is why $^{36}\text{Cl}^-$, $^{129}\text{I}^-$ and $^{79}\text{SeO}_3^{2-}$ are identified among the largest contributors to the performance assessment associated with radioactive waste disposal.

I^- sorption is still under debate^[4;7;9-11]. I^- speciation/redox change may occur during any experiment since generally no special care is taken regarding the speciation. In this case, the formation of IO_3^- may occur. Furthermore, the redox state of argillite may play also a major role as the COx argillite is known for its reducing conditions^[12]. Hence, it was shown that I^- uptake is strongly dependant on the anoxic conditions^[7]. Concurrently, a weak I^- sorption may also be an artefact since IO_3^- could be sorbed and reduced into I_2 at the FeS_2 surface whereas no sorption of I^- was found^[13]. Last, a rapid reduction of IO_3^- into I^- was observed during a diffusion test through the Opalinus Clay (OPA)^[14]. The same question arises with SeO_3^{2-} . Even though SeO_3^{2-} sorption onto clayey minerals was previously reported^[15], one may wonder if its sorption occurs without redox change as underlined by the very low D_e measured in COx^[4] and its reduction observed onto FeS_2 surface^[16]. To our knowledge, diffusive data regarding SeO_4^{2-} in

hard clay rocks are only available for the Boom clay formation^[17]. In this case, the diffusive parameters for SeO_4^{2-} are very close to those of SO_4^{2-} .

One may extend the definition of anionic species in the frame of migration of actinides in hard clay rocks from a deep geological waste disposal. The high sulphate and carbonate contents in porewaters drastically change the speciation of actinides since from cationic form as predicted in pure water whatever their oxidation number, they become mainly under anionic species as CO_3^{2-} and SO_4^{2-} complexes. The diffusive behaviour of such oxyanions of high molecular weight in hard clay rocks may differ from halides. Besides, redox transformations may also occur during interaction between argillite and actinides as illustrated by the reduction of $\text{U}^{(\text{VI})}$ observed on FeS_2 surface^[18-19]. Migration of actinides in hard clay rocks may therefore be delayed by the combination of sorption, redox transformation and anionic exclusion. Classical through-diffusion set-up which focuses on the incoming daily flux in the downstream reservoir, that is to say aqueous concentrations, can not be simply applied to these elements since duration of such diffusion tests can reach very long time. The recent use of imaging surface techniques such as μ -LIBS for Eu in the COx ^[5] or autoradiography for Pu in the OPA^[20] offers the opportunity to join the diffusive profile of a reactive tracer in the rock, to the aqueous concentrations in downstream reservoir.

This study aims at understanding the diffusive behaviour of redox sensitive anions (I, Se) and oxyanions of high molecular weight (U and some REE) in the COx argillite with a special emphasis on the coupling of the knowledge of both aqueous speciation and the diffusive profile of these reactive tracers in the studied rock.

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Relevance of redox conditions in phosphogypsum

UNICYPRUS

Phosphogypsum is an acidic by-product of the phosphate fertilizer industry, produced during the production of phosphoric acid from phosphate rock. Worldwide, large amounts of phosphogypsum have been produced up to now and it is estimated that if historic trends continue, production will increase to several hundred million metric tonnes annually. However, because of economic restraints (e.g. the price of the land) and pressing environmental issues the development of a safe disposal procedure is necessary. Although, the best option for dealing with the PG problem appears to be the commercial use of this material in the agriculture (e.g. amelioration of acid soils) and construction industry (building/road construction), only a relative small portion of the phosphogypsum produced (14%) is reprocessed, a significant part is dumped into water bodies (28%) and the main part of the material is accumulated in large sludge ponds and retaining stockpiles (Rutherford *et al.*, 1994, Burnett and Elzerman, 2001).

In order to understand the impact of the the physico-chemical conditions and in particular of Eh on the redox-stability of redox sensitive chemical species (e.g. sulfate and uranium(VI)), it is necessary to determine the physico-chemical parameters and evaluate the redox conditions (e.g. redox potential) existing in phosphogypsum stack solutions.

Based on previous data and the data obtained after the first project year's investigation about the phosphogypsum stack at a coastal area in Cyprus, there is a relatively clear picture regarding the physico-chemical conditions that exist within the open stack and in particular the stack solutions:

- the salinity (ionic strength) affects strongly solubility of phosphogypsum and leachability of uranium from the matrix.
- the of pH and temperature don't significantly affect the solubility of phosphogypsum.
- the redox conditions existing in the open stack are oxic/aerobic ($530 \text{ mV} < \text{Eh} < 575 \text{ mV}$), indicating that sulfate and uranium(VI) will the predominant redox species.



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WP6. Redox reactions affecting the spent fuel source-term

State of the art

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Corrosion of spent fuel in presence of corroding Fe

JRC-ITU

Underground storage of spent nuclear fuel is a generally accepted strategy for final disposal. In many European countries the disposal concept foresees a storage of spent fuel in a cast iron, stainless steel or carbon steel container with an overpack of copper or carbon steel [Bennet et al., 2008; Ferón et al., 2008]. In such a container spent fuel is in direct contact with the cladding material e.g. Zircaloy and steel. The principle of galvanic coupling of spent fuel with metals has been discussed at the example of defect spent fuel electrodes immersed in synthetic groundwater and 5 M NaCl solution [Grambow et al., 2000]. Studies on the effect of carbon steel and Zircaloy-4 in direct contact with UO_{2+x} have been carried out in salt brines and bentonite porewater under oxidising conditions. It was shown that in case of Zircaloy-4 UO_2 dominates the contact potential and the corrosion behaviour [Kupfer, 2000] while in the pair carbon steel and UO_2 the steel is dominating. In the latter case the corrosion of UO_2 is reduced when in direct contact with steel. This effect is enhanced in cases where less iron corrosion products were detected which form a passive layer on the steel surface [Engelhart, 1999]. The stability of this passive layer is influenced by hydrogen [Yu et al., 2002]. Hydrogen promotes the susceptibility of the passive film on iron to pitting corrosion especially under lower chloride ion concentrations. Therefore it is foreseen to investigate the behaviour of simfuel and spent fuel electrically connected to carbon steel in presence of hydrogen.

Influence of redox sensitive metals in the fuel

JRC-ITU

For a reliable assessment of the long-term storage behaviour of spent fuel a mechanistic understanding of the interactions of the waste forms with the surrounding environment is indispensable.

The dissolution of UO_2 and spent fuel has been extensively studied over the last years. Several key reactions within a failed container in contact with groundwater are widely agreed on. Anyhow the system is very complex and it is difficult to draw conclusions on the mechanisms from experiments within this complex system. Therefore a clear understanding necessary for long term predictions have not been achieved yet [Shoesmith, 2007].

Two reaction fronts are influencing the overall process that manifests in the measured spent fuel dissolution rate. On the one side there is the corroding fuel surface. Here H_2O_2 was identified as most important radiolytic oxidant and models were proposed to describe and predict the dissolution rates. On the other side a second reaction front due to the corrosion of the canister steel surfaces exists in the system. In recent years the effect of hydrogen, produced by this corrosion process, on the dissolution of spent fuel evolved from certain considerations and experiments. An inhibiting effect of H_2 on the dissolution was observed in leaching experiments in presence of H_2 as well as a reduced corrosion potential of SIMFUEL (containing ϵ -particle models) in presence of H_2 .

According to these findings a heterogeneous Pd-catalysed H_2 -dissociation reaction is proposed in the presence of the simulated ϵ -particles. As they are in galvanic contact with the fuel matrix they can act as an anode causing the reduction of oxidised uranium still retained at the fuel surface. The net effect in solution with radiolysis would be the recombination of H_2O_2 and H_2 to water [Brockzowski et al., 2005]. Recent experiments indicate that Pd catalyses as well the reaction between H_2O_2 and H_2 [Nilsson and Jonsson, 2008], as the reduction of UO_2^{2+} (aq) [Nilsson and Jonsson, 2008b] and the oxidation of UO_2 by H_2O_2 (in N_2 atmosphere) [Trummer et al., 2008]. Additionally a prevailing inhibiting effect of H_2 on following oxidation cycles is described [**Error! Marcador no definido.**]. However, it is not completely clear whether as well a UO_2 surface without the Pd inclusions may catalyse the H_2 reaction with UO_2^{2+} (aq) [Carbol et al., 2005].

Therefore laboratory experiments using simple model systems for single effect studies will be performed to elucidate the underlying mechanistic processes. The spent fuel models are UO_2 thin films produced by sputter deposition technique which allows a doping with additional elements for single effect studies. The production of Pd inclusions (to simulate ϵ -particles) in UO_2 , and eventually the introduction of rare earth elements into the UO_2 matrix to simulate the influence of M^{3+} on the reactions is planned. The investigation of (doped) UO_2 thin films is one of the current research fields of the surface science group at ITU and it was shown that these thin films can serve as reaction models for the fuel surface [Stumpf, 2008; Seibert, 2006, 2007; Miserque et al, 2001].

Gas adsorption reactions (with O_2 , H_2 , H_2O) are planned directly after film production and characterisation by XPS without handling the sample outside the ultrahigh vacuum preparation chamber. In the same manner the investigation of the more reactive radical species ($O\cdot$ and $H\cdot$) is possible [Gouder et al., 2007; Seibert et al., 2008].

Additionally the doped thin films are used as electrodes in electrochemical experiments with the electrochemical quartz crystal microbalance (ECQM) to determine corrosion properties as corrosion potential, cyclic voltammetric response etc. together with the mass change of the electrode, which facilitates conclusions on the mechanistic processes underlying the overall electrochemical behaviour [Snook et al., 2002; Seibert et al., 2008].

Corrosion of spent fuel in presence of H_2

JRC-ITU

It has been shown in a number of fuel corrosion experiments under hydrogen atmosphere that the concentrations of uranium and other redox sensitive elements as Np, Pu, Tc etc. decrease during the initial stage of the experiment, instead of increase as expected under the strong radiation field [Carbol et al., 2005]. There is a large amount of experimental evidence for the existence of surface-mediated processes causing the reaction of dissolved hydrogen with radiolytic oxidants and oxidized forms of radionuclides [Cui et al., 2008]. However, the mechanisms behind these reactions are unknown.

Different theories have been suggested to explain the effect of dissolved hydrogen in a fuel/groundwater system. These include: catalytic decomposition of H₂ on ε-particles, creation of H• due to surface defects as oxygen vacancies and Frenkel pairs, or activation of the H₂ due to radiation-induced excitons or lattice energies [Jonsson et al., 2007]. But none of them have been verified in laboratory experiments. Recent results indicate that the splitting of hydrogen might be an inherent property of UO₂ associated with the multiple oxidation states of uranium. Of special interest is the existence and role of pentavalent uranium [Wren et al., 2005].

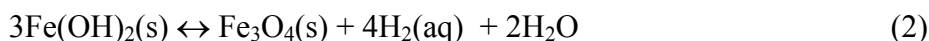
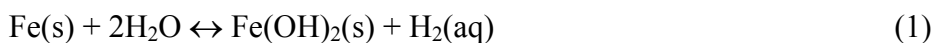
High burn-up, HBU, fuel corrosion under reducing conditions has not been studied before. The intense mixed radiation field will create a large number of molecular and radical oxidants that potentially will oxidize the fuel. Additionally, the damaged rim structure might have undergone structural changes making the hydrogen effect non-working. Nevertheless, as the HBU-fuel is largely UO₂, no major diverging behaviour compared to normal burn-up UO₂ regarding hydrogen is expected.

The effect of iron corrosion on spent fuel dissolution – the state of the art

NRI

The mechanism of alteration of spent fuel matrix after ingress of water in waste packages is very complex. Shoesmith et al., (2003) presented a general reaction scheme of processes occurring inside waste packages (Fig. 1).

It can be seen that a large number of factors affect spent fuel dissolution rate. Corrosion of spent fuel will be primarily affected by two corrosion fronts formed on fuel surface and steel surface, interconnected by diffusion processes in the groundwater. Dissolution of spent fuel and release of radionuclides from spent fuel will be determined primarily by reactions of less thermodynamically stable iron than by more noble metals of spent fuel structure materials or spent fuel matrix presented inside waste packages. Corrosion front on steel surface is given primarily by the reactions of iron with water (reactions (1) and (2)), reactions of iron ions with other species presented in water and the nature of iron corrosion products formed.



On the basis of a comprehensive literature review and a number of experiments performed within recently finished NF-PRO project [Arcos et al. 2008], it was concluded that 1) corrosion rate of carbon steel in anaerobic conditions will be lower than 5 μm/yr, 2) the processes affecting corrosion products nature are very complex so that the nature of corrosion products will depend significantly on composition of bentonite porewater. It cannot be expected that some equilibrium or some long-term steady state will be formed inside waste packages, because they are already open to flow of water to and from canisters. The maximum pressure of hydrogen achieved in canisters will depend on properties of compacted bentonite. After achieving the

maximum pressure, hydrogen will breakthrough through bentonite and the pressure will be decreased. This process will be repeated until the consumption of all the iron in waste packages or possible loss of sealing properties of bentonite (formation of a preferential path for hydrogen release) after which hydrogen pressure will decrease to some steady state level.

Both iron species and hydrogen have a strong influence on fuel corrosion rates (e.g. [Spahiu et al., 2000; Loida et al., 2004]). Hydrogen can reduce uranium matrix dissolution rate, but the main reasons underlying this decrease have not been sufficiently explained. An effect of Fe (II) on scavenging of radiolytically formed oxidants and reducing U (VI) species inside waste packages was studied by Johnson and Smith (2000), who derived the model for release of Fe^{2+} from an inside part of corroding steel canister after ingress of water on the basis of the assumption that the only corrosion product is magnetite (Fe_3O_4) and the flux of Fe^{2+} from magnetite can be equated to the rate of passivating maghemite ($\gamma\text{-Fe}_2\text{O}_3$) film grown on the surface of magnetite due to oxidation of magnetite. They found that the production of radiolytic oxidants decreases as a function of time, whereas the production of Fe (II) initially decreases but increases at longer times as a result of the formation of high surface area of corrosion deposits. The time at which production of Fe(II) first exceeds that of radiolytic oxidants is also the time at which the oxidising region reaches its maximum extent.

Not only iron, but also other spent fuel structure materials (e.g. stainless steels) presented inside waste packages can affect chemical conditions for spent fuel dissolution. For example in the papers of Domski (2000) or Pan et al. (2002) the inner environment in spent fuel waste package was studied using geochemical code EQ3. The major result of these studies was a strong decrease of pH inside canisters, which depended on the flow of water to and from canister, composition of water and the nature of inner components of waste packages. There was observed a decrease of pH reaching very low values (approaching 2.6) mainly from the oxidation of stainless steel structural components, particularly of Cr^{3+} species.

No papers have been devoted so far to experimental modelling of the effect of corrosion of iron on the development of chemical conditions inside waste packages. This will be the main subject of NRI experimental work.

Reductive Trapping of Actinides in Container Corrosion Products during Spent Fuel Corrosion

FZK/INE

With respect to the assessment of the long-term behaviour of the waste form spent nuclear fuel, it is of high importance to study the fuel alteration resulting from the contact with groundwater in presence of Fe based container material, or its corrosion products, respectively. Performance assessment of spent nuclear fuel disposal requires careful quantification of its long-term ability to re-immobilize individual radioelements. This may be achieved either by retention upon the surfaces of the solid phases, which are present in the system, or incorporation in newly formed secondary phases. Related

research comprises analyses of the (geo)chemical interactions of spent fuel with aqueous solutions (groundwater, brine), host rocks and near field components.

Various experimental data on the dissolution behaviour of the spent fuel matrix itself and in some cases in presence of container material (initial metallic Fe powder) as well, and the associated releases of radioelements were already obtained by extensive laboratory test programs and reported e.g. in [Shoesmith, 2000; Ferry et al., 2005; Loida et al., 1996]. However, only minor amount of knowledge is available on the extent and nature of radionuclide retention immediately after their mobilization from the fuel inventory in the course of long-term corrosion.

Thus, in the frame of this work we study the effect of the presence of magnetite (Fe_3O_4), representing the most important container corrosion product on the overall alteration behaviour of high burnup spent fuel in highly concentrated salt brine, over a long-term period of time. Special attention will be directed on the fate of radionuclides released from the fuel inventory. In this context issues are addressed to the fraction of radionuclides mobilized from the fuel inventory (1) either released into solution, or (2) re-immobilized by various processes upon the surfaces of the solid phases in the system. Processes under consideration are sorption upon the fuel sample itself, upon the magnetite or the vessel wall, or incorporation in the crystal lattice of newly formed secondary phases. A further question is related on the impact of Fe corrosion products on the dissolution rate of the fuel matrix, because magnetite is known to sorb uranium, the main constituent of spent fuel, at a high extent. This may possibly result in an accelerated dissolution of the fuel matrix (“pump effect”).

As an experimental approach, we investigate the alteration behaviour of a spent fuel pellet (50 MWd/kgHM) in presence of magnetite granulate (\varnothing about 5 μm) in 5M NaCl brine under anoxic conditions over a “long-term” period of time. We will terminate the related corrosion experiment, which is running over totally 9.3 years, where the last sampling interval was lasting about 4.4 years. To determine the reaction progress both, the gas phase and the solution will be analysed with respect to hydrogen, oxygen and released radionuclides. Special attention will be directed on the retention of radionuclides upon the solid phases. Studies aiming on their identification and characterization will be performed by means of “in-situ” Raman spectroscopy, directly upon the corroded spent fuel sample. The suitability of Raman spectroscopy in particular to study uranium bearing solid phases was recently described by Amme et al. (2002). SEM/EDS-techniques and XRD will be applied for Fe-corrosion products and small particles removed from the fuel surface. To determine the amount of actinides retained on the corroded magnetite in the course of brine contact, a part of it will be dissolved in concentrated nitric acid, and afterwards analysed radiochemically. Moreover, the amount of radionuclides sorbed upon the surface of the vessel wall will be identified by stripping the vessel with concentrated nitric acid and subsequent radiochemical analyse.

Presently, we perform general preparations in our hot cells, related to terminate the long-term spent fuel corrosion experiment in presence of magnetite in 5M NaCl solution. However, strong emphasis is placed on establishing the Raman probe inside of

the hot cell allowing “in-situ” Raman measurements upon the surfaces of the corroded spent fuel sample and the magnetite as well.

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