

Seventh International Conference on the  
**Chemistry and Migration Behavior of Actinides  
and Fission Products in the Geosphere**

# **MIGRATION '99**



## **Abstracts**

**Incline Village  
Lake Tahoe, Nevada/California, USA  
September 26 – October 1, 1999**



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## **Abstracts**

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**September 1999**

**Hyatt Regency  
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The Migration conferences focus on recent developments in the fundamental chemistry of actinides and fission products in natural aquifer systems, their interactions and migration in the geosphere, and the processes involved in modeling their geochemical behavior.

The primary mode dissemination of technical information will be early evening poster sessions designed to encourage intensive communication between the authors and participants. Daily oral sessions will be opened with invited lectures followed by contributed papers within the scope of each session.

Sessions cover:

A. Chemistry of actinides and fission products in natural aquatic systems

1. Solubilities and dissolution reactions
2. Complexation with inorganic and organic ligands
3. Redox reactions
4. Colloid formation
5. Experimental methods

B. Geochemical interactions and transport phenomena

1. Diffusion and migration in geologic media
2. Sorption/desorption phenomena
3. Natural analog studies
4. Effects of biological activities and organic materials
5. Colloid transport
6. Radionuclides in soils
7. Soil-remediation chemistries

C. Data base development and modeling

1. Data selection and evaluation
2. Data base management
3. Geochemical models and modeling
4. Application of models
5. Validation of modeling results

# ABSTRACTS



## COMPARISON OF $K_d$ AND SURFACE COMPLEXATION MODELING APPROACHES IN U(VI) TRANSPORT SIMULATIONS WITH SPATIALLY VARIABLE CHEMICAL CONDITIONS

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One-dimensional, reactive transport simulations were performed to compare different methods of describing radionuclide adsorption and retardation in solute transport modeling. Bounding values for hydrologic parameters and chemical conditions in the model simulations were based on field conditions at a site contaminated by uranium mill tailings. Chemical conditions within the shallow aquifer at the site vary spatially, with pH ranging from 6.9 to 7.4, alkalinity from 200 to 520 mg/L (as  $\text{CaCO}_3$ ), and U(VI) concentration from 6 to 1200 ppb. The transport simulations were performed along a hypothetical flow line within the aquifer, assuming a temporally invariant hydrologic gradient and spatially uniform hydraulic conductivity and mineralogy (adsorptive characteristics) for the porous medium. Variable aqueous chemical conditions were approximated by dividing the aquifer into several spatial domains along the flow path, with the chemical conditions of each domain based on actual groundwater conditions at the field site. U(VI) adsorption reactions within the solute transport modeling were described by: 1) a single  $K_d$  value applied to the entire flow path, 2) variable  $K_d$  values, with each spatial domain assigned a different value, and 3) surface complexation modeling using a generalized composite modeling approach. The results demonstrate that surface complexation modeling can be an effective tool for predicting  $K_d$  values for performance assessment calculations at sites with variable chemical conditions.

## MODELING OF HUMIC COLLOID BORNE AMERICIUM (III) MIGRATION IN COLUMN EXPERIMENTS USING THE TRANSPORT/SPECIATION CODE K1-D AND THE KICAM MODEL

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The humic colloid borne Am(III) transport was investigated in column experiments for Gorleben groundwater/sand systems. It was found that the interaction of Am with humic colloids is kinetically controlled, which strongly influenced the migration behavior of Am(III). The kinetic effects have to be taken into account for transport/speciation modeling.

The KICAM (KInetically Controlled Availability Model) was developed to describe actinide sorption and transport in laboratory batch and column experiments. It is an empirical approach based on association/dissociation kinetics of actinides onto or from humic collids. The application of the KICAM requires a chemical transport/speciation code, which simultaneously model both kinetically controlled processes and equilibrium reactions. Therefore, the code K1-D was developed as a flexible research code that allows the inclusion of kinetic data in addition to transport features and chemical equilibrium.

The application of the KICAM concept is presented using the K1-D code for column experiments comprising the unretarded breakthrough of humic colloid borne Am as well as the retarded Am migration. The model parameters were determined for a Gorleben groundwater system of high humic colloid concentration. A single set of parameters was used to model a series of column experiments. Model results correspond well to experimental data for the unretarded humic borne Am breakthrough. Modeling the distribution of Am sorbed onto sediment in a column was less successful due to the fact that the interaction between Am and the humic coated sediment surface could not be characterized in detail from experimental data.

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## NEAR-FIELD MIGRATION OF RADIONUCLIDES IN GROUNDWATER AWAY FROM AN UNDERGROUND NUCLEAR TEST

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Reactive transport simulations are being used to evaluate the nature and extent of radionuclide contamination within the near-field hydrologic environment surrounding a specific underground nuclear test at the Nevada Test Site. Interest is focused on determining the abundance and chemical nature of radionuclides that are introduced into groundwater as aqueous species, as well as the rate and extent of radionuclide migration and reaction in groundwater surrounding the working point of the test. This effort is being used to determine an improved "hydrologic source term" for use in other transport simulations designed to assess the fate of radionuclides over longer times and larger spatial scales.

For the current application, a technical approach has been pursued that involves (i) selection of a subset of radionuclides for formal analyses, (ii) estimation of their inventory and distribution among the melt glass and rubble phases about the test cavity, (iii) development of a dissolution model for the melt glass, (iv) calculation of the principal aqueous radionuclide species in groundwater, and (v) analysis of surface complexation and ion exchange reactions that occur between the radionuclides and reactive minerals in the host formation. Preliminary transport simulations will be used to illustrate the nature of radionuclide elution out of the near-field environment. Although the results can be particularly sensitive to the available surface area in the fractured melt glass, reactive mineral phase distribution in the near field, and overall groundwater flow configuration, they provide a rational basis from which defensible migration assessments can proceed.

This work was conducted under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-Eng-48. This work was funded by the Underground Test Area Project, Department of Energy, U. S. Nevada Operations Office.

## SOLUBILITY AND HYDROLYSIS OF TECHNETIUM (IV) OXIDES IN AQUEOUS SOLUTION UP TO 70°C, 0.1MPa

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The solubility of amorphous and crystalline TcO<sub>2</sub> in NaCF<sub>3</sub>SO<sub>3</sub> and NaCl solutions was determined as function of three physico-chemical parameters :

1/ pH (0 - 14)

2/ Ionic strength (0.1 and 1.0m)

3/ Temperature (5 - 70°C).

### Solubility of amorphous TcO<sub>2</sub>

In acidic solution ( $1.0 \leq \text{pH} \leq 2.0$ ), the concentration of dissolved Tc(IV), in equilibrium with amorphous TcO<sub>2</sub>, was in the range  $10^{-7}$  -  $10^{-8}$  mol/l and increased with the increasing acidity. The minimum of Tc (IV) solubility ( $10^{-8.2}$  mol/l) was observed in a wide range of pH from 3.0 to 10.0. In basic solution, the increase of pH from 10.5 to 14.0 led to an increase of the Tc(IV) solubility from  $10^{-8}$  to  $10^{-5}$  mol/l. The solubility curve log Tc(IV) vs pH was characterized by three slopes -1, 0, and 1 corresponding to three hydrolyzed species of the type Tc(OH)<sup>4-n</sup> (n = 3 - 5). Values of log Q and log K were determined for three solubility reactions as follows :



at 25°C and 0.1 MPa.

### Solubility of crystalline TcO<sub>2</sub>

The shape of the solubility curve of crystalline TcO<sub>2</sub> is similar to that of the amorphous phase. The solubility of Tc(IV) in the pH range 1 - 13 is approximately one order of magnitude lower than that of the amorphous phase. Values of log Q and log K were determined for three solubility reactions (equation 1) with crystalline TcO<sub>2</sub> and up to 70°C. The solubility of Tc(IV) appeared to be independant of the temperature in the range 5 - 70°C and of the ionic strength in the range 0.1 - 1.0m.

## THE PRECIPITATION OF CRYSTALLINE NEPTUNIUM DIOXIDE FROM NEAR-NEUTRAL AQUEOUS SOLUTION

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High-level nuclear waste disposal has become a serious issue for most of the modern world. In the U.S., the DOE is pursuing the establishment of a permanent, geological disposal site at Yucca Mountain, NV. Currently, the U.S. is using a conservative approach when conducting potential radiation dose and repository performance calculations. Incorporation of published neptunium concentrations observed in short term experiments has yielded calculated doses in excess of proposed long-term dose-based regulatory limits. These results may grossly exaggerate the long-term reality in an actual repository by ignoring the role of certain insoluble Np solids that may form only at very slow rates. Existing thermodynamic data at 25 degrees C show that experimentally observed, approximately  $1 \text{ E-}3 \text{ M}$  Np concentrations at pH 6 are supersaturated with respect to Np(IV) oxide. However, the only reported solid phases were Np(V) solids, both sodium neptunyl(V) carbonates and Np(V) oxide. Our hypothesis is that Np(IV) oxide is the thermodynamically stable solid phase in near neutral aqueous solution, but it is slow to form on the time scale of the earlier laboratory experiments. The precipitation of a crystalline Np(IV) oxide solid would go hand in hand with significantly lower aqueous Np concentrations. Such concentrations, if observed, would support calculated doses far below proposed long-term dose-based regulatory limits. Accordingly, we are studying the solubility and precipitation kinetics of Np at higher temperatures. Solubility experiments have been performed by introducing ionic Np(V) under mildly oxidic conditions into very dilute solutions of NaCl with initial pH values ranging from 6 to 10. The reaction vessels were then placed into an oven at 200 degrees C and allowed to react until steady-state aqueous Np concentrations were observed. In all cases, steady-state aqueous Np concentrations decreased significantly from the initial value of  $1 \text{ E-}4 \text{ M}$ . The resulting solids were collected and analyzed by XRD, XANES and EXAFS, and SEM. The solids were determined to be high-purity crystals of Np(IV) oxide. The octahedra ranged in size from a few tens of microns to nearly 100 microns. Experiments were repeated to confirm the results. This is the first time, known to the authors, that crystalline Np(IV) oxide has been observed to precipitate from near-neutral aqueous solutions. Work at elevated temperatures is continuing in order to model the reaction kinetics of this precipitation from ionic Np(V) as well as the dissolution kinetics from undersaturation using a well characterized, crystalline Np(IV) oxide solid.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

## THE INFLUENCE OF NEAR FIELD HYDROGEN ON ACTINIDE SOLUBILITIES AND SPENT FUEL LEACHING

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Large amounts of hydrogen are produced as a result of the anoxic corrosion of iron in the proposed container materials for some geologic repositories. Another hydrogen source, less important than the anoxic corrosion of iron, is the radiolysis of water by the spent fuel radiation. Gas phase formation occurs when the pressure of the hydrogen equals at least the hydrostatic pressure, around 5 MPa at 500 meters depth. The effect of a 5 MPa hydrogen pressure on spent PWR fuel leaching and on uranium oxide solubility has been studied in carbonated solutions at 70 °C. The experiments were performed in a 1 litre autoclave, filled with 950 ml of a solution 10 mM NaCl, 2 mM NaHCO<sub>3</sub> and with hydrogen at a pressure of 5 MPa in the remaining 50 ml free volume. The leaching behaviour of 2 g PWR spent fuel powder of the 0.25-0.50 mm fraction, placed in a gold basket was studied during several months by analysing 10 ml solution samples taken after regular time intervals. A few experiments were performed also with inactive U(IV) oxide. In both cases extremely low concentrations of uranium (less than 10<sup>-9</sup> M) were measured in the solution samples. Furthermore the uranium levels in solution remained practically constant during the whole leaching period (almost 10 months), indicating the absence of any oxidative dissolution of the spent fuel matrix. The same conclusion is confirmed by the constant (within analytical errors) levels of strontium, cesium, molybdenum, iodine and technetium during the whole leaching period. These results have been compared with the ones obtained during the leaching of a spent fuel pin in anoxic conditions, where the uranium and other radionuclides levels are several orders of magnitude higher.

The surface of spent fuel or U(IV) oxide is partially oxidised during storage, giving rise to relatively high levels of U(VI) in solution even during leaching in anoxic conditions. No such effect could be observed in the presence of 5 MPa hydrogen, indicating that this initial amount of U(VI) should have been reduced to U(IV). The experimental study of the influence of various parameters as temperature and pressure is still in progress.

## THE ROLES OF SOLID ALTERATION PRODUCTS IN LIMITING RELEASES OF U, Np, Pu AND LANTHANIDES FROM CORRODED NUCLEAR-WASTE FORMS

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Corrosion of actinide-bearing nuclear-waste forms under conditions comparable to those expected in the proposed repository at Yucca Mountain produces a suite of corrosion products that can limit releases of certain radionuclides (RNs). Combined analyses of solid corrosion products and leachates demonstrates how and which corrosion products can influence releases of RNs from various nuclear-waste forms, including spent fuel and nuclear-waste glasses. Uranium released from spent  $\text{UO}_2$  fuel will form U(VI) oxy-hydroxides when reacted in water vapor or small volumes of simulated groundwater, whereas U(VI) silicates form when fuel is exposed to greater volumes of Si-bearing groundwater. U(VI) silicates are also the dominant U-bearing corrosion products on borosilicate nuclear-waste glasses. Molar ratios Pu:U, Am:U and REE:U in leachates from corrosion experiments with spent fuel are commonly lower than their ratios in the fuel; whereas, Np:U ratios in leachates are commonly, though not always, similar to their waste-form values. Pu, Am, and REE tend to precipitate together with Ru and Zr to form a sparingly soluble electron-amorphous residue on the surfaces of corroded spent  $\text{UO}_2$  fuel, whereas Pu, Am, and REE commonly form crystalline phosphates in corrosion experiments on nuclear-waste glasses. Np is unusual, and its behavior is not readily generalized. Np will enter the structure of the uranyl oxy-hydroxide, dehydrated schoepite, formed on  $\text{UO}_2$  fuel reacted in vapor, but the uranyl silicate, Na-boltwoodite, formed on  $\text{UO}_2$  fuel corroded in Si-saturated groundwater, does not incorporate Np to a significant degree. Crystal-chemical considerations suggest that U(VI) silicates may not accommodate Np(V) as readily as uranyl oxy-hydroxides; however, certain uranyl silicates, such as weeksite can incorporate minor Np during corrosion of borosilicate nuclear-waste glasses. Np release may therefore be controlled by multiple factors, including (1) the nature of solid corrosion products, (2) solution chemistry, (3) local redox conditions, and (4) radiolysis effects, all of which can vary, depending on waste form and experimental conditions.

## OVERVIEW AND PERFORMANCE ASSESSMENT APPLICATIONS OF THE PALMOTTU NATURAL ANALOGUE STUDY

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The Palmottu Natural analogue Project is focused on a U-Th mineralisation in SW Finland. The mineralisation and its surroundings are investigated in order to improve the scientific basis for assessing the long-term performance of a disposal site for high-active nuclear waste in crystalline bedrock. The present international phase of the study is supported by the European Community and it consists of a two-phase structure: (1) Assessing of the present-day flow situation, and (2) Identifying and quantifying the processes related to radionuclide mobilisation and migration. The study in the latter phase is organised as 4 major tasks: (1) Geochemical evolution of the water-rock system, (2) Redox processes and trace-element mobilisation, (3) Migration of radionuclides, and (4) Conclusions related to repository performance assessment.

The Palmottu U-Th mineralisation is hosted by a Proterozoic (1800 Ma) crystalline bedrock, mainly mica gneiss with granite and granite pegmatite veins. The mineralised part is associated to the granitic veins and forms a vertical structure that extends to depths of some 400 m. Accordingly it covers both near-surface oxidative conditions and low-Eh reduced conditions, generally from 100 m downwards. The primary U-bearing mineral is uraninite that has been extensively altered to U(IV) silicate, mainly coffinite. Continuous mobilisation has transferred a portion of uranium onto fracture surfaces and in fracture infilling, mainly attached to calcite, kaolinite and iron oxides, and partly as U(VI) silicates, too. Generally, however, the large majority of the uranium is still fixed to its original host mineral uraninite and its old hydrothermal alteration product U(IV) silicate.

Based on a successful integration of structural, hydrogeological, and hydrogeochemical data, a conceptual groundwater flow model was constructed. The model is composed of an Upper Flow System above a depth of 100 m, a Dynamic Deep flow system, and a Stagnant Deep hydrogeological system. The Upper Flow system is characterised by young Ca-HCO<sub>3</sub> water (tens of years), whereas the Dynamic Deep Flow system has Na-HCO<sub>3</sub> water with residence times of hundreds of years to a few thousand years. The groundwater of the Stagnant Deep hydrogeological system has a Na-SO<sub>4</sub> or Na-Cl composition. The O-18 values of these groundwaters point to recharge during glacial periods, i.e. 10 000 years ago. High dissolved uranium concentrations (generally from 100 -500 ppb) are associated with the HCO<sub>3</sub> groundwaters around the uranium bearing mineralisation down to depths of 130 m. Deeper down clearly reduced conditions, around 300 mV, and Na-SO<sub>4</sub> and Na-Cl groundwaters prevail with uranium concentrations not exceeding 10 ppb. Also the groundwaters of the barren rock outside the mineralisation show equally low uranium concentrations independent on the prevailing groundwater type. The upper uranium-rich groundwater plume forms an horizontal tube-like system with a diameter of 100 m and a horizontal extension of 300 m. Presently it is still unclear whether this plume has any further extension within the direction of the groundwater flow. - Relevant areas of PA interest will be discussed: scenarios, redox processes, aspects of radionuclide retardation and migration.

## CHARACTERIZATION OF ALTERATION PRODUCTS OF URANINITE

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Alteration products resulting from oxidative dissolution of uraninite were studied by electron microprobe analysis (EMPA), scanning electron microscopy (SEM) and backscattered electron (BSE) imaging in order to determine the behavior and fate of trace elements, such as Pb, Ca, Si, Th, Zr, REE and lanthanides. The alteration of uraninite provides an informative natural analogue for the corrosion of the  $UO_2$  in spent nuclear fuel under oxidizing condition. In the samples examined, primary uraninite has altered partly or completely to a suite of secondary uranyl minerals. The primary uraninites contain PbO from 0.7 to 1.5 wt % and low trace element contents. The contents of trace elements in uranyl phases are also generally low. Soddyite (sample #603) from Caribon Mine, Colorado, has  $Y_2O_3$  as high as 0.9 wt %. An altered uraninite (sample #527) identified in a quartz sandstone from Gilpin County, Colorado contains unusually high  $ZrO_2$  (average 5 wt %). Other significant components in this phase include  $SiO_2$ , PbO, CaO,  $Al_2O_3$ ,  $K_2O$  and FeO, indicating the possible involvement of K-feldspar, zircon or quartz during the formation of the phase. Ca-rich calciouranoite (sample #369) hosted in limestone from Grants, New Mexico, also indicates reaction of host rock and uraninite. Coexisting phases in sample #637 from Jefferson County, Colorado, include schoepite, uranophane, fourmarierite and an Fe-rich uranyl phase. One 300  $\mu$ m compositional profile conducted on a concentric structure of uranyl phases in this sample shows that, with increasing alteration,  $UO_2$ , PbO and  $ZrO_2$  decrease from 80.2 to 70.3 wt %, from 6.6 to 0.5 wt %, and from 1.8 to 0.5 wt %, respectively, and  $SiO_2$ ,  $TiO_2$ , CaO and  $P_2O_5$  increase from 0.4 to 6.1 wt %, from 1.1 to 1.8 wt %, from 1.1 to 4.0 wt %, and from 0.3 to 1.2 wt %, respectively. Therefore, alteration processes cause loss of U, Pb and Zr and incorporation of Si, Ti, Ca and P into uranyl phases, and composition of alteration products of uraninite is controlled by compositions of the uraninite, host rock and ground water.

## POSTGLACIAL URANIUM MIGRATION IN A GRANITIC ROCK PART I: PHYSICAL AND CHEMICAL ROCK MATRIX PROPERTIES AND URANIUM DISTRIBUTION

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A summary of the investigation of geologically recent U migration in a granitic rock is given. Time scales, mechanisms and factors governing the migration were studied by characterising the relevant properties of the rock and U occurrence across the rock samples in relation to structural, physical and chemical parameters (Part I) and, by examining U-series disequilibria, U binding and its oxidation state (Part II). The purpose of the investigation is to increase understanding of the long-term migration of U under *in situ* conditions. A U enrichment was observed in a narrow band below the brown zone where Mössbauer spectroscopic results showed a significant decrease of the Fe(III) content in biotite, but loosely bound Fe(III) in felsic minerals in both zones. A brown weathering rim was macroscopically visible but petrographic and microprobe analyses of main minerals did not indicate significant alteration. The whole rock matrix was hydraulically very conductive and the porosity distribution was dominated by a regular grain boundary network. The weathered zone, however, showed open fissures and porous phases leading to roughly a doubling of the porosity ( $^{14}\text{C}$ -PMMA impregnation method and Hg-intrusion-computer tomography). Fission track results indicated (i) primary uranium fairly evenly distributed across the rock and (ii) secondary migrated uranium mainly along grain boundaries in the weathered zone. These findings were corroborated by detailed scanning electron microscopic investigation which identified both types of uranium in (i) mainly monazite and zircon and (ii) along grain boundaries mainly as uranophane.

## SORPTION OF STRONTIUM ON GOETHITE AND MAGNETITE

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Sorption of radionuclides is an important concern for modeling the migration behavior of high level nuclear wastes in the near field of a deep geological disposal. Carbon steel or low alloy steels are candidates as the containers or overpacking materials. Goethite and magnetite are the major corrosion products of these canisters expected under repository conditions.

Strontium sorption experiments were performed in NaCl medium on pure synthetic magnetite and goethite according to the batch method. Strontium was chosen because it is an important fission product (25% as <sup>90</sup>Sr) in the used fuel. Purity of the materials was verified by powdered X-ray diffraction (XRD) and electronic microscopy analysis. Specific surface areas (respectively 25.0 m<sup>2</sup>.g<sup>-1</sup> and 1.8 m<sup>2</sup>.g<sup>-1</sup>) were measured using a multiple point adsorption nitrogen process (BET method). The grain sizes were determined by laser granulometry and zero points charge by the Doppler velocimetry method. The densities of the surface sites (1.3 and 6.7 sites.nm<sup>-2</sup>) were determined by potentiometric titrations and pKa of the single amphoteric sites were calculated (5.7 ; 8.9 and 5.4 ; 10.5) using the surface complexation theory (Fiteql 3.2) with the double layer model (DLM). Sorption isotherms (percentage of sorption versus pH) were determined at different ionic strengths. Maximum uptake occurred in the pH range of 9-11 and desorption and kinetic were also investigated. The rate of cation sorption was determined by measuring by ICP and PIXE the concentration of strontium after sorption in solution.

Moreover, several spectroscopic methods have been carried out in order to characterize more precisely the sorbed surface complexes. X-ray photoelectron spectroscopy (XPS) pointed out two different binding energies for the sorbed strontium ions corresponding to Sr-O and Sr-CO<sub>3</sub> bounds. Photo induced X-ray emission (PIXE) and XPS showed that the complex SrCl<sup>+</sup> was not present on the surface of both materials. X-ray absorption study (EXAFS) at the Sr L<sub>III</sub> edge is now under investigation.

Sorption isotherms will then be modeled with Fiteql code using the informations of the spectroscopic studies.

## EUROPIUM(III) SPECIES SORBED ON CLAY MINERALS IN THE PRESENCE OF POLYCARBOXYLIC ACID STUDIED BY LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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Chemical species of actinide(III), or Eu(III), sorbed on natural particulate matter such as clay minerals and iron oxides have not been fully clarified yet. In the environment, the surface of such inorganic particulate matter is often coated with humic substances, due to the strong affinity between humic substances and the particulate matter surface. Therefore, it is of great interest to clarify the actinide(III), or Eu(III) species sorbed on the particulate mineral in the presence of humic substances.

In this study, laser-induced fluorescence spectroscopy was applied for characterization of Eu(III) species sorbed on organic-inorganic hybrids such as clay minerals (montmorillonite or kaolinite) coated with polyacrylic acid or polymethacrylic acid in aqueous media. These polyacids were employed as analogues of humic substances. The emission lifetime and the emission spectra of Eu(III) sorbed on the organic-inorganic hybrid showed that Eu(III) can be sorbed as an Eu(III)-polycarboxylate complex on the clay minerals. This implies that polycarboxylate or humate complex is important species for actinide(III), or Eu(III), sorbed on the organic-inorganic hybrid in natural aquifer. It is shown that the species of Eu(III), i.e., organic or inorganic, sorbed on the organic-inorganic hybrid can be estimated from the stability constants of the Eu(III)-polycarboxylate complexes and the distribution coefficients of Eu(III) sorption on the clay minerals. Speciation study on Cm(III) species sorbed on the clay minerals in the presence of humic acid is in progress, using laser-induced fluorescence spectroscopy.

## **SURFACE COATING EFFECT OF URANIUM(VI) ON THE ADSORPTION OF LANTHANIDE(III) ONTO THE OXIDE SURFACES**

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The migration of radionuclides in groundwater is greatly controlled by sorption. Among metal ions present in groundwater, the metal ion with the highest affinity to sorb, if relatively abundant, will occupy first the active adsorption sites on the oxide surfaces, coat the surfaces and finally provide new adsorption surfaces. Since uranium is much more abundant than any other ions in the near-field and strongly adsorbed on metal oxides, it is expected that uranium has a significant influence on the sorption of other metal ions.

In the present study, the adsorption behavior of U(VI) and Eu(III) on  $\text{TiO}_2$  and  $\text{SiO}_2$  has been investigated by fluorescence spectroscopy. When the concentration of metal ions used is lower than that of surface sites, the adsorption edge of U(VI) appeared at pH 3.2 for  $\text{TiO}_2$  and at pH 4.2 for  $\text{SiO}_2$ , and that of Eu(III) appeared at pH 3.7 for  $\text{TiO}_2$  and at pH 6.5 for  $\text{SiO}_2$ . The U(VI)-Eu(III) mixed system exhibited almost the same adsorption edge irrespective of the concentration ratio of U(VI) to Eu(III). From the analysis of fluorescence spectra for the sediments consisting of U(VI) and Eu(III) adsorbed on the adsorbents, it is noted that in the case of  $\text{SiO}_2$ , Eu(III) is adsorbed not on the adsorbent but on U(VI) adsorbed on the adsorbent. However, in the case of  $\text{TiO}_2$ , Eu(III) is adsorbed on the adsorbent as well as on the adsorbed U(VI). When the concentration of metal ions used is higher than that of surface sites, and that of U(VI) is ten times higher than that of Eu(III), the adsorption edge of U(VI) and Eu(III) appeared at pH 4.8 and pH 5.5, respectively for both  $\text{TiO}_2$  and  $\text{SiO}_2$ . This implies that the surfaces of adsorbent are completely coated by U(VI) ions. Eu(III) ions are bound mainly to U(VI) adsorbed on the adsorbent and partially to U(VI)-precipitates especially in the case of  $\text{TiO}_2$ , which is identified by the analysis of fluorescence spectra.

## DISTRIBUTION AND SPECIATION OF SORBED PLUTONIUM IN YUCCA MOUNTAIN TUFF USING MICROPROBE X-RAY ABSORPTION AND FLUORESCENCE TECHNIQUES

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Microprobe X-ray absorption spectroscopy applied using micro-focused synchrotron X-radiation is a valuable tool for probing the atomic and molecular states of elements in spatially heterogeneous matrices such as those often encountered in earth materials. This technique has been applied in the geochemical and environmental sciences to examine chemical speciation, precipitation and sorption processes. The transport of Pu from spent nuclear fuel disposal and storage sites is a process that will be dependent on Pu subsurface speciation chemistry. The sorption of Pu(V) from a synthetic groundwater on tuff from Yucca Mountain, NV was investigated *in situ* with the X-ray microprobes at beamline X26A at the National Synchrotron Light Source (Upton, NY), and at GeoSoilEnviro-CARS (Sector 13) at the Advanced Photon Source (Argonne, IL). The mineralogy of the tuff was highly zeolitic and it contained trace (<1%) quantities of hematite (Fe<sub>2</sub>O<sub>3</sub>), smectite and rancieite [(Ca,Mn<sup>2+</sup>)(Mn<sub>4</sub><sup>4+</sup>O<sub>9</sub>•3H<sub>2</sub>O)], which were present as fracture fill and pore space materials. Micro-probe X-ray fluorescence maps showed sorbed Pu to be highly localized in heterogeneously-distributed area and spatially associated with Mn oxides and smectites but not with iron oxides. Micro-X-ray absorption near-edge structure spectra obtained on these Pu-enriched regions indicate the average oxidation state of Pu is +V and +VI, based on the absorption edge energy. Micro-extended X-ray absorption fine-structure spectra lack evidence of Pu in the second shell, suggesting that Pu is surface sorbed rather than precipitated.

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## EXPERIMENTAL DETERMINATION AND CHEMICAL MODELLING OF RADIOLYTIC PROCESSES AT THE SPENT FUEL/WATER INTERFACE

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The chemical stability of a spent nuclear fuel repository is defined by its resistance to radionuclide release to the biosphere. This resistance is primarily dependent on the chemical stability of the UO<sub>2</sub> spent fuel matrix. The chemical conditions of the disposal concept, designed and engineered to minimise the radionuclide release, are normally described by the master variables: pH and Eh. The redox potential is the most critical variable to define the UO<sub>2</sub> stability.

The spent fuel matrix constitutes a dynamic redox system by itself, due to the time-dependent generation of oxidants and reductants at the spent fuel/water interface by alpha, beta and gamma radiolysis. In this context it is critical to understand the main processes and mechanisms that control the radiolytic production of redox components at this interface and their impact on the stability of the UO<sub>2</sub> matrix and in radionuclide release.

In order to achieve this, SKB commissioned a series of carefully controlled experiments in order to determine the time dependence of the radiolytic (H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>) production and radionuclide release (U, Pu, Np, Y, Nd, Tc, Mo, Sr and Cs) in an initially anoxic closed system, when PWR Ringhals spent fuel fragments are put in contact with 10 mM NaHCO<sub>3</sub> solutions.

The results of these experiments indicate quite a consistent and reproducible behaviour of the radiolytically generated reductants and oxidants. The data indicates that it is possible to define an equilibrium redox potential for the main redox pairs in the bulk system and that the experimentally determined radionuclide release can be rationalised in terms of the system redox potential.

In this work we will present the main experimental findings as well as some of the chemical interpretation of the data.

## CHARACTERIZATION OF ACTINIDE PHOSPHATES IN SILO WASTES

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Waste material from the Fernald Plant in Ohio was characterized by a range of techniques. The composition was determined with mass spectrometry (ICP-MS), the identification of individual phases by polarized light microscopy (PLM), and the nature of the actinide-bearing phases with analytical transmission electron microscopy, and x-ray absorption spectroscopy was used to look at the local coordination environment of the actinides in the Silo wastes. Finally, the particle size-range was estimated with laser-light scattering. According to the PLM and scanning electron microscopy analysis, the Silo wastes contained a significant amount of sulfur in the form of anhydrite  $[\text{CaSO}_4]$  and phosphorus in the form of magnesium and iron phosphates, structurally related to fairfieldite  $[\text{Ca}_2(\text{Mg,Fe})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$  and chalcosiderite  $[\text{FePO}_4]$ . The large quantity of sulfate and phosphate, which are not readily amenable to vitrification, makes this waste material problematic; however, the only radioactive elements in the wastes, U and Th, as well as the rare earth elements, were found to be almost always incorporated into extremely insoluble phosphate and arsenates structurally related to brabantite (monazite group) and thorium-bearing phases, related to the alunite group  $[\text{Th}_{0.1}\text{Mg}(\text{PO}_4)(\text{SiO}_4)_{0.8}]$ . Uranium was also observed in this material as discrete particles within the  $[(\text{Ca,Fe,Mg})\text{PO}_4]$  phase as a magnesium uranium phosphate phase, possibly saleeite  $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 9\text{H}_2\text{O}]$ . Owing to the complex nature of the Silo 3 material, we found that only the combination of diverse techniques provided enough information on the form of the actinides in the soils. In this paper, we will discuss the disposition of rare earths and actinides in phosphates and arsenates.

## RADIONUCLIDE RELEASE RATES AND CONCENTRATIONS IN UNSATURATED TESTS WITH OXIDE FUELS - FIRST 4.8 YEARS

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Release rates are reported for the isotopes U-238, Pu-239, Np-237, Cs-137, I-129, Tc-99, Mo-97, and Sr-90, which were measured at approximately six-month intervals for 4.8 years for ATM-103 and ATM-106, which are pressurized-water-reactor fuels. The corresponding radionuclide concentrations in the leachate, and the Pu colloidal fractions are also reported. These data provide information to assess the potential radionuclide source term under conditions expected in an unsaturated and oxidizing repository.

The tests, which are still in progress, are done at 90°C. A thin film of water, which is supplied by saturated water vapor, continuously contacts and reacts with the fuel fragments. Every 3 to 4 days ~0.75 mL of a simulated groundwater, EJ-13, is injected on the fragments. The EJ-13 is a 1E-3 molar sodium bicarbonate solution that is saturated with silica and has a pH of ~8.1. Also in the EJ-13 are trace amounts of Ca, K, Mg, F, Cl, nitrate, and sulfate.

The Tc-99 release rates are used as a marker for matrix dissolution under oxidizing conditions [1,2]. These rates are between 6E-6 and 8E-5 fraction/d for ATM-103 and initially at 2E-7 fraction/d and thereafter between 1E-5 and 4E-5 fraction/d for ATM-106. For the two fuels, the average release rate over the first 4.8 years of reaction is 80-90 mg/(m<sup>2</sup>d), based on a geometric surface area of 2.1E-4 m<sup>2</sup>/g. The release rates for all radionuclides, except I-129, are less than that of Tc. Most of the radionuclides that are released as the fuel reacts appear to be incorporated into alteration products. The Np concentrations, which range from 8E-9 to 2E-11 M after uranyl silicates form, are consistent with the co-precipitation of Np with the uranyl alteration products. The total Pu-239 release rates range from 7E-7 to 9E-11 fraction/d and are consistent with the formation of a Pu-rich phase on reacted fuel grains [2]. The Pu colloidal release rates in the leachate, which are measured after the leachate is in contact with the stainless steel vessel, range from 6E-9 to 2E-13 fraction/d.

The measured radionuclide release rates provide evidence that as the oxide fuel reacts, most of the released radionuclides are retained in alteration products. The resulting radionuclide concentrations in the leachate may be used in performance assessment calculations, if the alteration products that sequester these radionuclides can be identified, as well as their significance for the long-term control of the release of a radionuclide.

1. P.A. Finn, et al., Mat. Res. Soc. Symp. 465, 527 (1997).
2. P.A. Finn, et al., Mat. Res. Soc. Symp. 506, 123 (1998).

## EXPERIMENTAL AND MODELLING STUDIES OF URANIUM RELEASES FROM SYNTHETIC AND NATURAL BRANNERITES

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Brannerite occurs naturally as a uranium ore mineral,  $UTi_2O_6$ , and is also a constituent of ceramic waste forms designed to incorporate high levels of actinide elements, e.g. those associated with the immobilisation of wastes from weapons plutonium disposition. At ANSTO uranium brannerites have been studied to determine the chemical durability and the kinetics of uranium release from synthetic and natural samples, the extent of the analogy that can be drawn between synthetic and natural samples, and the effect of amorphisation of the crystal lattice arising from radiation damage.

Samples used in this study have been physically characterised by SEM, TEM, DTA, and  $\alpha$ -spectrometry. Preliminary transmission electron microscopy (TEM) has shown that the selected area diffraction (SAD) patterns of five natural samples consist of two broad, diffuse rings characteristic of titanate phases that no longer possess long-range periodicity. The diffuse rings have equivalent d-spacings of 3.1 Å and 1.9 Å, similar to many metamict (amorphous) oxide and silicate minerals. Many of the grains examined thus far also exhibit weak diffraction spots. The diffraction spots appear to be due to the presence of fine grained inclusions of another phase which is yet to be identified. In one sample, some of the brannerite grains are studded with 20 nm inclusions. Some of the grains in this specimen also contain 10-200 nm spherical voids, similar to previous observations on metamict zirconolite.

A significant amount of crystalline material is also present in two of the altered brannerite samples. The presence of crystalline material in these two samples is consistent with the SEM results which provide strong evidence for the presence of a  $TiO_2$  polymorph and a thorite-like phase. These additional phases and alteration products are under further investigation.

Leaching studies of powdered samples under static and flow-through conditions at 70°C in a range of pH buffers and in a synthetic, granitic ground water have also been carried out. Preliminary results from this work have shown that uranium leach rates from synthetic samples measured between pH 3 and 12 vary over about three orders of magnitude with the minimum leach rate obtained at pH = 8. These results will be further analysed using geochemical models to study the solubility of uranium from this phase.

Natural samples, after characterisation by SEM and TEM, will be used to assess the effect of amorphisation of the crystal structure arising from radiation damage on the durability of the brannerite phase. This will be carried out by using samples that have been split and annealed (providing pairs of amorphous and crystalline samples), followed by leaching experiments under the same conditions used for synthetic samples.

Overall, the results will be used to assess whether the results from natural samples can be used to aid in extrapolation of laboratory results over geological periods of time.

## EFFECT OF ISOSACCHARINATE ON $\text{NpO}_2(\text{am})$ SOLUBILITY UNDER ALKALINE CONDITIONS

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Experiments were conducted to determine the dominant Np(IV) complexes of isosaccharinate (ISA) and the influence of ISA on the solubility of  $\text{NpO}_2(\text{am})$  in alkaline conditions. The  $\text{NpO}_2(\text{am})$  solubility was measured in the presence of 0.0016 M sodium isosaccharinate (NaISA) over a large range of acidic to highly alkaline conditions (pH 4.5 to 4 M NaOH) and as a function of NaISA concentration ranging from 0.0002 M to 0.1 M at a constant pH of 12. The oxidation state of Np was determined by solvent extraction. The observed aqueous Np(IV) concentrations in the presence of ISA in the pH region 4.5 to near neutral decreased with increased pH and were up to several orders of magnitude higher than expected in the absence of ISA. Dramatic increases in aqueous Np(IV) concentrations in equilibrium with  $\text{NpO}_2(\text{am})$  at pH 12 were observed with increased ISA concentrations. Thermodynamic equilibrium constants for the Np(IV) complexes with ISA were determined that lead to reliable predictions of the  $\text{NpO}_2(\text{am})$  solubility as a function of pH and ISA concentrations.

## INCORPORATION OF RADIONUCLIDES IN THE ALTERATION PHASES OF SPENT NUCLEAR FUEL

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Rapid alteration rates may be expected for spent nuclear fuel exposed to groundwater under oxidizing conditions. Experimental studies examining the alteration of  $\text{UO}_2$  and spent nuclear fuel under conditions which simulate those of the proposed nuclear waste repository at Yucca Mountain have shown that the alteration products are primarily  $\text{U}^{6+}$  phases. The incorporation of spent fuel fission products (e.g., Sr, Cs, Mo, Se, Tc, I) and actinide elements (e.g., Np, Pu, Am) into the structure of  $\text{U}^{6+}$  phases will impact upon the release of the radionuclides into the environment. A series of tests were done to determine the incorporation of  $\text{Ce}^{4+}$  and  $\text{Nd}^{3+}$  (surrogates for  $\text{Pu}^{4+}$  and  $\text{Am}^{3+}$ , respectively) into dehydrated schoepite ( $\text{UO}_3 \cdot 0.8\text{-}1.0\text{H}_2\text{O}$ ). These experiments were conducted at  $90 \pm 2^\circ\text{C}$ . Analyses of both the leachant solution, and solid phase reaction products that were dissolved in a nitric acid solution were performed by ICP-MS. Results indicate that 0.22 ppm of Ce and between 6.8 to 16 ppm of Nd out of the initial Ce (2.10 ppm) and Nd (286 ppm) solutions, respectively were incorporated into dehydrated schoepite after 35 days. TEM-EELS and XRD will be used to further examine the solid synthesis products in order to confirm the extent of Ce and Nd incorporation into  $\text{U}^{6+}$  structures and to examine Ce and Nd incorporation mechanisms. Ce and Nd tests with ianthinite ( $\text{U}^{4+} \text{U}^{6+}_5\text{O}_{17} \cdot 10\text{H}_2\text{O}$ ), and  $\text{Hf}^{4+}$  (another surrogate for  $\text{Pu}^{4+}$ ) test with dehydrated schoepite and ianthinite are also being conducted.

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## LONG-TERM PERFORMANCE OF CEMENTED WASTE FORMS IN SALT BRINES

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Pore structure, leaching and corrosion behaviour, radionuclide retention and other properties of cemented waste forms can be influenced by the fabrication process. In order to investigate the scale-up and to determine the influence of the technical cementation process on the properties of the cemented waste forms, full-scale leaching tests were started between 1978 and 1989. Simulated and real cemented waste forms were investigated, traced with  $^{137}\text{Cs}$ , natural uranium and  $^{237}\text{Np}$ , respectively. Experiments still continue. The INE tests are performed at  $40^\circ\text{C}$ , the Asse tests at ambient temperature of  $28^\circ\text{C}$ . The tests are performed in tap water and salt brines typical for the hitherto German disposal concept. Visual inspection resulted that the waste forms stored at  $28^\circ\text{C}$  up to 20 years showed insignificant degradation. However, samples stored at  $40^\circ\text{C}$  showed already after periods of about 600 days the formation of cracks and after about 10 years the waste forms were disintegrated completely.

The corroding solutions are analysed regularly and the evolution of the concentrations of the main components and of the tracers are available. The pH of the tap water and NaCl brine samples increases from 6.7 to 12.5, whereas in the Q-brine samples the pH is buffered. Distinct Ca-Mg exchange reactions are found only for samples stored at  $40^\circ\text{C}$ . The Al concentrations are measured in the range of  $10^{-6}$  to  $10^{-5}$  mol/kg for all solutions. Fe concentration in Q-brine is about  $10^{-2}$  mol/l and  $10^{-5}$  mol/kg in NaCl brine.

Due to the increase of surfaces in these samples the Cs release is strongly correlated to the formation of cracks. Cs release is kinetically controlled, following a diffusive process. Uranium concentrations in the solutions increased initially, remaining constant over long periods of time. Np concentrations are close to the detection limit, showing no distinct kinetically controlled behaviour indicating that the release of these elements is controlled by solids.

## TECHNETIUM MICROBIAL REDUCTION PRODUCTS: AQUEOUS SPECIATION AND SOLUBILITY

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The solubility of Tc under reducing conditions is significantly less than that under oxidizing conditions due to the sparingly soluble nature of  $\text{Tc}^{\text{IV}}$  hydrous oxide. Our experiments have shown that the subsurface dissimilatory iron reducing bacterium, *Shewanella putrefaciens* sp CN-32, can enzymatically reduce  $\text{Tc}^{\text{VII}}$  under anoxic conditions, although the nature of the reaction products are not well known. Using XAS, TEM, and EDS measurements, we are attempting to identify the aqueous and solid Tc phases resulting from these microbial reactions. Results from these studies are generally consistent with known thermochemical data for reduced Tc species. In carbonate-free solutions, microbial reduction resulted in a decrease of the dissolved  $\text{Tc}^{\text{VII}}$  concentration from 500  $\mu\text{M}$  to  $<0.3 \mu\text{M}$  due to the formation of a solid dimeric  $\text{Tc}^{\text{IV}}$  hydrous oxide identified by XAS. The calculated solubility of Tc in equilibrium with  $\text{Tc}^{\text{IV}}$  hydrous oxide is  $<0.01 \mu\text{M}$ , and dominated by the complex  $[\text{Tc}^{\text{IV}}\text{O}(\text{OH})_2]_2^0$  (aq). The modeling results suggest that  $\text{Tc}^{\text{IV}}$  hydrous oxide in carbonate-free solutions would be stable over the pH range 4.0 to 9 and Eh values less than 50 mV. In carbonate-containing solutions, microbial reduction resulted in a decrease of initial  $\text{Tc}^{\text{VII}}$  concentrations to between 41 and 230  $\mu\text{M}$  at 21 hr depending on the electron donor and solution composition. Direct speciation measurements indicate that  $\text{Tc}^{\text{VII}}$  reduction resulted in the formation of a dimeric  $\text{Tc}^{\text{IV}}$  carbonate solid and soluble  $\text{Tc}^{\text{IV}}$  carbonate complexes that were equal to or more electronegative than  $\text{Tc}^{\text{VII}}\text{O}_4^-$ . The lack of published thermodynamic data for  $\text{Tc}^{\text{IV}}$  carbonate solids precludes calculation of Tc solubility with respect to such solid phases. However, modeling results based on the solubility of  $\text{Tc}^{\text{IV}}$  hydrous oxide indicate that dissolved Tc in the carbonate systems would be maintained at concentrations greater than those for carbonate-free systems due to the formation of aqueous complexes such as  $\text{Tc}^{\text{IV}}\text{OH}(\text{CO}_3)_2^-$ . Due to their anionic nature, aqueous  $\text{Tc}^{\text{IV}}$  carbonate complexes would be as or more mobile than pertechnetate ( $\text{Tc}^{\text{VII}}\text{O}_4^-$ ) in groundwater. Available thermodynamic data suggest that these complexes would be stable over a pH range of 5.5 to 10.5 and Eh values up to 100 mV, but uncertainty exists regarding the stoichiometry and stability constants for such species. Depending on groundwater composition, modeling results suggest that solubility-limited  $\text{Tc}^{\text{IV}}$  concentrations in carbonate systems under anoxic conditions may be greater, and less adsorptive and thus more mobile than commonly assumed.

## FORMATION AND INVOLVEMENT OF $\text{PuO}_{2+x}$ IN THE DISSOLUTION RATE OF ENVIRONMENTAL PLUTONIUM OXIDE

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Kinetic measurements for oxidation of  $\text{PuO}_2$  to a higher oxide,  $\text{PuO}_{2+x}$ , and  $\text{H}_2$  suggest that the dissolution rate of  $\text{PuO}_2$  in aqueous environmental media is determined by the rate at which Pu(VI) forms in the oxide phase. The rate of oxidation measured for  $^{239}\text{PuO}_2$  at room temperature in this study and the dissolution rate reported for that oxide are identical at 6 nmol Pu(VI) per  $\text{m}^2$  of oxide surface per day. The faster dissolution rate reported for  $^{238}\text{PuO}_2$  is consistent with the effect of oxide temperature on the rate of the  $\text{PuO}_2 + \text{H}_2\text{O}$  reaction. Kinetic results obtained at 25°C by pressure-volume-temperature methods show that the rates of Pu(VI) formation in the oxide are identical in liquid water, in 70 % saturated  $\text{H}_2\text{O}$  vapor, and in oxygen with a fraction of a monolayer of adsorbed water on the oxide surface. A catalytic cycle involving oxidation of  $\text{PuO}_2$  to  $\text{PuO}_{2+x}$  by  $\text{H}_2\text{O}$  and surface recombination of atomic hydrogen with atmospheric oxygen to reform water is identified. Existence of x values in excess of 2.25, continuous occurrence of the oxidation reaction at low humidity, accumulation Pu(VI) in the oxide, and slow leaching of hexavalent ion are consistent with seasonal surges in the Pu concentration of environmental water samples at Rocky Flats. Observations suggest that temperature is an important factor in determining the dissolution rate of environmental plutonium oxide.

## EFFECT OF COMPLEXATION ON SOLUBILITY OF NEPTUNIUM(IV) IN AQUEOUS CARBONATE SOLUTIONS

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The solubility of neptunium(IV) hydrous oxide was studied in  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  solutions from undersaturation direction at  $25.0 \pm 0.2$  °C in a controlled atmosphere containing high purity Ar (<1 ppm  $\text{O}_2$ ). Equilibration periods were up to 123 days.

The solubility was below  $10^{-8}$  M and constant in solutions with carbonate concentrations of <0.1 M, and increased dramatically with the increase in the carbonate concentrations of >0.1 M with the slope close to 4 on the logarithmic scale.

Solid characterization was made for the Np(IV) solid phases equilibrated with 0.01 M  $\text{Na}_2\text{CO}_3$ , 0.2 M  $\text{Na}_2\text{CO}_3$ , and 4.0 M  $\text{K}_2\text{CO}_3$  solutions for 67 days using X-ray diffractometry, UV-Vis-NIR and FT-IR photoacoustic spectroscopy. The results indicated that the solids formed in 0.01 M and 0.2 M  $\text{Na}_2\text{CO}_3$  solutions were a poorly-crystalline hydrous oxide, and the solid in the 4.0 M  $\text{K}_2\text{CO}_3$  solution appeared to be non-crystalline and contained hydroxyl groups and carbonate ions.

## THERMODYNAMIC DATA FOR THE SOLUBILITY OF TIN IN AQUEOUS CEMENTITIOUS ENVIRONMENTS

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The solubility of radionuclides under conditions relevant for nuclear waste repositories is an important parameter for safety analysis. For tin(IV), little is known about its chemistry under the alkaline conditions expected in the near field of a nuclear waste repository containing cement-based material. Little quantitative information exists in general on the solubility of solid Sn(IV) phases and the hydrolysis of Sn(IV) under alkaline conditions. Only recently has a systematic study been published [1] which investigates the solubility of crystalline SnO<sub>2</sub>(cassiterite) and poorly crystalline SnO<sub>2</sub>·xH<sub>2</sub>O (precipitated) in NaClO<sub>4</sub> electrolyte. At pH 12, Sn concentrations in the range of 0.01 M were reported. Based on these experiments, very high concentrations of Sn have to be expected in the near field.

However, in a previous paper [2] we could show that in cementitious environments, the solubility of tin(IV) may be drastically lower. Here, we demonstrate that the solubility of Sn(IV) in cementitious systems is largely controlled by the presence of dissolved Ca. In presence of typical Ca concentrations, solid Ca[Sn(OH)<sub>6</sub>](cr) is precipitated, resulting in dissolved tin(IV) concentrations that are about four to six orders of magnitude lower than observed in Ca-free systems.

In order to be able to set realistic upper limits for the solubility of tin in the near field of a cementitious repository, a number of experiments have been carried out (i) to confirm Ca[Sn(OH)<sub>6</sub>](cr) as the solubility limiting solid in cementitious systems and (ii) to obtain thermodynamic data that allow to predict the solubility of Ca[Sn(OH)<sub>6</sub>](cr) under repository conditions. The solubility of Ca[Sn(OH)<sub>6</sub>](cr) was approached in solutions containing 0.25, 0.5 or 2.0 M NaClO<sub>4</sub> as inert electrolyte from both under- and oversaturation in the pH range 11 to 13.1.

X-ray analyses showed that solid Ca[Sn(OH)<sub>6</sub>](cr) is formed in oversaturated solutions under alkaline conditions. The measured solubility of Sn and Ca at different ionic strengths agrees well with the precipitation of a solid phase with the composition Ca[Sn(OH)<sub>6</sub>](cr). From a number of different experiments carried out in initially oversaturated solutions, the respective solubility product is calculated.

[1]Amaya, T., Chiba, T., Suzuki, K., Oda, C., Yoshikawa, H. and Yui, M. 1997. Mat. Res. Soc. Symp. Proc. 465, 751-758.

[2]Ochs, M., Hager, D., Helfer, S., Lothenbach, B. 1998. Mat. Res. Soc. Symp. Proc. 506, 773-780.

## SOLUBILITY OF $\text{UO}_2$ UNDER REDUCING CONDITIONS

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The  $\text{UO}_2$ -matrix solubility is a critical parameter in predicting the stability of spent nuclear fuel under disposal conditions. This paper presents the results obtained from the dissolution experiments of  $\text{UO}_2$  in different synthetic groundwaters under anoxic conditions ( $\text{N}_2$ ) at 25 C. Additionally, a few results from experiments under reference conditions ( $\text{NaClO}_4$ ) are presented. The synthetic ground-water compositions simulating the deep granitic fresh and saline groundwaters for the experimental conditions were evaluated by modelling (EQ3/6) and stability tests. Solubility equilibrium was approached from undersaturation in the dissolution experiments with  $\text{UO}_2$  pellets, and from over-saturation in the precipitation experiments. The redox conditions included anaerobic ( $\text{N}_2$ ,  $\text{O}_2 < 1$  ppm) and reducing ( $\text{N}_2$ , low Eh) conditions. A low Eh (- 0.2 ... - 0.3 V) in the aqueous phase was maintained by the addition of reducing species, S(-II), to the aqueous phase. The oxidation state of uranium in solution was determined experimentally using a method based on the separation of the tetravalent and hexavalent states by ion-exchange chromatography in HCl medium.

The control of the Eh was shown to have an effect on the distribution of U oxidation states by the analyses. The dominant oxidation state at low Eh was the U(IV). The solubilities were at the level of the theoretical solubilities (EQ3/6) of the well-crystallized U(IV) oxide,  $\text{UO}_2$  ( $10^{-9}$  M). The composition of groundwater had a minor effect. In the experiments under anaerobic conditions without the Eh control, the measured solubilities were up to one order of magnitude higher. The effect was greater in the carbonate containing groundwater. The dominant oxidation state was the U(VI).

## EFFECT OF TEMPERATURE ON THE CRYSTALLINITY AND SOLUBILITY PRODUCT OF HYDROUS THORIUM OXIDE

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Studies were conducted to determine the effect of heating ThO<sub>2</sub>(am) to 90°C on the development of crystallinity and the solubility products of the resulting ThO<sub>2</sub> solid phases. The ThO<sub>2</sub>(am) was previously equilibrated at 25°C at a wide range in pH values. Studies were also conducted with the ThO<sub>2</sub>(c) at 25°C and 90°C as a function of pH. The data show that when ThO<sub>2</sub>(am) precipitates are heated to 90°C, they develop crystallinity with a concurrent decrease in solubility. Data also show that equilibrium is reached in these systems, and that the solubility products decrease by many orders of magnitude as previously reported in the literature and approach the values determined from the calorimetric data. Thermodynamic interpretations of the solubility data were done using the Pitzer model. Thermodynamic equilibrium constants, along with kinetic data obtained for this system, will be useful for predicting the Th behavior in high level waste repository environments.

## DISSOLUTION BEHAVIOUR AND RADIATION DAMAGE EFFECTS IN UO<sub>2</sub> CONTAINING $\alpha$ -EMITTING ACTINIDES

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After a few hundred years in a geologic repository,  $\alpha$ -emissions will constitute almost entirely the radiation field in and around spent nuclear fuel. In the event of failure of the spent fuel container, the dissolution behaviour of the uranium matrix in contact with groundwater could be enhanced by  $\alpha$ -radiolysis, which could create oxidizing conditions at the fuel surface. The radioactivity (hence the radiolysis) of the irradiated fuel available nowadays is characterized by a strong  $\beta$ - and  $\gamma$ - contribution, which is not representative of aged fuel in a repository. A possible way to single out the effects of  $\alpha$ -radiolysis on the dissolution behaviour of irradiated fuel is to study unirradiated UO<sub>2</sub> doped with a strong  $\alpha$ -emitter. The results of static (batch and sequential) leaching tests at room temperature in demineralized water under anoxic atmosphere on UO<sub>2</sub> containing ~0.1 and ~10 wt. % of <sup>238</sup>Pu showed a significant radiolysis effect, i.e. the amounts of U released were higher in the case of UO<sub>2</sub> containing <sup>238</sup>Pu than in the case of undoped UO<sub>2</sub>. The present work presents results of similar leaching experiments performed in carbonated water (0.01 molar) at room temperature under anoxic atmosphere. The tests were carried out using uranium oxide containing different types (namely <sup>238</sup>Pu, <sup>241</sup>Am, and <sup>239</sup>Pu) and concentrations of  $\alpha$ -emitters. The effects of different chemical compositions and of different levels of  $\alpha$ -activity, including that expected at the surface of irradiated fuel after several hundred years from discharge, have been investigated. The effects of different surface areas were also investigated by leaching crushed materials with two different particle sizes. The surfaces of the starting materials and of the leached samples were characterized using scanning electron microscopy and energy dispersive spectroscopy. The radiation damage build-up in the UO<sub>2</sub> matrix due to the  $\alpha$ -decay was also investigated by measuring the lattice parameter, hardness, and oxygen potential changes as a function of storage time, i.e. damage level.

## MAGNETIC, ELECTRONIC, AND STRUCTURAL PROPERTIES OF SELECTED ACTINIDES IN COMPLEX OXIDES

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The heavier actinides are generally believed to have physical properties similar to their 4f counterparts. Specifically the 5f electrons of actinides heavier than Pu are believed to be localized. We present synthetic conditions and property characterization for a number of complex actinide oxides, primarily of Am and Cm, and compare their measured properties with those of a lanthanide counterpart. The synthetic conditions necessary for formation of the actinide complex oxides, and the stable phases produced, are usually very similar to those of the corresponding Pr or Ce analogues. The cooperative magnetic interactions of the 5f ions are significantly enhanced over their 4f counterparts in isostructural compounds. Some of the phases under discussion are the actinide analogues of known mineral phases, and therefore this work provides information useful for geochemical modeling or surface science.

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## CONSEQUENCES OF AUTUNITE DEHYDRATION FOR PHASE CHARACTERIZATION AND STRUCTURE

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The family of calcium uranyl phosphate hydrates encompassing autunite and meta-autunite phases, i.e.  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot x\text{H}_2\text{O}$  where  $x$  is reported to vary from 4 - 12, represent an important group of weathering product in natural ore deposits and in contaminated soils and sediments. The literature is confusing with respect to the hydration status of the reported autunite and meta-autunite phases. In this work, we examine the dehydration of the autunite phases for the purposes of improving phase identification and clarifying the structural role of hydration water. Two autunite phases exhibiting different degrees of crystallinity were synthesized at room temperature via direct precipitation from supersaturated solution and by contacting chernikovite,  $[(\text{UO}_2)\text{H}(\text{PO}_4)]_2 \cdot 4\text{H}_2\text{O}$ , with 2 M  $\text{Ca}^{2+}$  solutions, and characterized using X-ray powder diffractometry (XRD), electron microscopy with energy dispersive spectroscopy (SEM/EDS), and high-resolution thermogravimetric analysis (HRTGA). XRD examination of initial products indicated the presence of more than one hydration state for both synthetic samples, as suggested by the co-existence of reflections corresponding to three distinct basal plane spacings of 10.0, 9.0, and 8.4 Å. Drying at 50 °C led to a more uniform product with a dominant d-spacing of 8.4 Å. However, increased drying temperatures above 60 °C led to the development and predominance of a fourth characteristic XRD reflection corresponding to 8.1 Å. HRTGA investigation of products dried at room temperature and 50 °C revealed three well-defined, low temperature weight loss events for both. Dehydration was similarly observed for samples subjected to vacuum and long-term storage under ambient conditions. While the observations seem to fall within the discrete categories traditionally used to distinguish the autunite hydrates (i.e. autunite, meta-autunite I, and meta-autunite II), our results suggest that continuous or semi-continuous hydration intervals better explain autunite dehydration behavior.

## SOLUBILITY OF Np(V) IN THE PRESENCE OF U(VI) HYDROXIDE SOLID

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The aqueous concentration of a trace element may be controlled by processes such as adsorption and mixed-crystal formation at values well below the solubility-limited concentration based on pure solid phases. These "heterogeneous solubility" processes are of particular interest in the case of Np because the solubility of Np(V) solids is generally greater than  $10^{-4}$  M under near-neutral pH conditions. If the pure phases are assumed to control Np concentrations, then Np-237 significantly impacts long-term radiological dose estimates for a spent-fuel repository. We are investigating equilibrium adsorption and mixed-crystal formation between Np(V) and U(VI) hydroxide (schoepite or dehydrated schoepite) in low ionic strength bicarbonate solutions. Experimental approaches to steady-state include addition of U(VI) hydroxide crystallites to aqueous Np(V) solutions followed by ripening, and coprecipitation of Np(V) with U(VI) followed by ripening. The effect of pH and Np concentration is being studied, and the experimental results are modelled using a Np/U exchange reaction. Solid phases are identified by X-ray diffraction and infrared absorption to the extent practical.

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## AQUEOUS DISSOLUTION KINETICS OF PYROCHLORE AND ZIRCONOLITE AT 25, 50, AND 75°C

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We have measured the rates of dissolution of pyrochlore and zirconolite in pH-buffered solutions of pH 2, 4, 6, 8, 10, and 12 at temperatures of 25, 50, and 75°C in flow-through reactors. The solids contain Ce, Gd, U, and Hf, which substitute for Ca (Ce and Gd), and Zr (Gd, U, and Hf), in zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) and analogous sites in pyrochlore. We are using these Ce-minerals as analogs for Pu-containing zirconolite and pyrochlore in a multi-phase Pu-ceramic waste form. The dissolution rates for both phases show a minimum near pH 8. The dissolution rate of zirconolite is always smaller than that for pyrochlore, with the difference varying between 0.04 and 0.7 log units. The rates increase with temperature, but the magnitude of increase varies with pH. Calculated activation energies for dissolution are generally in the range of 5-15 kcal/mole. Dissolution is non-stoichiometric at all pHs. Ti and Hf are released most slowly, and are often below our detection limits (1 ppb for Ti, 0.2 ppb for Hf). Releases of Ca, U, Gd, and Ce appear to be stoichiometric below pH 8. Above pH 8 only U and Ca are measurable in solution. Dissolution rates are slow under all conditions, and commonly in the range of 1-100 nm total dissolution/year (between  $10^{-3.5}$  and  $10^{-5.5}$  g/m<sup>2</sup>/day).

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## NEPTUNIUM REDOX SPECIATION

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The long half-lives of many of the radioactive actinide elements make their presence in the environment an issue of considerable concern. Once released, radionuclides may be transported over large distances in groundwaters. Difficulties in obtaining a predictive understanding of actinide transport and fate in the environment are compounded by complicated reduction-oxidation (i.e., redox) chemistry. For example, neptunium redox chemistry includes four oxidation states—III, IV, V, and VI. These cations have different solubilities and stabilities in aqueous solutions. Each can exhibit different reaction, precipitation, complexation, and sorption behavior with ions, minerals, soils, etc., in the aquifer. We have developed equipment for in situ X-ray absorption fine structure (XAFS) measurements of the redox speciation of ions in solutions at controlled potentials. To demonstrate its use, we have measured the formal potentials of the Np(VI)/Np(V) and Np(IV)/Np(III) redox couples. In addition to the neptunium redox properties, we obtained information about the coordination chemistry of the four pure Np oxidation states. The utilization of XAFS spectroelectrochemistry as a probe of fundamental chemical and redox processes in radionuclide migration and fate will be addressed.

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## REDUCING CAPACITY OF HUMIC SUBSTANCES AND URANIUM MIGRATION

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Humic substances may influence the migration of uranium in groundwater, directly, by forming complexes with uranium, and indirectly, by affecting the redox chemistry of groundwater, *i.e.* deoxygenation and reduction of ferric iron. Both direct and indirect influences were studied in nature and by laboratory experiments. At Bangombé natural reactor site (Gabon), the most reducing groundwater was found in the shallow organic matter-bearing aquifers. This suggests that humic substances play an important role in controlling the redox chemistry of the groundwater, and preserving the Bangombé uraninite core at 12 m depth from complete oxidative weathering over geological time. The reducing capacities of five humic substances, determined by measuring the amount of Fe(III) reduced, was found to increase three times by changing pH from 6.88 to 9.70. Two of the most reductive humic substances found, determined at pH 9.70 after 15-day reaction in the dark, are Dando humic acid and Dando fulvic acid with measured reducing capacities 5.2 meq/g and 4.6 meq/g, respectively. The effect of humic substances on the redox chemistry of groundwater was investigated by measuring Eh with Pt electrode in anoxic, neutral (buffered pH 7) aqueous solutions: (a) IHSS soil humic acid (b) blank water and (c) IHSS soil humic acid + ferricyanide. Eh values of the solutions (a) and (b) are almost identical, this may be explained by the fact that the functional groups in the humic acid colloids can not directly interact with the electrode surface. Eh of solution (c) continuously decreased with the reduction of Fe(III). Although the reductive effect of the humic acid is not directly measurable, it still probably governs the redox chemistry of groundwater with Fe(III)/Fe(II) as a redox-mediator. The result of another batch experiment showed that humic substances form complexes with U(VI), but direct reduction of U(VI) was not observed under groundwater conditions.

## REDUCTION OF Pu (V) AND Pu (VI) BY CITRIC ACID

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Interactions between organic complexants and actinides play an important role in defining the speciation of the actinide, hence it's potential for migration, in the subsurface. The reduction of the higher oxidation states of actinides by organic complexants, however, is an important interaction that has not received proper attention. We have completed studies of the reduction of Pu(V) and Pu(VI) by citric acid, tri-carballylic acid and oxalic acid to measure rates of reduction and establish the mechanisms and roles of the various functional groups. Rates of reduction were established by monitoring the Pu complexes using absorption spectroscopy and the concentration of the organic species using ion chromatography under pseudo first-order conditions. The overall mechanism for this reduction process is complex. A key observation of this work is that both overall rates and stabilities were complex-specific and affected by system pH. At low to moderate pH (pH 1-4), Pu(V and VI) is readily reduced to form stable Pu(IV) citrate and oxalic acid complexes in solution. At increased pH, however, the stronger organic complexes formed suppress reduction and stabilize the higher oxidation states. The functional group most responsible for reduction was the tertiary OH group on the citric acid. The carboxylate group led to rates of reduction that were significantly slower. Overall, Pu(IV) complexes predominated in the long-term.

## REDUCING BEHAVIOUR OF NATURAL ORGANIC MATTER AND ITS INFLUENCE ON THE URANIUM MOBILITY IN FLOODED MINES

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Large underground mines are being flooded by surface and groundwater during the restoration of the East German uranium mining sites. The mine shafts and galleries are heavily reinforced with wood, and the flooding process isolates the wood from exposure to air. In conjunction with the wood degradation, this may cause potentially reducing conditions.

To study this effect, redox potential measurements and redox titrations with potassium hexacyanoferrate(III) were carried out on hydrothermal wood leachates, lignin and humic acid using a platinum electrode in combination with a silver-silver chloride electrode in a cell with liquid junction. The redox potentials of spruce lignin and humic acid, extrapolated to pH 0 and infinite dilution, were determined to be  $570 \pm 5$  mV for both with a negative pH gradient of  $54.0 \pm 1$  mV/pH. The potential indicates that the organic matter produced by the wood degradation can reduce U(VI) to U(IV). We identified U(IV) as the reduction product by spectrophotometry of the U(IV)-arsenazo(III) complex. The capacity for lignin to reduce U(VI) increases from pH 5 to 8 from  $1.3 \cdot 10^{-2}$  to  $0.5$   $\mu\text{eq/g}$ , respectively. For comparison, iron(III) was reduced at pH 4.5 with a capacity of  $0.15$  meq/g.

We also studied how reducing conditions were generated by the decay of wood in a highland bog. We measured the redox potential in the field as a function of depth, and found that the redox potential decreased by more than 800 mV from the surface to the depth of one meter. In comparison, the redox potential in deeper layers of the flooded mines was diminished by about 700 mV. This is ascribed to the oxidation of sulfidic and arsenic minerals, especially of *pyrite*, *markasite* and *arsenopyrite*. This lowering of the redox potential causes the  $\text{UO}_2^{2+}$  to be immobilized as  $\text{UO}_2$ . Our results show that the degradation of the large quantities of wood in the mines also contribute to establish, maintain and enhance reducing conditions and, hence, to immobilize significant parts of the 100 tons of uranium and 50 tons of arsenic that are dissolved in Saxony's largest underground mine at Schlema.

## PHOTOCHEMICAL REACTIONS OF NEPTUNIUM IONS WITH WATER IN CARBONATE MEDIA

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It was shown earlier that americium ions in hydrocarbonate-carbonate solutions are involved in redox reactions at irradiation by UV light. The behavior of other actinides under the same conditions is not investigated. These reactions are of great importance since natural media are often a solutions contained  $\text{CO}_2$  and  $\text{HCO}_3^-$ . Photoreactions of actinides, change of form of their existence and of ability to migrate are possible in these solutions under irradiation of sun light.

This work presents the results of spectrophotometric study of influence of UV light on aqueous solutions of Np(VI), Np(V) and Np(IV) contained  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions. It was found that in carbonate solutions Np(VI) is reduced to Np(V), and simultaneously Np(V) is oxidized to Np(VI). Increasing of  $\text{Na}_2\text{CO}_3$  contents from 0.05 to 1.95 M or of  $\text{NaHCO}_3$  contents from 0.05 to 1 M accelerates the Np(VI) reduction and slows down the Np(V) oxidation. pH decreasing at constant  $[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$  leads to reverse effect. In 1 M  $\text{NaHCO}_3$  solution 94-95% Np(V) under UV irradiation turn into Np(VI). The presence of oxygen does not influence on rate of the process.

Np(IV) under conditions being investigated slowly turns into Np(V) and Np(VI).

## REDUCTION OF PLUTONIUM THROUGH CORROSION OF MILD STEEL IN HIGH IONIC STRENGTH BRINES

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The mobility of plutonium in the environment is strongly dependent on its oxidation state. The majority of wastes targeted for disposal in the Waste Isolation Pilot Plant (WIPP) and other planned salt dome repositories will be contained in mild steel drums. Possible contact of the drums with high ionic strength brines located underneath and above the disposal room can result in corrosion of the drum steel and produce reducing conditions in the disposal room. This situation can result in the reduction of plutonium to its lower oxidation states, +III and +IV, which have very low water solubility. Corrosion studies in the past have focused on corrosion rates of drum steel, but have not examined the mechanism of actinide reduction by iron. Experiments were performed to characterize the corrosion layer on the steel surface that formed when exposed to WIPP brines. Steel coupons leached in WIPP brines were examined by atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS). The leaching solutions were analyzed by Induction Coupled Plasma Mass Spectroscopy (ICP-MS). Experiments were also conducted using iron powder leached in WIPP brines to evaluate the effect of surface area on corrosion and possible actinide reduction. The results indicate a corrosion layer, possibly an iron hydroxy chloride, develops on the coupon surface and that corrosion rates are very slow. In additional on-going experiments, ASTM A36 drum steel coupons are being exposed to WIPP brines with added plutonium(VI) in an effort to determine the mechanism of Pu reduction. Plutonium concentrations and oxidation state will be monitored over time using absorption spectrophotometry and solvent extraction. These experiments will be described.

## LASER-INDUCED BREAKDOWN SYSTEM FOR COLLOID CHARACTERIZATION IN DILUTE AQUEOUS SUSPENSIONS

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Colloids play an important role in the migration of contaminants in natural waters. Colloidal transport is particularly important for "nonconservative" elements such as rare earths and actinides, which may form intrinsic hydrous oxide colloids or be strongly bound to natural organic or silicate colloids. One component to assessing colloidal transport in a particular natural water is an analysis of the number, size distribution and composition of the native colloidal particles. In groundwater systems the colloid concentrations may lie below the detection limits of common sizing techniques such as light scattering. Thus we are investigating a colloid detection and sizing method based on laser-induced breakdown which is appropriate for dilute aqueous suspensions. We will give a brief description of the instrumentation and results obtained with standard particles, groundwater samples, and core-flow samples.

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## ASSESSMENT OF CALIBRATION METHODS FOR *IN SITU* DETERMINATION OF OXIDATION STATES OF URANIUM BY X-RAY ABSORPTION NEAR EDGE STRUCTURE SPECTROSCOPY

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X-ray absorption near-edge structure (XANES) spectroscopy is a valuable tool for probing the oxidation state of radioactive and non-radioactive elements. XANES techniques have been applied in the geochemical, material, nuclear and environmental sciences to obtain oxidation state information about the speciation of surface sorbed species and in solid, liquid and gas phases. XANES spectroscopy can be conducted non-invasively *in situ*, making it a helpful analytical tool for examining samples without the introduction of potentially detrimental treatments or preparations that would be required with *ex situ* methods. Interpretation of XANES spectra ( $L_{III}$  absorption edge) has been conducted with a variety of mathematical methods. The primary chemometric for determining oxidation states of actinides from XANES spectra is a shift in the absorption energy ( $\mu$ ), which is attributed to de-shielding of core electrons. However, precise determinations of  $\mu$  are problematic due to overlapping spectral features. Researchers have applied several methodologies to phenomenologically and consistently determine  $\mu$ , including derivative analyses, curve fitting procedures and others. We have attempted to statistically quantify and assess the merits of each methodology with an extensive database of U XANES spectra. The applications, benefits, limitations and data acquisition requirements associated with each method will be discussed.

## **SURVEYING FOR ENVIRONMENTAL ALPHA CONTAMINATION USING NUCLEAR TRACK DETECTORS**

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In this work, we present a novel methodology for the detection of alpha particles from actinides and alpha emitting decay products based on the analysis of the tracks formed in organic polymers as a consequence of the interaction with the nuclear particles. A simple chemical process is used to develop the latent nuclear track. The track analysis can be made manually using an optical microscope or automatically through the use of digital image analysis and PC processors.

The methodology can be applied to very low-level count rates, i.e. fractions of a Becquerel. It also allows energy particle analysis in the range 0.5 to 15 MeV that can be used for isotope identification. These characteristics are very appropriate for the detection of low-level, alpha emitting nuclide contaminants in soils and waters.

This technique has been used at the Nevada Test Site to survey for large area surface contaminations, for small area point measurements and for depth profiling alpha contaminated soils. The details of the methodology and results from the survey will be presented.

## SPECIATION ANALYSIS ON LANTHANIDES USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Investigation of the chemical behavior of lanthanides and actinides in the geosphere is important for the safety assessment of high-level radioactive waste disposal. However, determination of speciation for lanthanides and actinides is difficult, because it is too hard to distinguish between metal ion and colloidal metal in aqueous solution. Laser-induced breakdown spectroscopy (LIBS) can detect both ions and microparticles of metals in aqueous solution, especially, high-sensitive to microparticles. In this study, we analyzed Eu(III) ion and  $\text{Eu}_2\text{O}_3$  particle in aqueous solution by LIBS, and measures the hydrolysis behavior of Eu(III) in aqueous solution. Furthermore, we tried to detect the plasma emission of Eu(III) ions sorbed on  $\text{TiO}_2$  particles.

Plasma emission of Eu was observed at 420.505 nm both in Eu(III) aqueous solution and in  $\text{Eu}_2\text{O}_3$  suspended solution. The emission line was generally used for quantitative analysis of Eu. The plasma emission intensity of  $\text{Eu}_2\text{O}_3$  was higher than that of Eu(III) ions when Eu concentration was same, and absorption band of Eu(III) ions was observed in LIBS spectrum of Eu(III) aqueous solution. These results indicated Eu(III) ions can be distinguished from  $\text{Eu}_2\text{O}_3$  particles in aqueous solution by LIBS.

The plasma emission intensity of Eu increased with Eu concentration. The intensity vs. concentration plot showed a good linearity in low concentration range (approximately  $10^{-2}$  to  $10^{-1}$  mol/dm<sup>3</sup> and  $10^{-5}$  to  $10^{-4}$  mol/dm<sup>3</sup> for Eu(III) ions and  $\text{Eu}_2\text{O}_3$  particles, respectively).

The plasma emission intensity of Eu increased with pH of Eu(III) aqueous solution, and drastic increase of emission intensity was observed above pH=6. The tendency was similar with solubility curve of  $\text{Sm}(\text{OH})_3$ , which calculated using stability constants in literature[1]. This result suggested that LIBS is useful for measurement of hydrolysis and precipitation behavior of Eu(III) in aqueous solution.

From plasma emission of Eu(III) ions sorbed on  $\text{TiO}_2$  particles, it was found that only Eu(III) ions on  $\text{TiO}_2$  may be detected by LIBS, because the emission from Eu(III) ions in solution was not observed. We also have tried to use time-resolved LIBS to analyze sorption form of Eu(III) ions.

[1] V. Moulin et al., *Radiochim. Acta.*, **44/45** (1988) 33

## DETERMINATION OF THE HYDRATION NUMBER OF ACTINIDES(III) AND LANTHANIDES(III) BY LUMINESCENCE LIFETIME MEASUREMENT AND ITS APPLICATION TO THE SPECIATION STUDY

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Highly sensitive and selective speciation methods of actinides are indispensable for in-depth understanding of the reaction mechanisms based on the identification and characterization of the species at the molecular level. The inner-sphere hydration number  $N_{H_2O}$  (i.e., the number of  $H_2O$  molecules in the first hydration sphere of a metal ion) provides significant information regarding the coordination environment of the chemical species in aqueous solution, in solid containing water, and at solid-water interface.

The correlation between the luminescence decay constant  $k_{obs}$  (i.e., the reciprocal of the excited state lifetime) and the  $N_{H_2O}$  of actinides(III) [An=Am, Cm] and lanthanides(III) [Ln=Nd, Sm, Eu, Tb, Dy] has been investigated systematically by Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS). The calibration relations of the  $k_{obs}$  vs.  $N_{H_2O}$  were derived on the basis of the linear correlation of the  $k_{obs}$  vs. mole fraction of  $H_2O$  in  $D_2O$ - $H_2O$  solutions and the  $N_{H_2O}$  in  $H_2O$ , i.e., nine for Am(III), Cm(III), Nd(III), Sm(III) and Eu(III) and eight for Tb(III) and Dy(III). The relationships were applied for studies on hydration states of An(III) and Ln(III) in various solution systems (e.g., concentrated aqueous salt solutions, water-non-aqueous solvent mixtures, etc.), on sorption behavior of the species onto silica and clay minerals in the presence or absence of organic ligands, and on separation behavior of the species into cation exchange resin-hydrochloric acid system with or without methanol. It was demonstrated that the determination of the  $N_{H_2O}$  of An(III) and Ln(III) by the luminescence lifetime measurement is an effective method for the speciation of these ions in various circumstances.

## FLUORESCENCE INHIBITION OF URANYL IONS BY CHLORINE IONS : INFLUENCE OF THE IONIC STRENGTH

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For a number of industrial applications uranium solutions of high acidity and concentration are encountered. However, little is known about uranium chemistry under conditions of high ionic strength. This situation calls for a better understanding of the influence of the ionic strength on uranium reactivity. The present study focuses on the influence of the ionic strength on the fluorescence life time of uranyl ions in the presence of chlorine ions.

Following photoabsorption of uranyl ions (350 - 450 nm wavelength range), the deexcitation probability by radiative and non-radiative processes defines a fluorescence life time. This time constant ( $\mu\text{s}$  range) as well as the shape of the emission spectrum are characteristic properties of the excited species.

Chlorine ions are known to quench the fluorescence of uranyl ions. This results in a decrease of both the fluorescence intensity and the life time as a function of chlorine concentration. The ionic strength is adjusted by adding  $\text{NaClO}_4$  in the concentration range  $10^{-2}$  – 3 M. The emission spectrum and the life times are measured with time-resolved laser fluorescence spectroscopy.

The fluorescence life times of uranyl ions are found to depend linearly on the chlorine concentration, following a Stern-Volmer behavior :  $\tau^{-1} = \tau_0^{-1} + k(\text{Cl}^-)$ , with  $k$  the rate constant for reaction between uranyl and chlorine ions,  $\tau$  and  $\tau_0$  the fluorescence life times with and without chlorine ions. This allows one to deduce reaction rate constants  $k$  as a function of the ionic strength. The  $k$  values decrease significantly in the concentration range of  $10^{-2}$  – 0.7 M in  $\text{NaClO}_4$ . For larger concentrations  $k$  remains constant. The experimental rate constants are in agreement with values derived from the models of Davies and Sun, within their respective ranges of validity ( $< 0.7$  M). Presently, the data are being confronted with the MSA model (Mean Spherical Approximation), which is applicable also for the larger ionic strengths.

Future experiments will be extended up to ionic strengths of 10 M which will allow to test models at high ion concentrations.

## TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY WITH PICO- AND FEMTOSECOND EXCITATION PULSES: STUDIES OF COMPLEX FORMATION OF U(VI) AND LIGNIN DEGRADATION PRODUCTS

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Time-resolved laser-induced fluorescence spectroscopy (TRLFS) is a very selective and sensitive method for the investigation of the complexation behavior of fluorescent actinides. For non fluorescent actinides and heavy metals ions, we developed a new method to study the complex formation with organic ligands by using pico- and femtosecond excitation pulses for TRLFS.

The change of fluorescence lifetime, fluorescence intensity and main fluorescence bands of the organic ligands in presence of heavy metal ions can be used to determine complex formation constants. The short fluorescence lifetimes of organic ligands (normally smaller than 20 ns) can be accurately determined by using pico- and femtosecond excitation pulses and a suitable detection system. We installed a femtosecond laser system using a double amplified 130 femtosecond pulse from a mode-locked Ti:Sapphire oscillator as excitation pulse. The wavelength of the laser pulse is tunable with a solid state laser system (OPA-system) between 250 nm and 10  $\mu$ m. The fluorescence emission is focused on a slit spectrograph vertically to the excitation pulse without using an optical fiber cable. The fluorescence signal is detected by an intensified 1 kHz picosecond CCD camera which is directly connected to a spectrograph via a multi-channel detector adapter. Fluorescence lifetimes between 200 ps and 20 ns can be determined.

The laser system was validated with protocatechuic acid and vanillic acid as well-known complexes of U(VI)-lignin degradation products. The obtained constants were compared with the conventionally determined complexation constants and with literature data.

## AN ADSORPTION STUDY OF URANIUM(VI) BY SURFACE ENHANCED RAMAN SCATTERING (SERS) AND AB INITIO HARTREE FOCK CALCULATIONS

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The application of Raman spectroscopy to surfaces has been difficult because of practical problems associated with weaker band intensities compared to those of infrared adsorption. One spectroscopic tool that helped this challenge is surface-enhanced Raman scattering (SERS) that can be observed on several roughened metallic surfaces. Our recent report [1] on SERS study of uranyl species adsorbed on silver surface has shown that the adsorption of uranium(VI) on silver surface proceeds without the release of hydroxo and carbonato ligands, and the uranium is strongly bound on silver surface.

Quantum chemical calculations, on the other hand, have been willing and able partner for the study of interface phenomena. In this study, Gaussian 94 code (Gaussian Inc.) have been used to carry out an ab initio Hartree Fock (HF) calculation of the optimized structure and molecular energy of uranium(VI) on silver surface. Hay's pseudopotentials and corresponding basis sets for uranium and silver were incorporated into Gaussian 94 to calculate uranium and silver containing systems. It was found out that the hydrated  $\text{UO}_2^{2+}$  ion may have strong adsorption onto silver surface via inner sphere structure, and the strong donation of uranium 5f orbitals to the uranium-silver bonding was observed. The effect of the uranyl "secondary ligand" (i.e. hydration water molecules) is important and should not be neglected in understanding the electronic structure of the surface bound uranyl.

Limitations to utilizing the enhancement provided by SERS include the relatively small number of metal surfaces which exhibit the requisite plasmon. Silver is the only SERS active substrate for uranium(VI) adsorption so far as we studied. A silver-island SERS substrate overcoated with a thin, continuous layer of silica was found to be SERS active, and serves as a model surface for adsorption studies of  $\text{SiO}_2$ . The SERS active  $\text{SiO}_2$ -overcoated silver-island films was used in this study, and the speciation of the uranium(VI) on silica layer was studied. The results were also compared with the ab initio HF calculations of uranyl adsorption on amorphous silica surface.

[1] Tsushima, S. et al., J.Phys.Chem. B 102,9029 (1998).

## NMR IMAGING OF TRIVALENT LANTHANIDE TRANSPORT

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The NMR imaging technique can be applied to heterogeneous systems using a wide range of flow conditions. The NMR technique is also inherently non-invasive and provides a means to investigate transport phenomena under precise environmental flow conditions. Research activities have focused on  $Gd^{3+}$ , a chemical analog of the trivalent actinides. The  $Gd^{3+}$  ion has the combined advantage of being chemically similar to  $^{241}Am$  and  $^{244}Cm$  and possessing the physical properties as an excellent NMR contrast agent. These combined properties of the  $Gd^{3+}$  ion makes it a superior candidate as a NMR tracer to simulate and model environmental transport. The development and testing of the NMR flow imaging system for investigating various radioactive analogs and environmental media is described. This flow system must be capable of ensuring air bubble free samples to reduce the NMR susceptibility effects inherent in granular flow systems. The flow system uses fluid deaeration followed by over-pressurization to accomplish this requirement. In addition, the flow system must be able to provide plug-type flow of a variety of fluids through complex granular samples with a high degree of reproducibility. The first approach in developing our NMR tracer technique is to validate the process using homogeneous media samples and known concentrations of a contrast fluid. Sand is chosen as the media. Very little sorption was observed. A heterogeneous environmental sample was examined next and showed preferential flow paths and retention. It is anticipated project results can be used to assist in transport model development.

## NATURAL ANALOG STUDIES OF Tc AND Np BEHAVIOR IN FRESHWATER EUTROPHIC AND DYSTROPHIC LAKES

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Model laboratory studies of the environmental behavior of two long lived and the most mobile radionuclides heptavalent technetium and pentavalent neptunium were undertaken. Two typical lakes were chosen according to different biological productivity: highly productive eutrophic lake and a dystrophic lake where organic matters present as humic and fulvic acids. The kinetics of radionuclides uptake by sediment from spiked water and substrate effects were examined in batch. The initial concentrations of Tc and Np were  $10^{-5}$ - $10^{-4}$  M. Two different uptake rates were characteristic for neptunium sorption: fast uptake during the first hour when 60% and 50% of initial input was sorbed by sediment of eutrophic and dystrophic lakes, and a slow bioaccumulation period when neptunium uptake was completed in 1 and 2 months for eutrophic and dystrophic lakes respectively. As for Tc, the uptake rate was almost constant, the time of half-uptake being 1/2 and 1 month for eutrophic and dystrophic lakes. The complete Tc accumulation by sediment took place after 1 and 2,5 months respectively. Speciation by centrifuging at 10000 rpm, ultrafilterfuging or filtration through 0.05 - 0.22  $\mu\text{m}$  membranes has shown that the Tc fraction remaining in water phase was present as truly ionic species up to 90%. The microflora of lake played important role in the accumulation and reduction of radionuclides. Some microorganisms being able of anaerobic respiration had competition relationships between  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  and  $\text{TcO}_4^-$ . Addition of  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  decreases the rate of Tc accumulation by sediment. Addition of lactate or cut reed as electron donors increased the Tc uptake rate. Being added to water phase of dystrophic lake about 3% of Tc and 30% of Np were bounded in water soluble complexes with natural humic acids precipitating on acidifying the water to pH=1. The sediments from freshwater lakes have a considerable sorption capacity. The consecutive sorption runs have demonstrated only small decrease of Tc uptake rate. The desorption of technetium was carried out with  $\text{H}_2\text{O}$ , 1M HCl, 1M  $\text{NaClO}_4$  or 15%  $\text{H}_2\text{O}_2$  and gave the desorption factors of 0.05, 0.05, 0.08 and more 0.99 thus indicating the reduction of technetium to be the main mechanism of its uptake.

## RADIOACTIVE WASTES CONTAINMENT IN SHALES: SORPTION / DESORPTION OF Cs, Sr and Eu

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The containment properties of shales towards radioactive wastes disposal are studied in the experimental site of Tournemire (southern France). Indeed, such argillaceous formations present interesting hydrogeological properties for this purpose: very low hydraulic conductivities ( $K \# 10^{-13}$  m/s), small effective diffusion coefficients ( $D_e \# 10^{-12}$  m<sup>2</sup>/s for tritiated water) and low porewater contents (from 3 to 5%). But besides these hydrogeological characteristics, migration of radionuclides also depends on sorption phenomena which occur in the pore space of the shales. The aim of this paper is to present a combined experimental and modelling study of the sorption by the shales of three radionuclides of interest, Cs, Sr and Eu. The last one is chosen as an analogue for Am. In a first step, chemical data concerning the porewater have been obtained using complex leaching techniques. Then, sorption laboratory experiments have been performed in gloveboxes under an anoxic atmosphere and with a synthetic water representative of the porewater in order to approximate *in situ* and *far-field* conditions. Sorption and desorption were studied through batch experiments. The liquid/solid ratio was set to 5 ml/g throughout the experiments. The experiments lead to the following conclusions: Cs is mainly sorbed through an ion exchange mechanism with the fixed natural cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) of interstratified illite/smectite minerals. Sr is also sorbed following a similar mechanism but to a lesser extent than Cs. The behaviour of Eu is particular as it precipitates with carbonates and hydroxyles even at low Eu concentrations. These sorption data were first fitted by a geochemical code including cation exchanges. When coupled with transport models these data allow one either to simulate or to validate common assumptions on the radionuclide migrations for conditions representative of the real Tournemire site.

## REACTIVE BARRIERS FOR $^{137}\text{Cs}$ RETENTION

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Plumes of  $^{137}\text{Cs}$ -contaminated groundwaters are a persistent problem at many DOE sites and at a number of commercial nuclear facilities. Engineered extraction is difficult and reactive barriers are increasingly being considered as a permanent solution. Clays are low-cost and effective chemical barriers, though their long-term effectiveness for Cs retention by ion exchange reactions is untested. To identify optimal clays for Cs retention we carried out Cs desorption studies with five common clays: Wyoming Montmorillonite (SWy-1), Georgia Kaolinites (KGa-1 and KGa-2), Fithian Illite (F-III), and K-Metabentonite (K-Mbt). Exchange sites were pre-saturated with 0.16 M CsCl for 14 days, readily exchangeable Cs removed by a series of  $\text{LiNO}_3$  and  $\text{LiCl}$  washes, the washed clay placed into dialysis bags and the Cs release to the deionized water outside the bags were measured. Rates were initially fast, but subsequently stabilized. Long-term release rates from 50 to 107 days for SWy-1, K-Mbt and F-III were similar; 0.017 to 0.021 % sorbed Cs released per day but the two kaolinites released Cs more rapidly (0.12 to 0.05 per cent of the sorbed Cs per day). In a second suite of experiments clays were doped for 110 days and subjected to an extreme and prolonged rinsing process. This, however, did not completely free any of the clays of excess Cs. Thus, all clays have at least some capacity for irreversible Cs sorption. Long-term uptake was greatest on K-Mbt and approached 0.33 wt% Cs. This, its commercial availability (as granulated shale), and its predictable release rate (0.021% per day), support K Metabentonite as an optimal reactive barrier component for  $^{137}\text{Cs}$  plumes.

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## BATCH AND COLUMN STUDIES OF URANIUM(VI) ADSORPTION BY QUARTZ IN THE PRESENCE OF CO<sub>2</sub>

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U(VI) adsorption on quartz powder was investigated by conducting batch adsorption experiments over the pH range of approximately 5 to 9 and at two partial pressures of CO<sub>2</sub> ( $10^{-3.4}$  and  $10^{-1.1}$  atm). The total U(VI) concentration in the experiments covered the range of  $10^{-8}$  to  $10^{-5}$ M. Increased levels of CO<sub>2</sub> decreased U(VI) adsorption in this pH range due to the formation of stable aqueous uranyl-carbonato complexes at pH > 5. The maximum uptake of U(VI) adsorbed was reduced from  $\approx 100\%$  under atmospheric ( $p\text{CO}_2 = 10^{-3.4}$  atm) to 85% at  $10^{-8}$ M U(VI) and 40% at  $10^{-5}$ M U(VI) at a  $p\text{CO}_2$  of  $10^{-1.1}$  atm. In addition, the higher level of CO<sub>2</sub> shifted the high pH edge of the adsorption envelope from pH 8.3 to 8.6 at atmospheric  $p\text{CO}_2$  to below pH 7 at  $p\text{CO}_2$  of  $10^{-1.1}$  atm. The time to reach U(VI) adsorption equilibrium increased by a factor of ten over the pH range from 4.8 to 8.5. Column studies were also conducted to investigate the effect of speciation on transport of U(VI) through columns packed with quartz. Experiments containing  $10^{-6}$ M U(VI) were conducted over a range in pH from 6.9 to 9.0, at  $p\text{CO}_2$  equal to  $10^{-3.4}$  and  $10^{-1.1}$  atm and at two different flow rates. At pH 6.9 and  $10^{-1.1}$  atm CO<sub>2</sub>, the breakthrough curve for U(VI) was nearly symmetrical and gave a retardation factor ( $R_f$ ) equal to 7.9. At pH 8.6 and  $10^{-3.4}$  CO<sub>2</sub>, the observed  $R_f$  was 7.2 and the peak showed significant tailing. The similar  $R_f$  values for these two breakthrough curves at significantly different pH values results from the similar distribution of U(VI)-CO<sub>3</sub> complexes in solution demonstrating the significance of aqueous speciation on transport. U(VI) was transported nearly conservatively at pH 9.0 and  $10^{-3.4}$  atm CO<sub>2</sub>. An increase in the velocity by a factor of 4 at pH 8.6 to 8.7 decreased the  $R_f$  approximately 15 percent suggesting that a kinetic process was slightly influencing the results. The batch and column results were modeled using a two-site surface complexation model (SCM) to describe adsorption equilibria. This model had been previously calibrated for similar batch and column studies in the pH range from 3.5 to 5; the previous model significantly under-predicted adsorption and retardation at above pH 7. The existing SCM was expanded to include the formation of ternary U(VI)-CO<sub>3</sub> surface complexes. Introducing these species improved the fit to the high pH adsorption envelope in batch studies and the observed retardation in the column studies. Different modeling approaches with respect to stoichiometries of adsorption reactions, surface species, electrical double layer and site densities will be discussed.

## ADSORPTION OF $^{241}\text{Pu}$ ON $\alpha\text{-Fe}_2\text{O}_3$ IN A REPOSITORY-RELEVANT BRINE

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To assess the long term safety of material-test reactor fuel elements (MTR-FE) in a salt mine repository, irradiated MTR fuel from the material test reactor (DIDO) in Jülich were subjected to leaching in a repository-relevant brine in the presence of iron (simulate for the POLLUX-container). From the irradiated MTR-FE the radionuclides were mobilized first and then trapped by the corrosion products.

In order to quantify the source terms for radionuclide release, the sorption effects of various radionuclides were studied on  $\alpha\text{-Fe}_2\text{O}_3$  in a repository-relevant salt brine at three different temperatures. The results indicated that there is a selective sorption between the nuclide  $^{241}\text{Pu}$  and the  $\alpha\text{-Fe}_2\text{O}_3$  matrix. To interpret these sorption data the equation of Langmuir was used and the values of various thermodynamic parameters have been determined. The sorption of  $^{241}\text{Pu}$  on  $\alpha\text{-Fe}_2\text{O}_3$  is an exothermic process. The  $\Delta H^\circ$  value is -37.88 kJ/mol. The negative  $\Delta G^\circ$  values which become more negative with increasing temperature show the spontaneity of the sorption process. The positive value of  $\Delta S^\circ$  indicates that the adsorbed ions are relatively immobile and that the displaced ions from the solid surface are greater in number than the adsorbed ions. The recorded adsorption isotherms of  $^{241}\text{Pu}$  on  $\alpha\text{-Fe}_2\text{O}_3$  at different temperatures are of the L-type (Langmuir-Type). The subsequent desorption experiments showed that there is a strong fixation between matrix and the radionuclide  $^{241}\text{Pu}$ .

In conclusion all these results indicated a chemical sorption process between the matrix  $\alpha\text{-Fe}_2\text{O}_3$  and  $^{241}\text{Pu}$ . To get information about the mechanism of this reaction additional knowledge especially of the matrix surface is needed and this work is in process.

## EXPERIMENTAL STUDY AND MODELING OF URANIUM(VI) TRANSPORT THROUGH Fe(II)-RICH OLIVINE ROCK COLUMNS

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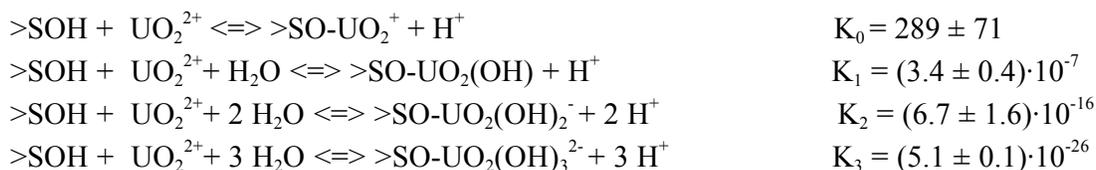
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Iron(II)-rich olivine has been proposed as an additive to the buffer material placed in high level radioactive waste final repository due, both to its reducing capacity given by its content in iron(II) as well as to its ability to sorb heavy metals and radionuclides.

In this work, the transport of uranium(VI) has been studied through columns filled with olivine and olivine-quartz mixtures. Experimental results have been modeled taking into account the following surface complexation constants:



Modeling has been performed by using two different transport reactive codes: ARASE and RETRASO. Both codes have satisfactorily reproduced the experimental uranium concentrations as well as pH changes as a function of time.

## ACTINIDES SORPTION PROCESSES ON ZIRCON

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Because of its low solubility and its resistance to radiation effects, zircon (zirconium silicate) is a potential candidate as host matrix for long term storage of actinides in an underground disposal. One of the most important processes which may affect safety during such a storage is the radionuclides migration through the geosphere. Thus, it appears very important to have not only a good understanding of the solubility of the zircon but also to well define the sorption mechanisms of aqueous ions on this mineral.

In a first step, in order to simplify the studied system, we have considered a synthetic material which present a high purity (about 99%). Moreover, we have also studied two others compounds ( $ZrO_2$  and  $SiO_2$ ) which can be considered as the elementary components of  $ZrSiO_4$ . Thus, the comparison of the results obtained for these three materials is very important to lead a detail knowledge of ions sorption mechanisms on zircon. All compounds were characterized using XRD, IR and microanalysis and their specific surface areas were determined ( $N_2$ -BET method). Potentiometric titrations and electrokinetic measurements were performed in order to determine the surface sites density and their amphoteric behavior.

Sorption experiments (using batch protocol at room temperature) were conducted to study uranyl and europium (III) ions sorption on the three materials versus pH and initial cation concentration in solution. Such ions were chosen because they can be considered as model for respectively hexavalent and trivalent actinides.

It is important to note that a thermodynamical approach of sorption phenomena, by direct modeling sorption isotherms, using surface complexation reactions for example, does not lead to accurate informations in regards to the nature and the structure of the sorbed species. Therefore, we have used XPS, EXAFS and optical spectroscopy in order to determine the nature of sorption sites and then to identify the sorbed species and the chemical bound between the sorbed ion and the substrate (mono vs polydentate complex, inner vs outer sphere complex).

## SURFACE SPECTROSCOPIC STUDIES OF Cs<sup>+</sup>, AND Ba<sup>2+</sup> SORPTION ON CHLORITE

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The radioactive isotopes <sup>137</sup>Cs ( $t_{1/2}=30.1$  y) and <sup>140</sup>Ba( $t_{1/2}=12.8$  d) are both fission products which are potentially hazardous to the biological environment. The sorption behavior of Cs<sup>+</sup>, and Ba<sup>2+</sup> on natural chlorite were investigated using TOF-SIMS, and XRD. Natural chlorite used in these studies was a clay mineral containing apart from illite some quartz, feldspar, and calcite. The major cations in the chlorite structure are Fe, Mg, Ca, and K in addition to Si and Al. Depth profiling up to 70 Å was performed utilizing TOF-SIMS to study the amount of sorbed Cs<sup>+</sup> and Ba<sup>2+</sup> as a function of depth in the chlorite matrix. The results suggest that Cs<sup>+</sup> and Ba<sup>2+</sup> are sorbed mainly by ion exchange coupled with physisorption. The fraction of the total sorbed amounts within 70 Å of Cs<sup>+</sup> and Ba<sup>2+</sup> that are bound to sites at the outermost clay surface are 0.20 and 0.22 respectively. The total amounts of Cs<sup>+</sup> and Ba<sup>2+</sup> sorbed within the same depth relative to (Si+Al) content are 0.32 and 0.38 respectively. Quantitative determination of the amounts of primary cations in the chlorite structure before and after sorption showed that Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> are the primary exchanging cations. The XRD spectra of both natural chlorite and those after Cs<sup>+</sup> and Ba<sup>2+</sup> sorption were analyzed. The Cs<sup>+</sup>-chlorite samples were not accompanied with any significant structural changes in clay framework. The XRD spectra of Ba<sup>2+</sup>-chlorite samples, however, showed the appearance of new peaks indicating some structural changes, possibly precipitate formation. In both cases, the quartz surface do not provide significant sorption sites.

## CHARACTERIZATION OF U(VI) SORPTION TO A NATURAL SUBSTRATE USING ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY

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The sorption of the uranyl ion ( $\text{UO}_2^{2+}$ ) to the surface of sediments is one of the major factors limiting or retarding migration in the natural environment. For the purposes of surface complexation modeling (SCM) the mechanisms by which the uranyl ion binds to individual phases within a complex substrate must be adequately defined in the laboratory before model development is undertaken. Some of the more common instrumental analyses such as secondary ion mass spectroscopy (SIMS), which can observe the interaction of ions at the mineral / water interface are of little value in defining the partitioning of U(VI) between different mineral phases due to the low sensitivity of the technique towards uranium.

This study sought to define the interactions between the uranyl ion and different minerals within a complex substrate by the use of analytical transmission electron microscopy (AEM). While the technique is not a pure surface analytical method, it was assumed that the measurement of all sorption processes including sorption, diffusion and surface precipitation would be adequately defined, enabling the development of a surface complexation model. This study used a substrate derived from, a weathered quartz / mica schist obtained from the locale of the Koongarra uranium ore deposit. The sediment was used in a number of sorption experiments in which different total concentrations of  $\text{UO}_2^{2+}$  were added. The samples were then observed under the AEM with spectra derived from individual particles found within the bulk substrate. The results of the study found that U(VI) sorption was dominantly controlled by ferrihydrite like minerals in the substrate, with clay minerals contributing little to the total U(VI) sorption.

## SORPTION OF Ni(II) AND Am (III) ONTO CARBONATE FLUOROAPATITES

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Among the apatitic minerals, the carbonated species (francolites) appear as the most efficient ones for the immobilization of radionuclides. Therefore, they could be used to improve the retention properties of the engineered barriers of a deep geological nuclear waste repository.

We focused our study on a synthetic carbonate fluoroapatite, with the stoichiometry  $\text{Ca}_{10}(\text{PO}_4)_5(\text{CO}_3)(\text{F},\text{OH})_3$ , and on a natural francolite, with high amounts of carbonates and impurities. The two apatites present different surface characteristics as well as different dissolution behaviors.

Sorption experiments have been performed on nickel and americium, chosen for their importance in the safety of a nuclear waste repository. The influence of various parameters has been investigated, such as pH, nature and concentration of the electrolyte, solid and radionuclide concentration.

For both apatites, the nickel retention is shown to be controlled by the formation of inner sphere complexes with the functional groups present at the solid surface. The constants associated to the complexation equilibria involved have been determined by applying the constant capacitance surface complexation model for fitting the sorption isotherms. These constants do not differ appreciably from one apatite to the other one.

The case of americium has been found to be more complex. Dissolution-precipitation phenomena due to the presence of phosphate anions in the solution have been considered to explain the high retention levels observed experimentally for both apatites.

## TRANSPORT OF Sr (II) THROUGH QUARTZ-BENTONITE COLUMNS

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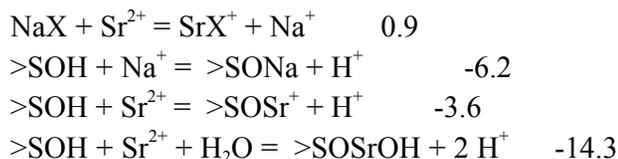
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Bentonite clay has been proposed as a buffer material in the final disposal concepts for spent nuclear fuel and other hazardous materials.

The aim of this study has been to understand the reactive transport mechanism of strontium through natural bentonites in order to find out a consistent set of equilibrium constant and make faithfully future predictions.

The cationic exchange capacity (CEC) and surface complexation approach have been both used to modelling sorption process on our minerals (Sodium and Calcium Montmorillonite forms) previously saturated with NaCl or CaCl<sub>2</sub> respectively.

The best fitting has been obtained with the next reactions and equilibrium constants



Aside, the transport of strontium (II) through quartz-bentonite barriers has been studied at laboratory scale at 25°C, using flow-through solid filled columns. Experimental data have been obtained for a series of total strontium concentrations  $1 \cdot 10^{-5}$  to  $1 \cdot 10^{-4}$  mol·dm<sup>-3</sup> for different ionic strength.

The experiments have been simulated with the reactive code RETRASO that couples advective transport and chemical reactions (aqueous complexation, precipitation, surface sorption and ionic exchange). The results have been compared with experimental data.

## INTERACTIONS OF CEMENT PORE FLUIDS WITH HOST ROCK AND THE EFFECTS ON HTO, Cs, Cl AND Mo DIFFUSION

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In the post-closure period of a deep disposal facility for low- and intermediate-level radioactive wastes, pore-fluids chemically equilibrated with cementitious components of the engineered barriers will migrate into the surrounding geology. Secondary calcium silicate hydrate phases might be formed in the micro pore system of the bedrock and change the available porosity for radionuclides. Since the retardation of radionuclides in bedrock is dependent on the sorption and matrix diffusion, these geochemical reactions are of concern. Experiments have been made to react discs of Swedish granite with hyperalkaline cement porewaters. 1 cm thick discs of Äspö grano-diorite mounted in diffusion cells were contacted with waters representative for fresh and leached cement porewater. The development of the water composition in the low-concentration containers were monitored by water analyses. The results were modelled using the computer codes CHEMGEO and PHREEQE. HTO, Cl, Cs and Mo diffusion experiments were done with both reacted and unreacted discs. In the case of Cs the ion diffusion behaviour was evaluated by sectioning the rock samples and measuring the radioactivity penetration profile.

## EVALUATION OF RADIOACTIVE NICKEL DISTRIBUTION COEFFICIENT BY ANALYZING BACKGROUND STABLE NICKEL

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Distribution coefficient ( $K_d$ ) is the most important sorption parameter for the safety assessment of underground disposal of radioactive wastes. Therefore an efficient and appropriate method for measuring the  $K_d$  is necessary. In this study, a simple novel method of evaluating the  $K_d$ 's of radioactive nuclides is proposed. The method is based on the measurement of the solid-liquid concentration distribution ratio ( $R_d$ ) of background stable isotopes. The present paper describes the application of this method to nickel (Ni), one of the most critical nuclides for shallow land disposal of low-level radioactive wastes generated from nuclear power plants.

The  $K_d$ 's of both the radioactive nickel (Ni-63) and its stable isotopes were simultaneously measured by batch sorption experiments in which the Ni-63 with a constant concentration and the stable Ni with various concentrations coexisted. The results showed that the  $K_d$  of Ni-63 and that of stable Ni agreed irrespective of the stable Ni concentration and that the  $K_d$ 's of both Ni-63 and stable Ni decreased gradually with an increase in the liquid-phase stable Ni concentration. This indicates that the  $K_d$  did not depend on mass number although the  $K_d$  was a function of the liquid-phase concentration of stable Ni. The solid-phase concentration of the background stable Ni was then measured by the extraction with 0.1N ammonium acetate solution or 0.1N hydrochloric acid. The  $R_d$  of the background stable Ni was calculated to compare the value of  $R_d$  from the extraction with the value of  $K_d$  from the batch sorption experiments. The background stable Ni concentration of the groundwater samples used ranged from 4 to 6 ng/ml, and the  $R_d$  agreed with the  $K_d$  obtained in the same liquid-phase concentration of stable Ni as a background level.

The above results illustrate that the method of evaluating  $K_d$  by the use of  $R_d$  is applicable to Ni. The advantages of this method are that the sorption experiments in laboratories using radionuclides are not necessary and the solid-liquid partitioning of background stable isotopes in the environment reflects the in-situ condition.

## SORPTION STUDY OF STRONTIUM ONTO CEMENT HYDRATE PHASES USING SEQUENTIAL DESORPTION METHOD

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Cementitious materials will be used as solidification, backfill, and construction materials for radioactive waste disposal. Therefore, long-term prediction of the dissolution and sorption mechanisms in cementitious material-water systems is very important for performance assessment of radioactive waste disposal.

We studied sorption and desorption behaviour of Sr onto/from several cement hydrate phases by applying a sequential desorption method. In this method, pure water,  $\text{NH}_4^+$  ion (0.1 N and 0.01N), EDTA (0.1N), and nitric acid (1N) were used to wash out weakly adsorbed ions, to exchange with the cations which were coordinated with  $>\text{SiO}^-$  sites of surface, to destruct the CaO layers of C-S-H, and to dissolve  $\text{SiO}_2$  chains, respectively.

The C-S-H at various Ca/Si ratio 0.8, 1.0, 1.3, 1.5, and 1.8 were put into polypropylene bottles and dispersed in the solutions containing Sr ( $1 \times 10^{-3}$  mol/L). The liquid-solid ratio of the samples was  $100[\text{mL} \cdot \text{g}^{-1}]$ . After 20 days, the solids were separated from the solution by filtration using a membrane filter with a pore size of  $0.45 \mu\text{m}$ . Then sequential desorption experiment was performed to investigate the sorption forms of Sr. The concentrations of Sr in the filtrates and each desorbed solution were determined by ICP-OES.

By using the sequential desorption technique to C-S-H, following results were observed: 1) Not only the surface coordination but also several other sorption reactions were considered such as the weakly adsorption and incorporation to C-S-H structure. 2) At Ca/Si ratio  $<1$ , the surface coordination is a dominant sorption reaction, and at Ca/Si ratio  $>1$  the weakly adsorption is a dominated reaction. We also performed the sorption of Sr on other cement hydrate phases (i.e. ettringite, monosulfate, and hydrogarnet) using this sequential desorption method. We will discuss these results at the conference.

## THE SORPTION OF $\text{Co}^{2+}$ , $\text{Pm}^{3+}$ AND $\text{Th}^{4+}$ ONTO $\text{UO}_2$

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The sorption of cobalt, promethium and thorium ions onto uranium dioxide from aqueous solution was studied as a function of pH and ionic strength (0.1, 0.01 M  $\text{NaClO}_4$ ) in a  $\text{CO}_2$ -free  $\text{N}_2$  environment at moderate radionuclide concentrations ( $\sim 10^{-8}$  M Co ( $^{60}\text{Co}$ ),  $\sim 10^{-8}$  M ( $^{147}\text{Pm}$ ),  $\sim 10^{-8}$  M ( $^{234}\text{Th}$ ). The desorption behaviour has been studied by reducing the pH. The first and second acid dissociation constants,  $\text{pK}_{\text{a}1}$  and  $\text{pK}_{\text{a}2}$  of the uranium dioxide surface were determined from potentiometric titrations. The dissolution of the solid has been studied as a function of pH as well for the time intervals used in the sorption experiments. The sorption was studied with an on-line equipment with samples withdrawn from the same solution at specific pH, separated by centrifugation and measured. Prior to all the sorption investigations the amount of the tracer sorbed on the equipment was checked under the same premises without the solid present. All the results are modeled with a double layer model surface complexation model using FITEQL. The resulting reactions are given as a function of the surface site density.

## SORPTION OF IODIDE ON PYRITE, MAGNESIUM OXIDE AND MG/AL LDH UNDER OXIDIZING AND REDUCING CONDITIONS

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The sorption of iodide on inorganic sorbents has been studied by several researchers because the migration of this anionic species is poorly retarded by geological barriers. It has been suggested that iodide can be sorbed on sulfide-containing minerals, such as pyrite ( $\text{FeS}_2$ ) and chalcopyrite ( $\text{FeCuS}_2$ ), by coprecipitation. The lead- or mercury-containing minerals, such as galena ( $\text{PbS}$ ), cinnabar ( $\text{HgS}$ ) and tiemannite ( $\text{HgSe}$ ), show a high capacity for the sorption of  $\text{I}^-$ . However, the toxicity of heavy metals must be considered if galena or cinnabar is to be used as an additive for backfill or buffer materials. The hydrous metal oxides, such as aluminium oxide and zirconium oxide, also have good properties of sorbing anions. Mg/Al LDH has an anion-exchange capacity and a composition of  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ . This mineral, which has a layered structure, can be readily synthesized under laboratory conditions.

The sorption properties of  $\text{I}^-$  on pyrite, magnesium oxide and Mg/Al LDH were investigated in this study. Batch sorption experiments were carried out under oxidizing and reducing conditions at  $25^\circ\text{C}$ . The experiments under reducing conditions were achieved by bubbling argon gas through the solution. Iodine-125 was used as a tracer. The experimental results of  $\text{I}^-$  sorption on pyrite are as follows : the distribution coefficient ( $K_d$ ) was about 100 ml/g when the initial concentration of  $\text{I}^-$  ( $[\text{I}]_0$ ) was  $1 \times 10^{-6}$  mol/L. The pH of solid-liquid suspension was in the range of 3.5 - 4.8. The sorbed concentration of  $\text{I}^-$  ( $[\text{I}]_{\text{sorbed}}$ ) increases as the  $[\text{I}]_0$  increases. The results of  $\text{I}^-$  sorption on magnesium oxide are as follows : the  $K_d$  value for the experiment of  $1 \times 10^{-6}$  mol/L  $[\text{I}]_0$  was about 350 ml/g. The pH of the solution was in the range of 10.4 - 10.8. The sorbed concentration of  $\text{I}^-$  increases in increments of  $[\text{I}]_0$ . The  $[\text{I}]_{\text{sorbed}}$  is affected by the ratio of solid to liquid amounts. The sorption of  $\text{I}^-$  on pyrite and magnesium oxide could be interpreted by the Freundlich adsorption isotherm. The sorption of  $\text{I}^-$  on Mg/Al LDH is explained by the Langmuir adsorption isotherm. The sorbed concentration of  $\text{I}^-$  under reducing conditions is higher than that under oxidizing conditions, showing the impact of carbonate anion on the sorption of iodide.

## NATURAL ANALOG STUDIES: APPLICATION OF ELECTROKINETIC DATA TO TEST THE ADSORPTION MODELS

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The effect of adsorption of Gd(III) on the electrokinetic potential of silica (Aerosil, 390 m<sup>2</sup>/g) was studied at various Gd(III) concentrations (ranging from 10<sup>-6</sup> to 10<sup>-2</sup> mol dm<sup>-3</sup>) and at various solid to liquid ratios (ranging from 0.05 to 8% of silica by weight). Up to some critical concentration of trivalent cations, their effect on the electrokinetic potential of silica is negligible and the sign is negative over the entire studied pH range. This critical concentration increases when the solid to liquid ratio increases, but proportionality is not observed. When Gd(III) concentration exceeds the critical value by about one order of magnitude, the magnitude of the negative electrokinetic potential of silica is reduced. This effect is substantial at pH 6 but it is rather insignificant when the pH is very high (pH>8) or very low (pH<4). When the Gd(III) concentration is even higher, the sign of the electrokinetic potential is reversed to positive over certain pH range, which depends on the solid to liquid ratio and Gd(III) concentration. The shape of experimental electrokinetic curves of silica in the presence of trivalent cations often shows maximums and double isoelectric points, thus, it is very complex in comparison with the shape of the percentage of uptake vs. pH curves. Therefore, a test of an adsorption model based on electrokinetic curves is much more demanding than a test based merely on uptake vs. pH curves. The parameters of surface complexation model (SCM) derived from analysis of a large set of uptake curves were used to predict the course of electrokinetic curves. The calculated and experimentally observed maximums and isoelectric points do not exactly match (a difference of one pH units or so), but the model curves qualitatively reflect the trends observed in electrokinetic experiments.

## STRONTIUM SORPTION ON HEMATITE AT ELEVATED TEMPERATURES

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Sorption onto iron hydrous oxide surfaces strongly controls the mobility of many trace metals in sediments and soils. To the most dangerous radioactive substances belongs  $^{90}\text{Sr}$  formed in nuclear reactions of the uranium fission.

We have used the experimental method representing a combination of acid-base potentiometric titrations with metal adsorption data to create a thermodynamic model for the heterophaseous system hematite ( $\equiv\text{FeOH}$ ) –  $\text{H}^+$  -  $\text{Sr}^{2+}$  depending on  $\text{p}[\text{H}^+]$  and sorbate/sorbent ( $\text{Sr}^{2+}/\equiv\text{FeOH}$ ) ratio at 25, 50, and 75°C. In the evaluation of experimental data, the Extended Constant Capacitance Model (Nilsson, 1995) has been used. Optimization of model parameters was performed via the nonlinear least square optimization program FITEQL 3.1 (Herbelin and Westall, 1994).

The best fit to the experimental data could be obtained by a model consisting of two surface complexes with the overall stoichiometries which can be interpreted as formation of a series of inner-sphere monodentate complexes according to the following equilibria:



The corresponding intrinsic equilibrium constants were calculated for 25, 50, and 75°C.

Sr adsorption enthalpies are 48 and 147 kJ/mole for  $\equiv\text{FeOHSr}^{2+}$  and  $\equiv\text{FeOSrOH}$  respectively. The difference between these values is caused by coadsorption of two hydroxide-ions. This also confirms a conclusion obtained from the fitting of experimental data that Sr adsorbs onto the hematite surface in a similar inner-sphere manner independent on pH. Moreover, this is confirmed by the entropy of  $\equiv\text{FeOHSr}^{2+}$  formation (196 J/K mole) which is to be related to the dehydration of  $\text{Sr}^{2+}$ . This value is very close to the entropy of hydration of  $\text{Sr}^{2+}$  ions in aqueous solutions amounts -205 J/K mole. It can be inferred that nearly the whole hydration entropy was gained when Sr adsorbs.

The combined effect of the  $\text{pH}_{\text{pzc}}$  decrease and the positive enthalpies of surface complexes formation is to favor Sr adsorption on hematite at enhanced temperatures. Sr adsorption and retardation in the natural aquatic environment is unlikely at ambient T and pH, but may be significant in the radioactive waste disposal at elevated temperatures.

## SORPTION OF $^{129}\text{I}^-$ ON ACTIVATED CARBON

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Anionic species are not retarded by the negatively charged Boom Clay at the slightly alkaline in situ pH. In the case of the geological disposal of non-reprocessed spent fuel, which will be a source for the long-living  $^{129}\text{I}^-$ , the highest calculated doses are due to  $^{129}\text{I}^-$ . If the geological barrier is not able to significantly spread the release in time (retardation) and if the dilution in the aquifer is not sufficient to reduce the  $^{129}\text{I}^-$  concentration, the confinement of  $^{129}\text{I}^-$  must be based on a robust engineered barrier. Adding anionic getters with high sorption capacity for  $^{129}\text{I}^-$  to the backfill material is a possible solution to spread the  $^{129}\text{I}^-$  release considerably.

Ag-impregnated and regular activated carbons (AC) are studied as additive to the gallery backfill material to act as a chemical engineered barrier sorbing the  $^{129}\text{I}^-$ . Batch sorption/desorption tests are performed to measure the sorption capacity of both activated carbons. Both activated carbons efficiently sorb  $\text{I}^-$ , especially the Ag-impregnated AC with a  $K_d$  value of 10000-100000 ml/g. The  $K_d$  value for the regular AC is lower but also quite high, between 1000-2000 ml/g. At high Iodide concentrations ( $\sim 1 \times 10^{-3}$  M), both AC reach the same sorption capacity:  $3.5 \times 10^{-5}$  mol/g ( $R_d=598$  ml/g) for the regular AC and  $3.3 \times 10^{-5}$  mol/g ( $R_d=433$  ml/g) for the Ag-impregnated AC. The activated carbons are however not ultimate sinks for  $^{129}\text{I}^-$  because the sorption is reversible.

Performance assessment calculations for the release of  $^{129}\text{I}^-$  resulting from spent fuel disposal in Boom Clay, showed that the dose calculated for the Normal Evolution Scenario is lower than the maximum acceptable limit. Adding an I-getter to the backfill material aims to enlarge the safety range. The influence of the value of the retardation coefficient for  $\text{I}^-$  on the release to the aquifer has been evaluated for different geometrical configurations and  $^{129}\text{I}^-$  release scenarios. At least an R-value of 1000 is necessary to obtain a significant reduction of the  $^{129}\text{I}^-$  flux to the aquifer. This means that for a backfill material containing 5% of an I-getter, a minimum  $K_d$  value of  $\sim 1500$  ml/g for the I-getter is necessary.

Both investigated activated carbons do obey this criterion and are considered for further investigation on their performance under geological disposal conditions.

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## INFLUENCE OF DISSOLVED SILICATES ON THE SORPTION OF CATIONS

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Dissolved silicates are one of the common and major species found in natural waters, coming from the dissolution of silicated solid phases. As silicates can be sorbed by surfaces, their presence in solution could influence the sorbing properties of these surfaces.

In this work, the sorption of silicates on two single oxide surfaces, magnetite and alumina, is pointed out and quantified. In a second step, the experimental study of the sorption of two cations, cesium and ytterbium, on magnetite and alumina is performed without and with silicates in solution. Yb well sorbs on neat alumina and magnetite, but the amount of cation sorbed becomes weaker when silicates are added in the solution. The sorption of Cs on the two neat surfaces is very weak, and increases when silicates are added in solution.

One mechanistic interpretation and one complexation modeling are proposed to account for the experiment observations. A comparison between the experiment results obtained with silicates in solution on one hand, and the sorption of Cs and Yb on binary mixtures of respectively alumina or magnetite with silica (which suspensions provide dissolved silicates) on the other hand is also made, and shows that the presence of silica alone could not explain the experiment results obtained for the binary mixtures. The same sorption model, taking into account the sorption of silicates on alumina and magnetite, can be used in both cases with the same consequences, the increase of the Cs uptake and the decrease of the Yb sorption.

## SORPTION OF U(VI) ON QUARTZ AS A FUNCTION OF EQUILIBRATION TIME AND SOLUTION PARAMETERS

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In this work, we investigated the retention of U(VI) on quartz as a function of mineral/solution equilibration time and solution parameters like pH (3-8), ionic strength (0.1 and 0.001 M NaClO<sub>4</sub>), initial uranium concentration (U=10<sup>-8</sup>-10<sup>-6</sup>-10<sup>-4</sup> M), and with or without the presence of carbonates (CO<sub>3</sub><sup>2-</sup>=0-10<sup>-3</sup> M).

In a first part we examine the influence of the mineral/solution equilibration times (from a few hours to one month) on the fractional uptake of 10<sup>-8</sup> M U(VI) on 25 g/L of quartz in CO<sub>2</sub>-free 0.1 M NaClO<sub>4</sub> solutions, at pH values equal to 4.40±0.05 and 6.8±0.1. The most remarkable result is a decrease of uranium uptake both with increasing pH and equilibration times. Such a behaviour can be related to the kinetic of quartz dissolution. The long-term sorptive behaviour of U(VI) in such a system results from a competition between surface complexation and aqueous complexation of uranyl ions with silicic acid, which is not negligible under the conditions of pH and Si concentrations investigated.

The pH-dependence of U(VI) sorption was also studied under CO<sub>2</sub>-free conditions, at different ionic strengths (0.1 and 0.001 M NaClO<sub>4</sub>), for a three days equilibration time. It is found that a lowering of the ionic strength of the solutions induces an increase of U(VI) uptake, due to the formation of outer-sphere complexes at quartz surface.

In a second part we have examined the adsorption processes of U(VI) on quartz surface in presence of carbonates in solution. An increase of the concentration of carbonate in solution induces a lowering of the percentage of U(VI) adsorbed at high pH values, certainly due to a competing effect between hydroxo surface complexation of uranyl and the formation of uranyl carbonate complexes in solution. However, a surface complexation modeling only based on such a competing effect did not provide a sufficient description of our experimental results for carbonated solutions, suggesting the retention of uranyl carbonate at quartz surface. Therefore, X-ray photoelectron spectroscopy (XPS) was used to get information on the kind of complexes formed at mineral / solution interface under conditions leading to different major uranyl species in solution.

The thermodynamic and kinetic code KINDIS, in which a non-electrostatic surface complexation model was introduced, was used to describe the evolution of the U(VI)-quartz- carbonates-0.1 NaClO<sub>4</sub> system. We took into account in modeling kinetic laws and rate constants for quartz dissolution and U(VI) complexation constants reported in the literature, as well as a binding constant of uranyl ions at quartz surface derived from our short-term experiments. We propose here a model which takes into account several processes occurring in a mineral / U(VI)-solution system, like dissolution, aqueous complexation and surface complexation of uranyl ions, and provides an accurate description of our experimental datasets for the sorptive behaviour of U(VI) on quartz as a function of time, pH and carbonates concentration.

## INTERACTION OF GRANITIC BIOTITE WITH LANTHANIDES AND ACTINIDES

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The interaction of granitic biotite with aqueous solutions containing lanthanide (La, Nd) and actinide (Th, U) elements (conc. 10-1000 mg/L) was investigated using radiochemical (INAA) and accelerator-based (<sup>12</sup>C-RBS) techniques. La and Nd have themselves a limited significance in respect of nuclear wastes (in contrast to Th and U) but can be used in experiments to simulate the chemical behavior of trivalent actinides, such as Am and Cm which belong to the long-living constituents of high-level nuclear wastes (HLW). The experimental results showed that biotite considerably interacts with La and Nd (even better than pure zeolites) removing, in the case of most diluted solution used (10 mg/L), almost the total amount of the elements (mostly by ion-exchange). The interaction with Th and U is also remarkable but the sorption mechanisms seem to be more complicated and related, as indicated by the spectroscopic measurements, to adsorption/surface-precipitation phenomena taking place at the surface of the reacted biotite crystals. The same behavior against the above mentioned elements was also observed for the other two main mineral constituents of granite (quartz and feldspar).

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## CATION SORPTION ON UNTREATED BENTONITE. EFFECT OF CATIONIC INVENTORY

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Many countries consider to use bentonite as one of the engineered barriers in their repository concepts for spent nuclear fuel. Often when the diffusion behaviour of radionuclides is studied pH and initial solution composition is varied.

To understand the effects of pH and composition of the solutions used to equilibrate untreated bentonite in diffusion experiments, it is essential to know those parameters (pH and composition of the solutions) after interaction with the clay. We have therefore carried out a series of experiments using Volclay MX-80 bentonite.

In batch sorption experiments with  $\text{Na}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Co}^{2+}$  two solid to solution ratios were studied. NaCl and  $\text{NaClO}_4$  solutions with initial concentrations in the range between  $10^{-5}$  and 1M were used and pH was varied between 2 to 9.

The sorption data is modelled taking into account the variation in the concentration of the dominant cations  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

## SORPTION OF Se(IV) ON HYDROXYAPATITE

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In the conceptual design of depositories for the disposal of high level radioactive waste, clay minerals have been often proposed as host or backfill material. Most of clays exhibit high immobilizing properties for cationic radionuclides but only weak retention properties for anions. Among radionuclides,  $^{79}\text{Se}$ , with its long half life ( $t_{1/2} = 60,000$  y), would have significant effects on the cumulative dose if released from the depositories to the geosphere. Selenium exists predominantly in the anionic form in aqueous environment with the species  $\text{SeO}_3^{2-}$  and  $\text{HSeO}_3^-$  being present in glass matrix molten in oxidizing conditions. Considering hydroxyapatite as a potential backfill material, the sorption of  $\text{SeO}_3^{2-}$  and  $\text{HSeO}_3^-$  from aqueous solutions was studied using a multidisciplinary approach, including sorption isotherms, kinetics, reversibility, influence of pH, ionic strength and calcium ions, electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS). The influence of pH revealed a maximum retention around pH 8 and a decrease for lower pH values, which is unusual for the sorption of anions on a mineral surface. Sorption isotherms showed a saturation of  $2.5 \cdot 10^{18}$  at.m<sup>-2</sup> and a 1 to 1 release of phosphate ions. The results are interpreted as an exchange process, leading to the replacement of phosphates by selenite ions. XPS and X-ray diffraction showed that this is a superficial process, selenite ions occupying crystallographic sites normally occupied by phosphates in the framework of the apatite. This process leads to a very efficient removal of selenite ions from aqueous solutions.

## ACTINIDE SORPTION ONTO IRON COLLOIDS: CASE OF Am, Co, U and Np

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Iron colloids are ubiquitous in the environment of a radwaste disposal either in the near field (containers) or the far field (natural waters). As a potential role on the radionuclide migration is generally assigned to colloids, experimental studies have been performed in order to characterize the sorption mechanisms which could occur with radioelements. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) colloids have been selected as model colloids for a systematic and detailed study on their sorption properties towards different radioelements such as Co(II), Am(III), Np(V) and U(VI). The influence of different physico-chemical parameters such as pH (2 to 10), the ratio adsorbate/adsorbent, ionic strength (0.01 to 0.1 M) and the characteristics of hematite colloids has been investigated through batch experiments. Results obtained (percent of radionuclide fixed or log K<sub>d</sub> as a function of pH) are presented and discussed. The sorption data are described by using two models based on surface complexation theory: the Kurbatov model (without electrostatic term) and the diffuse layer model (with an electrostatic term). Both models allow the description of Co, Am, Np, U retention onto hematite colloids by considering equilibria which involve different hydroxo surface complexes. The retention mechanisms obtained through these models as well as the associated surface complexation constants, are compared to each other and to literature.

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## EFFECTS OF HUMIC SUBSTANCES ON Np SORPTION ONTO SAND AND GRANITE

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Humic substances (HS) are present in groundwaters at concentrations between 0.1 and 100 mg/L and may play an important role on the transportation of actinides. Studies on the influence of humic substances on sorption properties of actinides onto sediments and rocks provide basic information for modeling to predict the migration behavior of actinides in the geosphere. In this study, three HS, which mainly consisted of fulvic acid, were isolated from groundwaters in sandy and granitic layers and were used in the sorption experiments. Purified Aldrich humic acid was also used as a reference.

Sorption experiments of Np onto sand and granite were carried out in 0.01M NaClO<sub>4</sub> solution at the HS concentration between 0 and 100 mg/L. The reaction time was 7 days. The final pHs of the solutions after the experiments were pH 5-6 at the Np-HS-sand systems and pH 9-10 for the Np-HS-granite systems.

In the Np-HS-sand systems, the distribution coefficient (K<sub>d</sub>) in the presence of Aldrich humic acid increased with the humic concentration from 0.6 mL/g at 0 mg/L to 1.1 mL/g at 23 mg/L, and then decreased to 0.26 at 50 mg/L. On the other hand, the K<sub>d</sub> value of Np in the presence of the groundwater HS exhibited the lowest value (ca. 0.2 mL/g) at the HS concentration of 1-10 mg/L, and then increased. The dominant molecular size fraction of HS was 100,000-30,000 daltons for the Aldrich humic acid (61%) and less than 5,000 daltons for the groundwater HS (50-60%). Therefore, the difference in the variation of K<sub>d</sub> depends on the characteristics of HS. In granitic simulations, the K<sub>d</sub> of Np was almost constant (3.4 mL/g), and hence the effects of HS on the Np sorption were low.

## INNER-SPHERE COMPLEXES OF $\text{NpO}_2^+$ AND $\text{SeO}_4^{2-}$ ON DISPERSED PARTICLES OF AMORPHOUS FERRIC OXIDES

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It is important to understand the sorption mechanism of fission products and actinides for the safety assessment of radioactive waste disposal. There are two types of surface complexes, namely an inner-sphere complex and an outer-sphere complex. Ions sorbed as inner-sphere complexes bond directly with the surfaces of rocks and materials of engineered barrier, while those sorbed as outer-sphere complexes are located at least one water molecule layer away from the surfaces. In this work, we measured the volume changes through the sorption of  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$  on the amorphous ferric oxide particles dispersed in 0.01 M  $\text{NaClO}_4$  at pH = 6 and pH = 5, respectively. Comparing the initial volume of liquid phase with the volume of it after sorption equilibrium, it was found that the volumes of liquid phases increased during the sorption of  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$  and that the increased volumes per mole of their sorption were approximately 9 ml/mol and 20 ml/mol, respectively. This may indicate that some fractions of water molecules hydrated to aqueous  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$  and dispersed amorphous ferric oxide particles were released to the bulk liquid phases. It is well known that  $\text{H}_2\text{PO}_4^-$  is strongly sorbed on ferric oxides as an inner-sphere complex, and reported that the volume change per mole of  $\text{H}_2\text{PO}_4^-$  sorption was estimated at 15 ml/mol and its hydration number is 6 [1]. Assuming that (i) the effective volume of hydrated water molecule of  $\text{H}_2\text{PO}_4^-$  is similar to that of  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$ , (ii) the hydration numbers of  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$  are 6 and 9, and (iii) the volume change owing to surface protonation per mole of  $\text{H}^+$  sorption is 6 ml/mol, it suggested that  $\text{NpO}_2^+$  and  $\text{SeO}_4^{2-}$  are sorbed on the dispersed amorphous ferric oxide particles as inner-sphere complexes under the experimental conditions. For  $\text{NpO}_2^+$ , this is consistent with our previous studies [2,3].

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## SORPTION EQUILIBRIUM AND KINETICS OF Np(V) ON DISPERSED PARTICLES OF Na-MONTMORILLONITE

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According to the performance allocation analysis on multi-barrier system for high-level radioactive waste disposal, it was found that the retardation of TRU elements in the bentonite-filled buffer region of the engineered barrier plays essentially an important role in the multi-barrier system, and that Np dominates the hazard at the exit of the natural barrier. In this work, the sorption equilibrium and kinetics of  $\text{NpO}_2^+$  and Np(V) carbonate complexes (mainly  $\text{NpO}_2\text{CO}_3^-$ ) on dispersed particles of Na-montmorillonite were experimentally investigated by using batch technique and spectroscopic method, respectively. In the experiment on sorption equilibrium, we examined the influence of the heterogeneous surfaces (outer surface and interlayer surface) of Na-montmorillonite on sorption. The sorption data could be fitted with Langmuir-Freundlich type isotherm, but not with Langmuir type isotherm, suggesting the heterogeneity effect on the sorption equilibrium. Considering the heterogeneity of sorption sites, we showed the affinity spectra for the sorption of  $\text{NpO}_2^+$  and Np(V) carbonate complexes and found the monomodal distribution functions for both cases. However, the spectrum for  $\text{NpO}_2^+$  was asymmetrical, and that for Np(V) carbonate complexes was relatively symmetrical. This suggests the difference of sorption sites between  $\text{NpO}_2^+$  and Np(V) carbonate complexes. In the experiment on kinetics, kinetic spectra were calculated. From the kinetic spectrum for  $\text{NpO}_2^+$ , two sorption processes could be distinguished. It was considered that the fast process is attributable to the sorption of  $\text{NpO}_2^+$  on the easily accessible outer surface of Na-montmorillonite particles and the slower process is assigned to the sorption on the interlayer surface. On the other hand, the kinetic spectrum for Np(V) carbonate complexes illustrated the fast process only, suggesting that the sorption sites in the interlayer of Na-montmorillonite particles can not be accessible for Np(V) carbonate complexes. The half widths of spectra for both cases were also broader, indicating the heterogeneity effect on the sorption kinetics.

## SORPTION AND DESORPTION KINETICS OF Np(V) ON MAGNETITE AND HEMATITE

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Sorption kinetics of Np(V) on magnetite and hematite was investigated. It was found that sorption process consists of a fast sorption followed by a slow sorption and that the sorption reaches nearly equilibrium in 1 hour.

Desorption experiment was carried out with 1N KCl and 0.1N  $K_2C_2O_4$  to investigate the variation of the Np sorption forms as a function of time contacting with Np solution at pH = 5.5 and 7.5 and at pH = 4.2 and 8.0 for magnetite system and hematite system, respectively. For magnetite system, 100% of sorbed Np was found to be desorbed by  $K_2C_2O_4$  and 80% was desorbed by KCl at 4 minutes, but after 1 hour, about 15% of Np could not be desorbed by KCl and  $K_2C_2O_4$ , and the fraction of Np that could not be desorbed by KCl and  $K_2C_2O_4$  increased to 25% at 1 week at both pH. For hematite system, 100% of sorbed Np was found to be desorbed by  $K_2C_2O_4$  and 60% was desorbed by KCl at 4 minutes and even at 1 hour. The fraction of Np that could not be desorbed by KCl and  $K_2C_2O_4$  was 25%, and 75% of sorbed Np was desorbed by KCl after 1 week at pH = 4.2. On the other hand, at pH = 8.0, about 90% of sorbed Np could not be desorbed by KCl and  $K_2C_2O_4$  after 4 minutes. These results indicate (i) that a fast sorption is attributable to the sorption on/into the non-crystalline phase of the magnetite and hematite, (ii) that the sorption on/into crystalline phase also contributes to the fast sorption of hematite in alkaline solution, and (iii) that a slow sorption represents the diffusion into crystalline phase of magnetite in both acidic and alkaline solutions and that of hematite in acidic solution. These results also suggest that the surfaces of magnetite in both acidic and alkaline solution and that of hematite in acidic solution were covered with non-crystalline phase, while the surface of hematite in alkaline solution was covered with non-crystalline part sporadically. For hematite, it was considered that there are many effective sorption sites inside of the crystalline and non-crystalline phases especially crystalline phase.

From the results of sorption kinetics and desorption, it is considered that the sorption equilibrium is achieved in about 1 week from the viewpoint of sorption forms, although the amount of Np sorbed reaches nearly equilibrium in only 1 hour.

We also investigated the surface conditions of magnetite and hematite in acidic and alkaline solutions using of SEM and XPS and combined these investigations with sorption, desorption and kinetics results.

## URANIUM(VI) SORPTION BEHAVIOR ON MIXED SILICATE MINERALS

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An important mechanism for retarding radionuclide migration from geologic repositories for high-level nuclear waste is sorption onto mineral surfaces. In this study, mixtures of quartz and clinoptilolite, which are present in rock matrix and fractures at the proposed U.S. repository at Yucca Mountain, Nevada, were reacted with  $^{233}\text{U}$ -bearing solutions to evaluate the sorptive behavior of a binary silicate mineral system. Data from the experiments were used to test the ability of surface complexation models to predict U(VI) sorption onto mineral mixtures based on parameters derived from single mineral experiments.

Sorption experiments were conducted over a range of pH in electrolyte solutions of 0.1 M  $\text{NaNO}_3$  with an initial U(VI) concentration of  $2.0 \times 10^{-7}$  M. Prior to the start of the experiments, minerals were treated to remove impurities, clinoptilolite was converted to Na-form by ion exchange with NaCl solutions, and the surface areas of the individual minerals and mineral mixtures were measured. The M/V ratio of quartz in experimental solutions was kept constant at 28.6 g/L, whereas the M/V ratio of clinoptilolite was varied from 0.0 to 20.0 g/L. Experiments were carried out with solutions in equilibrium with atmospheric  $\text{CO}_2(\text{g})$  (open containers) and with solutions having limited  $\text{CO}_2(\text{g})$  (capped containers).

Results of the U(VI) sorption experiments using single minerals (i.e., quartz-only and clinoptilolite-only) were used to derive binding constants for the diffuse-layer surface complexation model. Experimental data on mineral mixtures were then compared to U(VI) sorption predicted by the diffuse-layer model using the derived binding constants.

## SORPTION OF Am(III) AND Eu(III) ONTO $\gamma$ -ALUMINA: EXPERIMENT RESULTS AND MODELING

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A large number of investigations are available in the literature to describe surface complexation processes of different metal ions, particularly abundant for divalent metal ions but much less for trivalent or higher charge metal ions. For the latter ions the surface sorption is overlapped by multitudinous processes and hence their surface complexation is well described.

The present paper investigates the surface complexation behaviour of trivalent metal ions,  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ , on well characterized  $\gamma$ -alumina. Experiments are conducted at different pH (4 - 8) and ionic strength (0.001 – 0.1  $\text{NaClO}_4$ ). By varying the metal ion concentration from  $10^{-9}$  to  $10^{-4}$  mol/L, the sorption isotherm is established under each given experimental condition. To ascertain the carbonate ion effect, experiments are also carried out either in the presence or in the absence of  $\text{CO}_2$  contact to sample solutions. Different surface complexation models are applied to the present experimental results to interpret and appraise the surface sorption processes under different experimental conditions. The underlying surface complexation constants are evaluated and compared with the values hitherto available in the literature. A comparison is also made with the Eu(III) sorption onto hematite mineral surface investigated previously. For the interpretation of the surface sorption of binary metal ion complexes at higher pH, the formation constants for hydrolysis and carbonate complexation are taken from the literature.

## RETARDATION CAPACITY OF ORGANOPHILIC BENTONITE FOR ANIONIC FISSION PRODUCTS

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Sorption and diffusivity of the anionic radionuclides iodide and technetium on MX-80 bentonite with different hexadecylpyridinium (HDPy<sup>+</sup>) loadings, were studied using equilibrium solutions of different ionic strengths. Experiments were carried out with ~37 kBq of <sup>125</sup>I and <sup>95m</sup>Tc (~5·10<sup>-1</sup> mol·l<sup>-1</sup>) and the corresponding carriers in concentration ranging between 10<sup>-8</sup> and 1 mol·l<sup>-1</sup>.

Additionally, the mineralogical characteristics, like regular and *in situ* powder X-ray diffraction (XRD), thermogravimetric (TG) and calorimetric (DTA) measurements, IR spectral analysis of the organo-bentonite samples, and the exchange behavior of HDPy<sup>+</sup> (chemical analysis) were investigated.

On the basis of these analyses it was concluded that the alkylammonium ions are adsorbed as 1. HDPy<sup>+</sup> cations, 2. HDPyCl molecules and 3. micelles with decreasing binding intensities in this order.

In HDPy<sup>+</sup>-modified MX-80 bentonite, iodide and pertechnetate ions exhibited increasing sorption (characterized by the distribution ratio, R<sub>d</sub>), while cationic radionuclides showed decreasing sorption with increasing organophilicity. In case of medium saturation levels, the simultaneous sorption of anions (I<sup>-</sup> and TcO<sub>4</sub><sup>-</sup>) and cations (Cs<sup>+</sup> and Sr<sup>2+</sup>) was observed.

Sorption as well as reversibility of the process were influenced by the composition of the electrolytes employed. The sorption of the radionuclides decreases gradually with increasing ionic strength of the electrolyte solutions.

The experiments revealed the general tendency that the diffusivity (Da [cm<sup>2</sup>/s]) for iodide and pertechnetate decrease with increasing organophilicity and increase with increasing ionic strength of the equilibrium solutions, confirming the implications of the sorption experiments.

## EFFECTS OF THE HUMIC ACID ON SORPTION OF Am(III) AND Cm(III) ONTO KAOLINITE

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Sorption coefficients of Am(III) and Cm(III) on kaolinite were measured at pH from 3.5 to 10 and humic acid (HA) concentrations of 0 to 20 ppm at ionic strength of 0.1 (NaClO<sub>4</sub>). The Am(III)- and Cm(III)-humate stability constants were also measured at the same ionic strength at pH from 3.0 to 5.5. In the absence of HA, the sorption coefficients of Am(III) and Cm(III) ions increased with pH over the whole pH range. By introducing HA, the sorption coefficients were enhanced at pH up to around 5, above which there was a considerable decrease in the coefficients. Sorption of HA-bound Am(III) and Cm(III) onto kaolinite results in higher sorption coefficients at low pH, while sorption of the HA-bound Am(III) and Cm(III) at higher pH decreases. The effects of humic acid were interpreted by a linear additivity model, modified for partial dissolution of humic acid in aqueous phase. The model based on the stability constant of Am(III)- and Cm(III)-humate complexes, fractional sorption of HA on kaolinite, and sorption coefficients of Am(III) and Cm(III) on kaolinite in the absence of HA. The model was found to be in fairly good agreement with the experimental data.

## EFFECT OF HUMIC ACID ON THE URANIUM(VI) SORPTION ONTO PHYLLITE AND ITS MINERALOGICAL CONSTITUENTS

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Organic materials, such as humic and fulvic acids, that are present in natural aquifers interact with dissolved inorganic contaminants and affect their sorption behavior on geological materials and thus, their migration in aquifers. Consequently, a quantification of the influence of humic material on radionuclide sorption is necessary.

Phyllite was used as site-specific rock material because it is quite common in the Western 'Erzgebirge' in Saxony, Germany, and is closely associated with uranium deposits of the uranium mining areas in East Germany. Site specific humic acid, isolated from the bog 'Kleiner Kranichsee' and a <sup>14</sup>C-labelled synthetic humic acid were used for the experiments.

The effect of humic acid was studied on the sorption behavior of uranium(VI) onto phyllite and its mineralogical components muscovite, albite and quartz in air-equilibrated batch experiments as a function of pH. The uranium sorption is strongly affected by both the pH and the presence of organic material. The kinetics and reversibility of the uranium and humic acid sorption were studied using the <sup>14</sup>C-labelled humic acid. Furthermore, the influence of competing sulfate ions on the uranyl and humic acid sorption onto phyllite was determined, because seepage waters of the uranium mining areas in Saxony contain, among other anions, relatively high concentrations of sulfate ( $3 \cdot 10^{-2}$  M).

## MODELLING OF THE SORPTION OF EUROPIUM ON BENTONITE IN THE PRESENCE OF HUMIC ACID AND CARBONATES

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The sorption of europium(III) was studied as a function of pH (ranging from 4.5 to 9) in the systems consisting of Czech Na-bentonite SABENYL and synthetic granitic water containing the humic acid (HA) and spiked with  $^{152,154}\text{Eu(III)}$ . The experiments were accomplished using the batch method ( $V/m = 400 - 600$  ml/g, time of equilibration 48 - 60 h;  $V$  - volume of aqueous solution,  $m$  - weight of bentonite) and the following starting concentrations of important components of granitic water were used:  $1 \times 10^{-6} - 1 \times 10^{-5}$  M  $\text{Eu(III)}$ , 2 - 20 mg HA/l (approx.  $1 \times 10^{-5} - 1 \times 10^{-4}$  M),  $1.8 \times 10^{-3}$  M  $\text{CO}_3$ , ionic strength 0.1 ( $\text{NaClO}_4$ ). Three types of surface complexation models (SCM) (Constant Capacitance Model, Diffuse Double Layer Model and so called Chemical Equilibrium Model) were used for the modelling of the sorption systems and new computer codes were constructed for this purpose. The experiments were realized to ensure the input data (surface complexation constants) needed for the SCM models, namely, apart from the sorption of Eu in the absence of HA, also the distribution of HA alone and the mutual effects of HA and Eu were determined, always as a function of pH. In all cases, the sorption of HA decreased and that of Eu increased if pH increased from 4.5 to 9. It was also evident that the sorption interactions between HA and Eu existed. Other input data needed, i.e. the protonization constants of the bentonite edge sites and surface complexation constants characterizing the sorption of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  on bentonite, were taken from our papers published earlier. The stability constants for Eu complexation in solution partly were taken from literature and partly were obtained from our experiments.

## THE STRUCTURE OF URANIUM (VI) SORPTION COMPLEXES ON SILICA, ALUMINA, AND MONTMORILLONITE

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We have investigated the adsorption of the uranyl ion ( $\text{UO}_2^{2+}$ ) in contact with silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and montmorillonite surfaces between pH 3.1-6.5 using extended x-ray absorption fine structure (EXAFS) spectroscopy to observe the local structure around the uranium. Preliminary analysis shows that in all samples the uranyl ion structure is preserved, with two axial oxygen atoms detected at 1.8 Å. For the montmorillonite samples a single equatorial oxygen shell is observed at 2.4 Å, with a coordination number of  $5 \pm 1$ . The samples of uranyl on silica and alumina are all observed to have two separate equatorial shells with bond lengths of approximately 2.3 Å and 2.5 Å. A uranium shell at 4.0 Å is observed in the samples of uranyl on silica and on alumina at high pH (6.2, 6.5). Some evidence exists for the presence of a silicon shell at approximately 3.10 Å in the sample of uranyl on silica at pH 6.5.

These results suggest there is some inner-shell adsorption in the samples of uranyl on silica and alumina which may be pH dependant, but that no inner shell adsorption occurs between uranyl and the montmorillonite.

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## SORPTION OF $^{241}\text{Am}$ ON KAOLINITE MODIFIED BY HUMIC ACID

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Mineral-bound humic substances modify inorganic surfaces in subsurface environment, changing the nature and number of complexation sites for contaminants including radionuclides. In this respect, sorption of  $^{241}\text{Am}$  on kaolinite was studied in  $\text{NaNO}_3$  solutions considering effects of ion strength and pH. Batch tests were employed to carry out sorption of humic acid on well-prepared kaolinite and succeeded  $^{241}\text{Am}$  sorption. With characterization of kaolinite, humic acid and humic-coated kaolinite, we suggested structure of the modified surface. Sorption mechanism of  $^{241}\text{Am}$  was discussed based on information available in this study and literature.

The study was funded by Nuclear Industry Science Foundation, CNNC.

## EFFECT OF THE LEACHING OF CONCRETE BARRIERS OF L/ML RADIOACTIVE WASTE REPOSITORIES ON Cs MIGRATION THROUGH SURROUNDING SOILS

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Concrete matrixes are largely used in low and medium level radioactive wastes repository (notably as confining barriers). Lixiviation of such matrixes result in saline and high pH solutions, able to migrate through surrounding soils. These particular physico-chemical conditions can have an impact on the migration behaviour of the fission products contained in nuclear wastes as Sr or Cs. The aim of this study is to investigate Cs sorption capacity of different kinds of soil, when these are submitted to hyper-saline and hyper-alkaline solutions. Synthetic solutions simulating concrete matrixes leachate (CBS) were made, the effect of different parameters (the concentrations of Ca, Si, Na, K and pH), on Cs sorption were studied. Five synthetic soils were made, they are a mix of quartz, carbonates (calcite, dolomite) and clay minerals (kaolinite and montmorillonite). Soil 1 is quartz, soil 2 is a mix of quartz + calcite, soil 3 associates quartz, calcite and dolomite, soil 4 and 5 are mixes of quartz calcite and clays minerals. Batch adsorption experiments are conducted and the percentage of Cs removed from solution and the distribution coefficient between soil and solution ( $K_d$ ) are calculated in each case. In order to compare sorption of Cs with or without CBS and to appreciate the modification, improvement or drop, of Cs sorption capacity of soils, the Cs fixation on each type of solid phase was previously studied for neutral pH solution and very low competitor (Ca, Na, K) concentrations. From a general point of view, we can notice a significant effect of CBS, which involve in every case an extensive decrease of  $K_d$  value, and, in a smaller part, a decrease of the Cs adsorbed percentage.

Studied ions, especially  $\text{Na}^+$  and  $\text{K}^+$ , are good competitors for  $\text{Cs}^+$ , not only on clay minerals, as expected, but also for carbonated soils (soils 2 and 3). Fixation is high for soils containing clays minerals even the part of clay is low (<3/18 w/w), but it can be noticed a good affinity of Cs for dolomite (soil 3).

## THE SORPTION OF URANIUM AND NEPTUNIUM ONTO CEMENTITIOUS MATERIALS

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Cementitious materials are expected to be present in nuclear waste repositories in significant quantities. Consequently, they would have a high probability of interacting with radionuclide-bearing fluids derived from failed waste packages. We are reporting the experimental results of batch sorption experiments to obtain partition coefficients of uranium 6+ and neptunium 5+ oxidation states on untreated (fresh) and hydrothermally altered concrete under various conditions relevant to either near-field or adjacent geological environment of the repositories. The observed partition coefficients vary by several orders of magnitude depending on the type of concrete, pH, carbonate concentration in the solution, and the time. The nuclides associated with silica-rich colloids were also observed in our experiments. The effect of these colloids on the partition coefficients and the results of recent XAFS studies of the nuclides sorbed on the concrete under different conditions will be discussed.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

## INTERLABORATORY STUDY OF SORPTION MECHANISMS FOR RADIONUCLIDE MIGRATION PREDICTION

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Sorption/desorption processes are basic factors controlling the migration of radionuclides in artificial or natural barriers surrounding radioactive waste depositories. It is necessary to acquire sorption data and to develop reliable sorption models, able to be used in migration calculation and long term safety predictions. One of the major problems of these calculations is the uncertainty on the validity of sorption models, which may result in hazardous predictions especially if data have to be extrapolated to several millions of years. It has been decided to develop an interlaboratory study in order to examine the validity of models and to increase the knowledge of the real sorption mechanisms and sorption sites through a multidisciplinary approach, using a panel of microscopic and spectroscopic methods. Fourteen laboratories participate to this common work, in which sorption studies of several elements modeling long-lived radionuclides were conducted on solids such as oxy-hydroxydes, silicates and phosphates. One of the approaches of this common study, is the use of a "reference" sorbent (goethite) which was thoroughly characterized in a pool of laboratories. After four years, it is possible to evaluate the results, which lead to a marked progress in the knowledge of sorption processes. Among results, it was possible to point out cases where this approach allowed to discriminate among several possible models all able to fit sorption data. It was also possible to detect and study several effects not considered in usual sorption models, such as non-equilibrium, formation of new solid phases, partial or total irreversibility, diffusion into the solid. Several examples of results will be given, together with the future developments of this study.

## COMPONENT ADDITIVITY AND GENERALIZED COMPOSITE APPROACHES TO SURFACE COMPLEXATION MODELING OF COMPLEX MINERAL ASSEMBLAGES

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Two types of surface complexation modeling approaches are illustrated for describing radionuclide adsorption in aqueous environments: 1) the *component additivity approach*, and 2) the *generalized composite approach*. Each approach is applied to simulate U(VI) adsorption by a subsurface weathered schist sample collected near the uranium ore body near the Koongarra ore deposit in Australia. U(VI) adsorption by the weathered material was studied in laboratory batch experiments with a range of pH and U(VI) concentrations selected to encompass conditions observed in the shallow aquifer at the site. In the generalized composite approach, one- and two-site surface complexation model parameters were calibrated with the experimental data over the pH range 5.5 – 8.5 with the computer program FITEQL. The pH dependence of U(VI) adsorption was simulated without explicit representation of electrostatic energy terms. Surface acidity constants and ion pair formation by major electrolyte ions were also not required in the model, thereby minimizing the number of fitted parameters. Predictions of U(VI) adsorption with the component additivity modeling approach did not simulate the experimental data adequately without manipulation of surface area or site density parameter values. To apply the component additivity approach to environmental sorbents, further research is needed to better characterize the composition of sediment surface coatings. The generalized composite modeling approach requires less information and can be viewed as more practical for application within performance assessment modeling. With only a few adjustable parameters determined once by calibration, this modeling approach could simulate U(VI) adsorption over a range of chemical conditions that would cause two orders of magnitude variation in the distribution coefficient ( $K_d$ ) for U(VI) within the aquifer.

## THE EFFECT OF BICARBONATE ON THE RATE OF DISSOLUTION OF URANINITES FROM OKLO (GABON) UNDER OXIDIZING CONDITIONS AT 25°C

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Uraninites from Oklo (Gabon) have the unique characteristic of being the remnants of fossil natural fission reactors. This makes the study of such samples interesting not only from the geological point of view but also for the performance assessment of a hypothetical future repository of high level nuclear wastes, because they are the closest known example of a geologically old spent nuclear fuel.

In the present work the dissolution rates of four uraninite samples from Oklo (Gabon) have been determined as a function of bicarbonate concentration and at 25°C. The solid phases selected correspond to reactor zones 9, 10 and 13, representative of uraninites with different degrees of alteration. The fourth sample comes from the surroundings of reactor zone 9, what is known as *Argile de Pile*. Previously to the experiments, the samples have been characterized by means of X-Ray Powder Diffraction (XPD) and X-Ray Photoelectron Spectroscopy (XPS) techniques. BET surface area determinations have been carried out as well for all the uraninites studied.

The experiments have been performed under oxidizing conditions in contact with air. The dissolution rate determinations have been performed using a tank stirred continuous flow-through reactor to minimize the possibility of secondary solid phase formation. The dissolution of some trace elements as Nd, Mo, Ba, Yb and Sb, has also been followed to check how their release rates relate to the uraninite matrix dissolution. The dissolution rate of the minor elements has been normalized to their initial content in the solid sample, determined by the dissolution and subsequent analysis (by ICP-MS) of a known weight of uraninite.

## DOMINANT URANIUM UPTAKING MINERALS IN FRACTURE-FILLINGS AT PALMOTTU FINLAND

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The nucleation of a mineral crystal and its growth in groundwater carrying fractures provide an impressive example of chemical selectivity. Using a microscope connected to a Laser Enhanced Raman Spectrometer, we selected 100  $\mu\text{m}$ -size single mineral crystals, calcite, pyrite and biotite from reducing zone fracture-fillings (R348, 74.8m) and hematite from oxidizing zone fracture fillings (R348, 27.8m) above the Palmottu uranium deposit (Finland). Thin-section SEM and porosity measurements showed that the fracture-fillings at Palmottu are very porous ( $\epsilon > 10\%$ ). The stable isotope analysis of the fracture-fillings suggests that they were formed at low temperature. Assuming that the fracture-fillings reached equilibrium with the groundwater, *in situ* uranium distribution ratio  $K_d$  was estimated from the uranium concentration in mineral crystals and in the groundwater. Calcite and hematite, with uranium  $K_d$  in a range of  $10^4$ - $10^5$  ( $\text{cm}^3/\text{g}$ ), were found to be the two dominant uranium up-taking minerals in reducing and oxidizing fractures, respectively. The mechanism of uranium up-take was studied in laboratory experiments. 4 g calcite (a) was precipitated in a 2.38 ppm U(VI) solution (vol.  $1000 \text{ cm}^3$ ) and in another vessel the same amount of calcite (b) was precipitated in U free solution. After 2-day aging, the same concentration of U(VI) was added to vessel (b). During further aging, part of U(VI) in calcite (a) gradually returned to the solution. After one-month aging, calcite(a) (BET  $1.23 \text{ m}^2/\text{g}$ ) contained 164 ppm U(VI). This is six times more than that in calcite (b)(BET  $1.46 \text{ m}^2/\text{g}$ ). A  $^{233}\text{U}/^{238}\text{U}$  isotope exchange experiment with the U(VI)-bearing calcites described above was carried out. The result of 10-day isotope exchange showed that, the fraction of unexchanged U(VI) in calcite (a) was 90 %, much higher than in the calcite (b)(40%). Similar observation was made for the hematite case. In the assessment of long-term radionuclide migration, nucleation of mineral crystal, its growth and dissolution in the groundwater carrying fractures should not be ignored, and therefore, coprecipitation should be considered as an important mechanism beside adsorption.

## SORPTION/DESORPTION PROCESSES OF URANIUM AND REE IN ROCK SAMPLES OF THE BANGOMBÉ NATURAL REACTOR ZONE, GABON

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The Bangombé natural reactor (Oklo, Gabon) is located at a very shallow depth and has been submitted to intense weathering. In this work, mineralogical, chemical analyses and sequential extraction experiments were undertaken in order to provide new insights on the relative efficiency of the different minerals and sorption processes for the control of U and REE retention in the weathering zone above the reactor. An experimental study of U adsorption/desorption processes was carried out using an U isotope exchange technique in order to estimate the proportion of uranium adsorbed on mineral surfaces. Clayey (illitic) and Fe-oxides rich samples were examined. Concerning the Mn- and Fe-crusts close to the reactor, it is found that the HREE are locally enriched. Extraction treatments evidenced the role of Mn-oxides and phosphate phases for HREE uptake. The fraction of total U in exchangeable position on clays or adsorbed at mineral surfaces is low. U is mainly associated to Fe-rich amorphous phosphate phases occurring as coatings on iron oxides, or to autunite-like minerals. Concerning the clayey illitic samples in the upper weathering zone, a strong depletion of HREE compared to LREE is observed. A large proportion of U is adsorbed at mineral surfaces and is accessible to solutions.

The <sup>233</sup>U sorption data obtained on an illitic Bangombé sample were modeled using a surface complexation modeling approach. It was assumed in modeling that uranyl binding occurs at aluminol edge sites of illite. The binding constant required for modeling was firstly determined for the non-electrostatic model (NEM) from experimental work on the U(VI)/hydrargilite ( $\alpha$ -Al(OH)<sub>3</sub>) system. The fractional uptake of U(VI) on hydrargilite was measured as a function of pH under CO<sub>2</sub>-free conditions or in carbonated solutions. Modeling provided a reasonable description of the pH-dependent sorption of U(VI) on both a well-characterized hydrargilite and on the clayey sample of Bangombé.

## CAN WE USE IN-SITU $K_d$ -VALUES AS A VALIDATION TOOL FOR LABORATORY SORPTION DATA ?

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The distribution of the naturally occurring rare earth elements (REE), Th, Zr, and U between sediment and groundwater is determined. These trace elements are taken as chemical homologues of tri-, tetra- and hexavalent actinides. Samples are originated from aquifers overlying the German repository for low level nuclear waste at Morsleben and the Gorleben repository site anticipated for high level waste. In both cases the natural distribution coefficients, the so-called in-situ  $K_d$ -values, are higher by some orders of magnitude than the respective  $K_d$ -values obtained for tracers in the laboratory. The difference is ascribed to the fact that in the case of the in-situ  $K_d$ -value not only surface-sorbed metal species are considered but also the fraction bound in the bulk sediment. In the case of the Morsleben samples, which are poor in colloidal components, the surface-bound metal species are separated by leaching the sediment with 1 mol/L acetic acid. The in-situ  $K_d$ -values normalized to the fraction of acetic acid leachable metal species are found to be comparable with the respective laboratory  $K_d$ -values for Am, Th, Pu and U. For sediments containing calcite, considerable amounts of REE and to a less extent Th and U are dissolved by acetic acid together with the calcite. Calcite represents a host mineral phase especially for the trivalent REE. In general, the in-situ  $K_d$ -values are consistent with laboratory sorption data. Some deviations can be explained by the coprecipitation process occurring during the geological time scale in the natural system.

For the humic acid rich Gorleben system the in-situ  $K_d$ -values are more or less similar for different elements, indicating that sediment bound and dissolved humic acid is primarily responsible for the distribution of trace elements. The sediment-bound humic acid, therefore, is extracted by 0.1 mol/L NaOH and analyzed for the trace elements. The in-situ  $K_d$ -values normalized to the metal ion fraction extractable by the NaOH solution again are comparable with the respective laboratory  $K_d$ -values.

The use of in-situ  $K_d$ -values to validate laboratory sorption data for actinides concerned is discussed.

## SPECTROSCOPIC PROPERTIES OF URANIUM(VI) MINERALS STUDIED BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY (TRLFS)

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About 160 uranium minerals are known. Although many of these minerals show fluorescence properties, detailed fluorescence spectra are not published in the literature. We studied the fluorescence properties of 120 uranium minerals in order to provide a data base of potential solids that may form in the flooding process of defunct uranium mines<sup>\*)</sup>.

In the series of alkaline earth uranyl phosphates, we measured the minerals saleeite,  $\text{Mg}(\text{UO}_2\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ , autunite,  $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ , and uranocircite,  $\text{Ba}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . We studied the influence of the changing alkaline earth ion on the fluorescence of the uranyl phosphate group. We found differences of up to 2.2 nm in the fluorescence emission between these minerals. From the band spacing of the spectral data, we calculated the wave numbers of the vibration in the ground state. The ground state vibrational frequencies for saleeite, autunite and uranocircite are at  $828\text{ cm}^{-1}$ ,  $825\text{ cm}^{-1}$  and  $820\text{ cm}^{-1}$ , respectively.

We also studied the fluorescence properties of the uranyl arsenate minerals troegerite,  $\text{UO}_2\text{HAsO}_4 \cdot 4\text{H}_2\text{O}$ , novacekite,  $\text{Mg}(\text{UO}_2\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$ , abernathyite,  $\text{KUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ . Using the data of troegerite, we could assign the fluorescence properties of the solution complex  $\text{UO}_2\text{HAsO}_4(\text{aq})$ .

Our study of copper-containing uranium minerals showed that for voglite,  $\text{Ca}_2\text{Cu}[\text{UO}_2(\text{CO}_3)_4] \cdot 6\text{H}_2\text{O}$ , the copper changes the well-established fluorescence emissions of liebigite  $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 10\text{H}_2\text{O}$ , to a broad maximum. Torbernite,  $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , shows fluorescence bands like the alkaline earth uranyl phosphates, but zeunerite,  $\text{Cu}(\text{UO}_2\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is a non fluorescent mineral.

These fluorescence data can be used as fingerprint for the determination of secondary minerals grown on rock material, and for aiding with the deconvolution of spectra of solution species.

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## CONCENTRATIONS AND ACTIVITY RATIOS OF URANIUM ISOTOPES IN THE GROUND WATER

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Concentrations and activity ratios of uranium isotopes were determined by the chemical separation and alpha spectrometry for underground water samples in Korea. The concentrations of uranium isotopes in the ground water were variable, depending on the sampling time and sampling site. In the rainy season the concentrations of uranium isotopes were lower than in any other seasons. The concentrations of uranium isotopes at the hot springs area were higher than those at any other regions. The increase of the concentrations of uranium isotopes at the hot springs area could be attributed to physicochemical reaction between the ground water and the mother rocks. Owing to a violent material exchange between the subterranean hot waters and the rock stratum, the erosion of the rocks has been greatly increased. Hence, uranium isotopes of underground in hot springs area easily dissolved in the ground water and increased the concentration of uranium isotopes. The activity ratio of  $^{234}\text{U}/^{238}\text{U}$  in the ground water was not unit, ranging between 1.04 to 3.58, depending on the reactive character of water and rock and residence time of water. The activity ratios of  $^{234}\text{U}/^{238}\text{U}$  in the hot springs area were lower than those at any other regions, although the concentrations of uranium isotopes were higher than those of other regions. This indicates that in hot springs waters much of the  $^{238}\text{U}$  located in the lattice is dissolved and the superiority of being leached owing to daughter's recoil is reduced. Hence, the activity ratio of  $^{234}\text{U}/^{238}\text{U}$  is close to that in the rock.

## SOME UNUSUAL U-SERIES DISEQUILIBRIA IN BEDROCK AS INDICATORS OF CONTINUOUS U EXCHANGE

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Traditionally U-series disequilibria (USD) have been utilised in dating, assuming Th immobile and closed system behaviour after initial U accumulation. Here we present observations from dynamic systems that can not be explained by the closed system model. Furthermore, some observations require a multistage description of the U accumulation/loss processes. Unusually large deviations from radioactive equilibrium in  $^{238}\text{U}$ -decay series were observed in granitic rocks from two different sites in southern Finland. The lowest U-234/U-238 activity ratios (0.29 - 0.39) were measured in a smectite, coating the surface of an open fracture within granite pegmatite at a depth of 70 m. Low U-234/U-238 values indicate preferential loss of U-234 isotope from the fracture solids exposed to groundwater, and that this process has been active for a considerable time. In the whole rock samples from the other site, low U-234/U-238 values (between 0.6 and 0.7) were also measured. In the same rock samples, very high Th-230/U-234 activity ratios (around 4) were observed as well. Qualitatively, high Th-230/U-234 activity ratio indicates geologically rapid U leaching. As possible explanation to the USD observations we test three different open system models. Constant release rate (mimicking  $\alpha$ -recoil), and constant release fraction (mimicking chemical release) models are classical open system models. A new model that combines the two release processes was developed because of the unusual observations, and the fact that  $\alpha$ -recoil and chemical release complement each other. By sensitivity analysis we could bracket release rates, and e.g. the time for start of release. The real difficulty in modelling, however, is to obtain independent values for the release rates of U isotopes.

## THE BOOM CLAY FORMATION AS A NATURAL ANALOGUE FOR THE GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTE: A CHEMICAL ANALOGUE STUDY.

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The Boom Clay is studied as potential host rock for the deep disposal of radioactive waste. To fill the lack between informations on the radionuclides behaviour from the short term laboratory or *in situ* experiments and the need for performance assessment, SCK•CEN studies the Boom Clay as natural analogue since 1996. In general, the Boom Clay (Rupelian, 32 My) can be considered as a homogeneous clay deposit. However, variations in grain size, organic matter and carbonate content, giving the Boom Clay its characteristic layered structure, point to a heterogeneous composition on a smaller scale. The behaviour of REE, U, Th and their natural isotopes is studied in both solid fraction and interstitial pore water as chemical analogues to critical radionuclides. This presentation will focus on the chemical and mineralogical aspects of the study.

Samples were collected from three drilling cores in the Boom Clay. Pore water was extracted from core samples by the technique of squeezing. XRD mineralogical analyses and XRF, ICP-MS, INAA chemical analyses were performed on the solid samples. ICP-AES, IC and ICP-MS chemical analyses were performed on pore water samples.

The uranium content varies from 3 to 7 ppm in the solid fraction and from 1 to 16 ppb in the pore water. The thorium content in the solid samples varies from 8 to 15 ppm. LREEs are slightly enriched relative to the NASC composition, conversely HREEs are slightly impoverished. Multivariate statistical analyses allow to divide the Boom Clay in three groups according to their influence on the chemical analogue behaviour:

- quartz, muscovite and feldspath have a trace element dilution effect;
- clay minerals, such as chlorite, illite, smectite and intersratified illite-smectite, sorb thorium, caesium and LREEs;
- carbonates, pyrite and organic matter concentrate HREEs and redox sensitive elements like U, Cu and Ni.

The current distribution of the chemical analogues (U, Th and REE) is completely explained by their behaviour during deposition and early diagenetic processes. No more recent geochemical process seems to have influenced their distribution.

The ratio between uranium content in solid and liquid fraction (around 1000) allows to give an upper limit on Kd values obtained from laboratory experiment and used for performance assessment studies.

Future work concerns both the improvement of the squeezing technique and the study of uranium and thorium distribution in the solid fraction by a.o. sequential leaching in order to approach more precisely the Kd values.

## ACTINIDE MIGRATION CASE STUDY IN THE GORLEBEN AQUIFER SYSTEM

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Humic colloids are recognized to have a great potential for the enhancement of actinide migration in groundwater. Over many years research has been conducted to quantify relevant processes. These investigations include the actinide humate interaction, stability and mobility of humic colloids in real aquifer systems and chemical characterization of actinide homologues in real groundwater. In order to apply the present state of knowledge, an actinide migration case study is conducted for the Gorleben aquifer system.

For a part of the aquifer system above the center of the Gorleben salt dome, namely inside the so-called "ring-wall", important hydrological and geochemical conditions are identified. Distribution of groundwater main components and isotopic composition ( $H^2$ ,  $H^3$ ,  $^{18}O$ ,  $^{14}C$ ) are used to describe the hydrological situation. The geochemical situation in this area of the aquifer system is described by the distribution of different groundwater constituents, pH and Eh, and especially the humic colloid concentration. Furthermore, occurrence of some important geochemical reactions such as the in-situ generation of humic colloids and generation of dissolved inorganic carbon are described by the help of (isotope)geochemical data.

Saturated salt solution with dissolved actinides from disposed HAW is assumed to be released from the salt dome at the bottom of the case study area (approximately 250 m depth). Groundwater is strongly intermixed over the entire depth of the case study area and different isotope geochemical methods lead to differing results for the groundwater transport velocity. Based on different results, for the case study a vertical groundwater transport time of 1000 y is used. For the mobility of the actinide ions, emphasis is given to the influence of the humic colloid mediated actinide migration. Key issues are the interaction of actinide ions with mobile humic colloids and their stability and mobility. Analysis of geochemical data show no indication of retention or decomposition of humic colloids. The actinide humic colloid interaction is described by a mixed equilibrium and kinetic approach. A part of the natural actinide homologue elements is shown to be practically irreversibly bound to humic colloids. To what extent actinide ions will show the similar behavior is a critical aspect for the humic colloid mediated actinide migration.

## TRANSPORT BEHAVIOR OF IONIC AND COLLOIDAL FORMS OF Pu WITH SELECTED SOIL MATERIALS

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We have investigated the transport behavior of both ionic and colloidal, aqueous forms of plutonium in selected matrices of environmental interest. A goal of these studies was to provide information for supporting cleanup activities at DOE sites. Such information provides a basis for evaluating/predicting migration behavior of plutonium in multiple circumstances encountered in the environment. Both ionic forms of plutonium together with real- and pseudo-colloids were considered in this work. The ionic materials and colloids were studied using both batch-type and flow-through experimental techniques.

The solid matrices chosen for these studies were sand, alumina, charcoal, kaolin and bentonite; some of these materials are of interest as general geologic barriers for migration of actinides in the environment. The plutonium colloids were characterized regarding their morphology, size and physical properties to better understand their behavior in the studies. Their stability under different conditions was also explored to establish either transport or removal processes based upon the particular aqueous conditions and/or the physical properties of the colloids. In this regard, the apparent pH, colloid diameter and various sorption behaviors were considered as opposed to some chemical phenomena.

The kaolin and bentonite matrices were found to be effective in removal of both ionic and colloidal species from the aqueous plutonium media employed. Colloid instability was a primary concern. Reactions at the matrix surface involving anion exchange of the colloid's stabilizing counter-ion and/or generating pH conditions unfavorable to the colloid's stability were observed frequently. Sorption at mineral surfaces appeared to be a major mechanism in controlling removal of the plutonium from solution by the solids. With some ionic forms of plutonium, alteration of its oxidation state and/or the plutonium species were complicating events in the study.

The presentation will address important facets of the above studies with both ionic and colloidal forms of plutonium and will suggest simple models to explain the processes observed in the work. The chemical and physical nature of the colloids controlling attachment or de-attachment with the matrices, and the colloid dynamics in terms of their molecular characteristics will also be discussed.

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## KINETIC ASPECTS OF THE TRIVALENT METAL ION BINDING ONTO HUMIC COLLOIDS

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Groundwater colloids play a carrier role for the migration of radionuclides with charge  $z \geq 2+$  in natural aquifer systems. However, the colloid-borne radionuclide migration depends on the kinetic stability of radionuclide binding onto aquatic colloids. This paper deals with the kinetics of the metal ion desorption from humic colloids in order to elucidate how stable a given metal ion is bound on aquatic colloids.

In the present experiments the behaviour of rare earth elements (REE), Th, Zr, Sr and Ba is investigated. These elements are chosen as chemical homologues for radionuclides of different oxidation states present in nuclear waste. Tri- and tetravalent elements occur in the two investigated Gorleben groundwaters (Gohy 532 and 2227) as bound to colloids, which are primarily composed of humic/fulvic acid. Their desorption kinetics from colloids are examined in the unaltered groundwater (pH  $\approx$  8) under anaerobic conditions (Ar/1% CO<sub>2</sub>) by addition of a chelating cation exchanger resin (Chelex 100). The time dependency of the Eu(III) desorption is described by a pseudo-first-order kinetics with two different components (time constants:  $\tau_1 \approx 10^2$  h,  $\tau_2 \approx 10^3$  h). The process is compared with the Eu(III) desorption from its humate complex prepared with purified Aldrich humic acid and brought in contact with the Chelex resin in a buffered aqueous solution ([HA]=30 mg/L; [Eu(III)]= $1 \cdot 10^{-6}$  mol/L; pH=8.0; I=0.1 mol/L NaClO<sub>4</sub>). The Eu(III) dissociation is found to follow the same pseudo-first-order kinetics as found in the groundwater but time constants are about a factor 10 lower. This suggests that under natural aquatic conditions the Eu(III) binding in colloids is chemically different from the simple humate complexation as observed in the comparative experiment. The size characterization indicates that natural trace elements are found predominantly in the groundwater colloids of larger size. The slower kinetics and the larger size suggest that the Eu(III) binding in natural humic colloids might be associated to polynucleation with other co-present trace metal ions.

## THE NAGRA/PSI THERMOCHEMICAL DATA BASE: NEW DEVELOPMENTS

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PSI's Waste Management Laboratory has been developing thermodynamic databases for more than 15 years. A milestone was reached with the issue of the internationally recognised Nagra/PSI Thermochemical Data Base in 1992.

A major update of this database is in progress. It retains the division into core and supplemental data groups and aims at (1) Establishing thermodynamically consistent patterns among groups of chemically similar elements with respect to relevant ligands, (2) Improving the quality of individual equilibrium data by reviewing experimental results and by adopting internationally reviewed data, (3) Identifying gaps in the matrix of chemically consistent data, (4) Providing comprehensive and detailed reasoning for the proposed improvements and (5) Discharging non-essential ballast such as irrelevant high temperature solids, highly soluble salts, unstable compounds, etc.

However, there are always important problems with any practical, specific database application. Examples include the possible impact of missing or uncertain data (or the selection of inappropriate solubility limiting solids). Unfortunately, even a database of high quality is not sufficient to avoid such problems. Additional efforts based on sound chemical knowledge and on good system understanding are needed to perform adequate and sensible modelling (e.g. problem oriented estimates of missing data).

Our present studies are in several areas: (A) Carbonates form solids and complexes with almost all groundwater constituents and radionuclides. A status report on carbonate complexation and solubility of radionuclides and major groundwater constituents will appraise the quality of the thermodynamic data. It will further define the measures to be taken to fill identified gaps in the data. (B) Sulphides are important in reducing environments. Whereas data of questionable quality are found for many sulphide solids, aqueous sulphide complexation data are largely missing in thermodynamic databases. A comprehensive status report on sulphide complexation and solubility is in preparation. (C) Hydroxides and carbonates are the most important ligands for all redox states of the actinides. We aim at a chemically consistent set of actinide equilibrium and solubility data with an extension to chemical analogues like Zr and the lanthanides. This work complements NEA's detailed review series with respect to practical applicability. (D) Since appropriate ion interaction data are scarce, geochemical modelling of trace elements in highly saline waters poses serious problems. We aim at developing an empirical approach based on the SIT method which will provide a sufficiently good description of nuclide speciation in saline groundwaters.

## THE AQUEOUS GEOCHEMISTRY OF NEPTUNIUM: A MODEL FOR CONTROL OF SOLUBLE CONCENTRATIONS BY SOLID PHASE SOLUBILITY AND SYSTEM REDOX POTENTIAL

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Potential release scenarios for high-level nuclear waste repositories include alteration of spent fuel and migration of actinides in oxidizing groundwater. The redox state of the groundwater influences the geochemical behavior of redox-sensitive radionuclides such as neptunium, which occurs in the +IV and/or +V oxidation state in most natural waters. We evaluate how solids and redox potential interact and influence neptunium solubility and speciation in a natural aqueous system. The geochemical codes EQ3/6 and Geochemist's Workbench are used to model these interactions, and the model is tested with spectroscopic and redox experiments. Databases resident in these codes are updated with experimental results published during the last fifteen years to correct inconsistencies in neptunium thermodynamic data. The most significant database changes are: (1) crystalline  $\text{Np}_2\text{O}_5$  is now more stable than its amorphous hydration product,  $\text{NpO}_2\text{OH}$ , and is a solubility-limiting phase, (2)  $\text{NpO}_2(\text{OH})_2^-$  is now a valid species, (3) the stability of  $\text{NpO}_2\text{OH}(\text{aq})$  is corrected, (4)  $\text{Np}(\text{OH})_5^-$  is disregarded, and (5) mixed Np(V) hydroxo carbonato species are included. These changes significantly decrease the solubility of solid  $\text{Np}_2\text{O}_5$  above pH 10. This relationship is important for effective nuclear waste package design, such as including cement as an engineered barrier, and for evaluating releases of highly alkaline wastes from nuclear waste storage facilities.

At the low electrolyte concentrations of many natural aquifers, Np(IV, V) oxides and oxyhydroxides control neptunium solubility while  $\text{NpO}_2^+$ , Np(V) carbonato complexes, and  $\text{Np}(\text{OH})_4(\text{aq})$  predominate in solution. Np(IV) solids and  $\text{Np}_2\text{O}_5$  govern the solubility of neptunium at neutral pH at extreme reducing (below -0.1 V) and oxidizing conditions (above approximately +0.3 V), respectively. Under reducing conditions, Np(IV) solids provide several orders of magnitude lower solubility than Np(V) solids only at pH below 11. At higher pH, neptunium solubility is nearly independent of redox potential and the neptunium oxidation state. At pH 5 to 8 and the redox potential of many groundwater systems (about -0.1 to +0.3 V), the redox potential of the aquifer controls soluble neptunium concentrations. In this redox interval, Np(IV) remains stable in the solid phase while aqueous Np(V) increases exponentially with increasing Eh until limited by  $\text{Np}_2\text{O}_5$  solubility. Thus, evaluation of radionuclide mobility in aqueous systems proximate to nuclear waste repositories must account for soluble radionuclide concentrations controlled by both solid phase solubility and the redox potential of the system.

## CRITICAL EVALUATION OF THERMODYNAMIC PROPERTIES OF ACTINIDE-BEARING PHOSPHATES

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Reliable data on thermodynamic properties of actinide-bearing phosphates are needed urgently to solve the ecological problems: prediction of behavior of actinides upon their entry into the environments or migration of the actinides from the sites of radioactive waste disposals in the form phosphate glass. All available published results of experimental measurements of the thermodynamic properties of actinide-bearing phosphates, including also a new one which obtained recently by Nizny Novgorod University Group, have been collected and analyzed within the framework of the "DIANIK-99-win" database (Expert Version). The results obtained by various methods were compared. Where it was possible, temperature dependencies of thermodynamic properties have been given. Equilibrium solubilities of a number of uranium-bearing phosphates was calculated from available thermochemical data. The discrepancies between the experimental data, obtained by various researches, and the thermodynamic calculations results are analyzed. Necessity of further studies of thermochemical measurements, solubility of actinide-bearing phosphates will be discussed.

## HYDROLYSIS REACTIONS AND SOLUBILITY PRODUCTS OF TETRAVALENT ACTINIDES: THERMODYNAMIC EVALUATION

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Tetravalent actinide ions are known, because of their high electric charge, to have an inordinate tendency toward hydrolysis. They undergo polynucleation or further to colloid formation in aqueous solution. Such underlying problems complicate the thermodynamic evaluation of their hydrolysis constants and solubility products. Therefore a wide scattering appears in the published data. This fact prompts us to revisit the subject and to reevaluate critically the data and experimental results hitherto available in the literature. At first the hydrolysis constants available from less ambiguous experiments, like spectroscopy ( $U^{(IV)}$ ) and solvent extraction ( $Np^{(IV)}$ ,  $Pu^{(IV)}$ ), are correlated with those of actinides of other oxidation states for the  $z/d$  function ( $z$  = charge of the actinide ion,  $d$  = distance An-OH). From this systematic functional correlation the unknown mononuclear hydrolysis constants of tetravalent actinide ions are estimated and used together with known constants to describe the solubility of  $AnO_2 \cdot xH_2O(s)$  or  $An(OH)_4(am)$  as a function of pH. Correlating the experimental solubility data available in the literature with the evaluated hydrolysis constants, the following solubility products of hydrous oxide or hydroxide solid phases are obtained:  $\log K_{sp}^{\circ} = -58.7 \pm 1.1$  for  $Pu^{(IV)}$  -  $56.4 \pm 0.5$  for  $Np^{(IV)}$  -  $55.0 \pm 1.5$  for  $U^{(IV)}$  and  $-52.3 \pm 0.9$  for  $Th^{(IV)}$ . The SIT is used for the calculation of activity coefficients with the interaction parameters given in the NEA-TDB. The semi-empirical method applied in the present work provides the possibility of evaluating unknown thermodynamic constants of actinide ions.

## ANALYSES CONCERNING THE ESTIMATION OF THE RELEASE BEHAVIOUR OF HEAPS OF THE FORMER MINING ACTIVITIES AND URANIUM ORE MINING

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Three heaps as remains of historical and uranium ore mining in Germany were subjected to a thorough investigation of their geochemical, mineralogical and radioactive inventory and the hydrochemical composition of their leachates. Besides, the elution behaviour of the heap material was simulated in column laboratory experiments. The investigations are aimed to get an idea about the geochemical processes which control the solubility and mobility of radionuclides within the heaps.

Results of the field and laboratory experiments will be used as input data for a subsequent geochemical model calculation as well as for the purpose of model calibration. Geochemical processes essential under outdoor conditions (e.g., oxidation/reduction, equilibrium reactions between solution and solid phase, sorption and buffer effects) are intended to be simulated as realistic as possible. Model calculations will be conducted with the geochemical code PHREEQC (PARKHURST 1995).

When a sufficient reproduction of the geochemical process sequences is reached by the modelling approach, the sensitivity of the input data will be checked by parameter variations. This step shall lead to an identification of parameters having a substantial influence on the radionuclide solubility and mobility, and therefore, which should be analysed conscientiously during future investigation programs.

Finally, the geochemical source term calculation will be applied to other and in less detail analysed heaps. It is planned to develop a simplified model for determining the source term of heaps with a similar type of deposited material. Hence, the overall aims of the project are firstly, a definition of requirements for a site-specific investigation guideline for heaps from former mining activities and uranium ore mining and secondly, a categorisation of heaps according to their magnitude of long-term radionuclide release and the need for further remedial actions.

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## SPECIATION, SOLUBILITY AND DISTRIBUTION COEFFICIENTS OF RADIONUCLIDES IN DEEP ALKALINE GRANITIC GROUNDWATERS CONDITIONS

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The aim of this work is to evaluate the impact of deep alkaline granitic groundwater composition on radionuclides (RN) behaviour (solution chemistry, solubility -s- and sorption coefficients onto minerals -Kd-) in the context of nuclear waste deep storage. It concerns elements present in the nuclear fuel cycle management : actinides, fission and activation products. First, it was necessary to define variation range of deep groundwaters parameters (compositions, temperature) and redox potential values. Using a geochemical model for alkaline granitic waters (thermodynamical equilibria with mineralogical assembling), it is possible to characterise a water (pH, ionic strength...) only by its temperature and chloride concentration. In a second step, we calculate radionuclides speciation (complexes and hydroxides formation in solution), solubilities (total concentration of the RN in a saturated solution) and distribution coefficients (ratio of concentration of sorbed RN on concentration of RN in solution) in the waters using equilibrium constant values (thermodynamical database). For each RN, it was thus possible to develop analytical expression of s (or Kd) as a second degree polynoms of log [Cl<sup>-</sup>] and temperature :  $\log (s \text{ or } Kd) = a_0 + a_1.T + a_2. \log[Cl^-] + a_{11}.T^2 + a_{22}. (\log[Cl^-])^2 + a_{12}.T.(\log[Cl^-])$ . The variation domain of temperature [20, 80°C] and log [Cl<sup>-</sup>] [-3, -1] was chosen to cover most of deep alkaline granitic groundwaters. The conditional values of solubility and distribution coefficient thus obtained are representative of these groundwaters and are ready to be used in radionuclides migration calculations and safety assessment exercises.

## **THERMOHYDROCHEMICAL (T-H-C) COUPLING AND THE IMPLICATIONS TO RADIONUCLIDE TRANSPORT**

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Thermohydrochemical (T-H-C) processes result from the placement of heat-generating radioactive materials in unsaturated, fractured geologic materials. The placement of materials in the proposed Yucca Mountain repository will result in complex environmental conditions. Models are developed linking the thermohydrological effects simulated with TOUGH2 to system chemistry, with an example presented for chloride. Perturbations to near-field chemistry may have a significant impact on the migration of actinides and fission products in geologic materials. Various conceptual models to represent fractures are utilized in TOUGH2 simulations of thermohydrological processes. The simulated moisture redistribution is then coupled to simple chemical models to demonstrate the complexity and potential magnitude of T-H-C processes. The concentration of chloride in solution (returning to the engineered barrier system) is demonstrated, in extreme cases, to exceed 100,000 mg/L. The complexity of the coupling process is demonstrated to induce error when process metrics are being determined. The implication of the presented work is that the system (typically ambient chemical and hydrological conditions) in which radionuclide transport is simulated and measured may be significantly different from the perturbed system.

## MODELING THE DIFFUSION OF AN ALKALINE PLUME IN A CLAYEY PLUG

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The diffusion of an alkaline plume from a concrete container in a clayey plug has been modeled over a period of 100,000 years by using the geochemical code Phreeqc. The objectives of the calculations were the description of : (i) mineral surface modifications, (ii) minerals dissolution, (iii) precipitation of new mineral phases, (iv) migration in the barrier of the radioactive cesium released from the concrete. Input data corresponded to a CPA concrete, a clayey plug composed of MX80 and their related equilibrated interstitial waters. A new database, derived from that of EQ3/6 for aqueous speciation and mineral phases solubility, has been created. Ion exchange equations for this new database are those defined by Fletcher and Sposito (in Clay Minerals 1989, 24 : 375-391) for a bentonite MX80. A first selection of mineral phases able to precipitate in both media was made allowing the restriction of a number of mineral phases considered in the modeling. Simulations were carried out at 25°C and 1 bar. The length of the clayey plug considered was 3 or 6 meters. Transport modeling was based on a pure 1 dimension diffusion model by considering constant concentrations at the boundary conditions. Bromide, used as the conservative tracer, shows an almost stabilized diffusion profile at about 50,000 years for a 6 m barrier. The alkaline plume is directly in relation to a continuous increase of pH with time. At the interface, the more aggressive conditions lead to (i) the dissolution of the barrier minerals and especially of Na-montmorillonite and cristobalite and (ii) the precipitation of new phases typical of these hyperalkaline media like a CSH (tobermorite) and an hydroxyde (brucite). The evolution of most of the solution species depend both of dissolution/precipitation reactions and surface reactions. The montmorillonite, initially in a sodium form, progressively loses its sodium character against potassium via ions exchange reactions which also control the cesium concentration. At 100,000 years and a distance of 3 meters from the interface, the radioactive cesium concentration is of 4 orders of magnitude less than the initial concentration in the concrete. The modeling results are in good agreement with laboratory experiments described in the literature. Nevertheless, some improvements can be envisaged like for instance taking into consideration new mineral phases and sorption of alkaline ions on new mineral phases.

## DEPENDENCE OF MASS TRANSPORT ON SPATIAL VARIABILITY OF THE RETARDATION EFFECT

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The relation between the mass transport rate and the spatial distribution of retardation coefficient,  $R_d$ , has been examined by using two-dimensional (2-D), advection-dispersion model. In the calculated breakthrough curves, this study focused on the peak height and its arrival time. To compare them easily, the dimensionless mean residence time was always set at unity. In the results, as the  $R_d$  values were distributed perpendicular to the flow direction, the peak height and its arrival time strongly depended on the  $R_d$  distribution. This study, for simplicity, considered two kinds of  $R_d$  layers and assumed that the small  $R_d$  and the large were arranged parallel to one another. The smaller the alternation frequency of the layers became, the higher peak and the shorter arrival-time the breakthrough curve showed. In contrast, when the frequency was large enough, the peak-arrival time almost agreed with the homogeneous case. Further, this study confirmed that the variation of the skewness of  $R_d$  had no appreciable influence on the whole mass transport rate. When the 2-D distribution of  $R_d$  was described by, e.g., log-normal distribution, the average mass transport rates showed agreement with those on the other probability density functions defined by the same set of the arithmetic mean and the standard deviation of  $R_d$ . These tendencies mentioned above were confirmed in the range of Peclet number from 10 to  $10^2$  for the dimensionless standard deviation at least up to around 1.

## MODEL CALCULATION OF CONSISTENT DIFFUSION AND DISTRIBUTION COEFFICIENTS IN COMPACTED BENTONITE

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Disposal concepts for high-level radioactive waste in Japan as well as other countries rely on the use of engineered barrier systems based on compacted bentonite. For performance analysis, radionuclide migration/retention in the bentonite barrier is typically quantified through diffusion and distribution coefficients, which can be combined to calculate apparent (overall) diffusivities of radionuclides. It is, therefore, essential that the selection of such key parameters is done in a consistent fashion.

It is in general not possible to predict or explain experimentally obtained apparent diffusivities ( $D_a$ ) through geometric factors (tortuosity, constrictivity, porosity) relevant for compacted bentonite and distribution coefficients ( $K_d$ ) obtained in batch experiments. For cations, the selection of the wrong  $K_d$  value often contributes to this discrepancy. In addition, an additional diffusion pathway for cations ('surface diffusion') and a reduction of the accessible porosity for anions ('ion exclusion') are frequently used to explain the apparently high and low diffusivity of cations and anions, respectively. We showed in a previous paper [1] for the case of Cs how (i) the calculation of  $K_d$  values with the help of a thermodynamic speciation model [2], and (ii) the interpretation of constrictivity as the ratio of the average concentration of an ion in the pore to its concentration in the bulk solution with the help of an electrostatic model [3] can predict  $D_a$  for a range of dry densities.

Here, these models are combined to yield a surface chemical model that treats porewater chemistry, ion exchange, and the influence of charged pore walls on diffusing ions in a consistent fashion. Based on the Stern-Gouy model of the electrical double layer, the distribution of simple cations (Cs, Sr) between ion exchange sites, diffuse layer, and bulk solution is calculated. The siloxane surface of the clay and the Stern plane are treated as constant-charge, variable-potential surfaces.

The contribution of Stern and diffuse layer to the compensation of the permanent surface charge is calibrated for the diffusion of Cs in Kunipia-F bentonite (> 95% Na-montmorillonite), at a dry density of 400 kg/m<sup>3</sup>. The calibrated model is then applied to calculate apparent diffusivities of Cs, Sr, Cl<sup>-</sup>, I<sup>-</sup> and TcO<sub>4</sub><sup>-</sup> in different bentonites as a function of dry density. Further, effective diffusivities for Cs, HTO, and TcO<sub>4</sub><sup>-</sup> are calculated. All calculated values are compared with published, measured data. This comparison shows that the model allows reasonably good prediction and a consistent explanation of (i)  $K_d$  values in batch and compacted systems, and (ii) apparent as well as effective or pore diffusivities for cations, anions, and neutral species in compacted bentonite.

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## **KINETIC MODELING OF MICROBIALLY-DRIVEN REDOX CHEMISTRY OF RADIONUCLIDES IN SUBSURFACE ENVIRONMENTS: COUPLING TRANSPORT, MICROBIAL METABOLISM AND GEOCHEMISTRY**

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Understanding of the migration and transformation of multi-valent radionuclides in subsurface environments is important for nuclear waste management and environmental remediation. The mobility of a radionuclide depends on various chemical factors including the oxidation state of the radionuclide, solution pH, the concentrations of both inorganic and organic complexants, and the availability of sorption substrate. The chemical behavior of a radionuclide is subjected to the overall chemical environment created by the chemical processes of major elements such as C, O, N, S, Fe, and Mn. An appropriate approach to model radionuclide migration in a subsurface system must fully take into account the coupling of radionuclides with these major elements. Microbial reactions, acting as a driving force for subsurface redox processes, have a significant impact on the chemical behavior of both major elements and radionuclides. In this communication, we develop a general methodology for modeling the migration and transformation of multi-valent radionuclides in subsurface systems. We developed a one-dimensional reaction-transport model for simulate microbially-driven redox chemical processes of C, O, N, S, Fe, and Mn and the coupling of these processes with radionuclide redox reactions. The model is used to simulate various scenarios of U migration in subsurface environments.

## INTRINSIC SORPTION CONSTANTS OF RADIONUCLIDES AT THE MINERAL/WATER INTERFACE AND INTERSTRATIFIED-CLAY—WATER INTERFACE

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Oxidative dissolution of nuclear waste will result in the formation of oxy-cations, such as  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ , and  $\text{AmO}_2^{2+}$ . The cations will interact with the surfaces of minerals and clays. The sorption on minerals is an important mechanism of radionuclide retardation. According to the surface complexation model, the sorption of an ion  $j$  onto a solid surface  $k$  is represented by the sum of "intrinsic" and coulombic terms, that is

$$\log K_{\text{ads}, j, k} = \log K_{\text{int}, j, k} - (zF/2.303RT)\psi_0$$

In the equation,  $\log K_{\text{ads}, j, k}$  and  $\log K_{\text{int}, j, k}$  are overall adsorption constant and intrinsic sorption constant, respectively.  $\psi_0$  is surface potential of the mineral  $k$ , and is a function of environment. The parameter "z" is charge of the cations. For the divalent cations, z is 2. The intrinsic sorption constant is related to the dielectric property of the solid and aqueous chemistry of the cation (Sverjensky, 1993), and can be expressed as  $\log K_{\text{int}, j, k} = -(\Omega_j/2.303RT)(1/\epsilon) + \log K_{\text{ii}, j}^0$ . In the equation,  $\Omega_j$  is a conventional Born coefficient for the cation  $j$  specifically for sorption (Shock and Helgeson, 1988). The term  $\log K_{\text{ii}, j}^0$  is related to the standard non-solvation energy of the cation  $j$  ( $\Delta G_{\text{n}, j}$ ).

The divalent oxy-cations can be treated as normal divalent cations. Therefore, the intrinsic sorption constants of the cations on the mineral can be calculated. All the equilibrium sorption constants refer to the surface reaction of  $\text{SO}^- + \text{M}^{2+} = (\text{SOM})^+$ , where  $\text{M}^{2+}$  is a divalent cations, and are consistent with only the triple-layer model. The model can also be used for the calculation of the sorption of divalent cations on the surfaces of interstratified clays (smectite—illite series, biotite—vermiculite series, and chlorite—biotite series) based on calculated dielectric constants for the interstratified clays. The physical surface-complexation model may provide insight into the differential sorption on mineral surfaces, because the dielectric constant is a tensor.

## EQUILIBRIA OF COMPLEX FORMATION AND ION EXCHANGE OF METAL IONS WITH SOIL SURFACE SITES

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For quantitative description and prediction of behavior of metal ions, in particular radionuclides, in soil it is necessary to consider relation of equilibrium parameters of ions sorption with distribution coefficient. Methods for quantitative description of complexation equilibria of metal ions, monobasic and polybasic organic molecules of cationic, anionic and amphoteric type with soil surface sites were developed and appropriate isotherms of sorption were deduced. Appropriate equations of adsorption isotherm taking into account acidic dissociation of surface sites, inorganic or organic ions and competing ligands in the solution were derived. These sorption isotherms have the general form:

$$[LM]=[L]_0[M]_{eq}/(FK_d+[M]_{eq}),$$

where F is function which depends on the type of adsorption site, nature of the adsorbed molecules and availability of competition;  $[L]_0$  - concentration of complex-forming adsorption sites in the sorbing particle;  $[M]_{eq}$  - equilibrium concentration of ions in solution;  $[LM]$  - equilibrium concentration of surface complexes;  $K_d$  - dissociation constants of surface complexes (affinity of ions to the surface adsorption sites). From these isotherms distribution coefficient can be derived, which is equal to the ratio between the ion concentration in adsorbed and soluble state:

$$D=[LM]/[M]_{eq}=[L]_0/(FK_d+[M]_{eq}),$$

For determination of the surface sites dissociation constants of soil particle and the kinetic parameters of adsorption data of experiments, received in flow column mode, can be used. Description of breakthrough curve in plug flow reactor is offered. This model can be used for description of metal ions migration in soil. Adsorption rate constants of K and loading rate constants for surface sites k at given concentration of ions in the solution are taken into account:  $\ln(1/1-X)=\ln KL\tau-kt$

where  $X=( [M]_0-[M] )/[M]_0$  - degree of ions adsorption, L - concentration of adsorption sites capable of adsorbing an ions at certain concentration ( $L = LM$  at  $t = 0$ ),  $\tau = m/v$  - residence time, v - flow rate of solution, t - progress time of adsorption process.

Use of this model permits from experimental breakthrough curve to determine adsorption rate constants (extraction of ions from solution), loading of adsorption sites, and capacity of the adsorbent at given equilibrium concentration of ions on input of a column.

## A NON-ELECTROSTATIC SURFACE COMPLEXATION APPROACH TO MODELING RADIONUCLIDE MIGRATION AT THE NEVADA TEST SITE: THE ROLE OF IRON OXIDES AND CARBONATES

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Reliable quantitative prediction of contaminant transport in sub-surface environments is critical to understanding the risks associated with radionuclide migration. Radionuclide mobility is controlled to a large extent by surface complexation (SC) reactions. Reactive transport models that describe radionuclide retardation with SC are more flexible than those that use traditional  $K_d$  values because the effect of ionic strength, pH, and aqueous complexation are taken into account. Radionuclide transport at the Nevada Test Site (NTS) was modeled using the GIMRT reactive transport code (Steeffel and Yabusaki, 1995) which accounts for non-electrostatic (NEM) SC reactions. A set of NEM SC reactions was fit to literature sorption data for use in GIMRT simulations. A single-site NEM adequately fit iron oxide data available in the literature without need for bidentate or ternary surface species. The decrease in U(VI) sorption as a function of carbonate alkalinity was accounted for by aqueous uranyl-carbonate complex formation.

Though the interactions of carbonate minerals with radionuclides are rarely discussed in terms of radionuclide migration, information in the literature suggests that calcite can be an important sorbent. Surface complexation on calcite was calculated from a limited set of sorption data available in the literature. Unlike goethite SC reactions, calcite reactions were modeled as surface exchange reactions. In the NEM case, surface complexation and surface exchange are, in essence, equivalent. Surface complexation on calcite approximately followed the Doerner-Hoskins rule. Variations from the D-H rule were due to the limited SC data and the fundamental limitation of the D-H rule. GIMRT simulations for some areas of NTS suggest that iron oxides and calcite will play a major role in radionuclide retardation. Our NEM SC data set for Sr, Sm, Eu, U, Np, Pu, and Am indicates that migration of Sm, Eu, Np, Pu, and Am can be significantly retarded by sedimentary carbonates. Though iron oxides are usually thought to be the major contributors to radionuclide retardation via SC, carbonate surfaces will be of paramount importance in areas where they are present (e.g. calcareous regions of NTS as well as buried carbonate paleosols at Hanford, calcareous soils of the Marshall Islands, and weathered cementitious materials at waste disposal facilities).

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## TWO-DIMENSIONAL NUCLIDE DECAY CHAIN TRANSPORT AROUND THE DEEP GEOLOGICAL REPOSITORY

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A general two-dimensional numerical solution for nuclide transport through the buffer and the fractured porous rock media is introduced. One of the main advantages of the model over previous models is that it is based on rather physically exact manner by utilizing a control volume formulation method, by which the governing equation can be directly integrated over each control volume. Assuming linear sorption isotherm, nuclide transport of arbitrary decay chain length due to diffusion in the buffer, which is in contact with spent fuel rod canister, and advection and dispersion along thin rigid parallel fractures existing in a saturated porous rock matrix as well as diffusion through the fracture wall into the matrix are considered. To verify the model and to illustrate the usability and exactness in simulating multi-chain decay transport, a three-member decay chain  $^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$  is chosen. The results for some various cases are compared with available analytical solutions. Since the model can employ a variable temporal and spatial discretization sizes, a larger practical problem associated with geological repository system that requires a number of nodes and time steps and then needs a significant computing efforts can be reduced.

## A MICRO-LEVEL MODEL FOR DIFFUSION AND ANION EXCLUSION CONSIDERING THE MODIFIED GOUY-CHAPMAN THEORY

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A theoretical micro-level model, based on a modified form of the Gouy-Chapman (GC) theory of the electrical double layers, for the diffusion of hydrated molecules between locally planar charged solid surfaces is presented. The modifications to the GC theory stem from such unconventional features as ionic hydration, dielectric saturation and finite ion-sizes, which are found to have a significant influence on the physicochemical characteristics of the pore fluid. The model provides a unifying framework for explaining the macroscopically observed anion exclusion and greatly debated surface diffusion for cations in a consistent fashion. With due consideration for the electroviscous effect and specific adsorption, the model is shown to yield apparent diffusivities for  $\text{Na}^+$ ,  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  in compacted mont-morillonite in excellent agreement with literature values.

## COORDINATION CHEMISTRY OF HEXA-VALENT ACTINIDE IONS (U, Np, Pu) UNDER HIGHLY ALKALINE CONDITIONS

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Hexa-valent  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  ions are fairly soluble in 2 - 3.5 M NaOH and LiOH solution due to formation of anionic species,  $\text{AnO}_2(\text{OH})_n^{2-n}$  (An = Np, Pu; n = 4, 5). The  $\text{UO}_2^{2+}$  ion forms similar species in tetramethylammonium hydroxide (TMAOH) solution. Single crystal x-ray diffraction studies revealed discrete molecular  $\text{AnO}_2(\text{OH})_4^{2-}$  (An = U, Np) complexes in the solid state. Strong bonding of equatorial OH- ligands result in a lengthening of the An=O bond and large shifts ( $100 \text{ cm}^{-1}$ ) to lower energy in the Raman-active  $\nu_1$  stretch of these species. EXAFS spectroscopy indicates the presence of  $\text{AnO}_2(\text{OH})_5^{3-}$  (An = U, Np, Pu) in solution.  $^{17}\text{O}$ -NMR and  $^{18}\text{O}$ -Raman spectroscopy on  $\text{UO}_2^{2+}$  ions in 2.5 - 3.5 M OH<sup>-</sup> reveals a chemical exchange between An=O and An-OH units. Luminescence spectroscopy of the U(VI) system at liquid nitrogen temperature indicated the presence of two species in solution. Changes in luminescence with OH<sup>-</sup> concentration are consistent with an equilibrium between  $\text{AnO}_2(\text{OH})_5^{3-}$  and  $\text{AnO}_2(\text{OH})_4^{2-}$  complexes. The penta-valent systems are also under investigation and the most recent results will be discussed.

## THE ROSSENDORF BEAMLINE ROBL – A DEDICATED EXPERIMENTAL STATION FOR XAFS MEASUREMENTS OF ACTINIDES

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X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool for obtaining basic molecular-level information, which is required for a qualitative description of the mechanisms of radionuclide transport in the environment. A unique XAFS station dedicated to the study of actinides has become operational at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, in January 1999. XAFS spectra of solid and liquid samples can be recorded in fluorescence and transmission modes at ambient and low temperatures in the energy range of 5 – 35 keV. A maximum activity of 185 MBq (5 mCi) of the actinides Th-nat, Pa-231, U-nat, Np-237, Pu-239, Pu-242, Am-241, Am-243 as well as Ra-226, Po-208, and Tc-99 can be handled inside a glove box. The presentation will describe the main characteristics of this synchrotron beamline and its radiochemistry end station. The potential of XAFS spectroscopy will be demonstrated by showing results of speciation studies performed at ROBL on U and Np in aquatic systems and complexes with inorganic and organic ligands.

## ELECTROSPRAY-MASS SPECTROMETRY AS A NEW POWERFUL TOOL FOR SPECIATION STUDIES

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In the framework of migration studies, new analytical techniques for speciation studies are of great interest. They have to be sensitive (in order to work below solubility limit and at representative concentration), selective (since natural matrix are very complex) as well as non-intrusive (in order to keep the image of the real solution).

Among them, time-resolved laser-induced fluorescence (TRLIF) as well as extended X-ray absorption fine structure (EXAFS) are by their performances more and more used. However, they have some limitations such as elements that can be studied in the former case or concentration in the latter case. Electrospray ionization - mass spectrometry (ESI-MS) is a new analytical technique that seems promising for speciation studies in the framework of waste disposal. Hence, first developed for biological applications since it allows to reach very high mass by making multicharged species, it is also very suitable for speciation studies due to its soft mode of ionisation. Hence, it is the first time that it is possible to directly couple a liquid at atmospheric pressure to a mass detection working at reduced pressure. However, mechanisms taking place in the different section of the apparatus are very complex and special cares should be taken in terms of results interpretation.

Principle, advantages and limitations of ES-SM will be presented. Results obtained with the use of ESI-MS on different systems of interest including actinides, lanthanides, fission products in interaction with simple organic molecules to very complex structure will be presented and discussed. In certain cases, comparisons will be made with results obtained by TRLIF.

## **X-RAY ABSORPTION FINE STRUCTURE AND TIME DIFFERENTIAL PERTURBED ANGULAR CORRELATION STUDY OF HAFNIUM(IV) SORBED ONTO AMORPHOUS SILICA**

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Sorption of Hf(IV) onto amorphous silica at pH values between 1 and 7 is investigated by Time Differential Perturbed Angular Correlation (TDPAC) and X-Ray Absorption Fine Structure (XAFS) spectroscopy. Hafnium(IV) is studied as a chemical analogue for understanding the speciation of tetravalent actinides. In addition,  $^{181}\text{Hf}$  is a frequently investigated TDPAC probe. Results from TDPAC measurements show that there are two similar surface binding sites for Hf(IV) at low pH values. At a pH above 3, a third, unspecific surface binding site for Hf(IV) begins to dominate. The TDPAC signal of all three sorption sites differs from that for polynuclear hydrolysis product formed in Hf(IV) solutions at  $\text{pH} > 3$  and are, therefore, different from precipitated hydrolysis species. It is, therefore, assumed that sorbed Hf(IV) species are present. XAFS investigations of the sorption samples are performed on the Hf  $L_3$ -edge, in order to elucidate Hf(IV)-species structure for the sorption sites and to detect any presence of polynuclear surface species. Analysis of Extended X-Ray Absorption Fine Structure (EXAFS) spectra show that sorption samples exhibit changing Hf-coordination with sample preparation pH. Changes in the X-ray Absorption Near-Edge Structure (XANES) for the sorbed samples, compared to reference samples, indicate a direct interaction of Hf(IV) cations with the silica substrate. Short Hf-O distances obtained from theoretical fits to EXAFS oscillations also indicate formation of an inner-sphere surface complex.

## INTERPRETATION OF ACTINIDE-DISTRIBUTION DATA OBTAINED FROM NON-DESTRUCTIVE AND DESTRUCTIVE POST-TEST ANALYSES OF AN INTACT-CORE COLUMN OF CULEBRA DOLOMITE

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The U.S. DOE has been developing a nuclear waste disposal facility, the Waste Isolation Pilot Plant (WIPP), located approximately 42 km east of Carlsbad, New Mexico. Performance assessment analyses indicate that human intrusions by inadvertent, intermittent drilling for resources provide the only credible mechanisms for significant releases of radionuclides from the disposal system. For long-term brine releases, migration pathways through the permeable layers of rock above the Salado formation are important. Major emphasis is placed on the Culebra Member of the Rustler Formation because this is the most transmissive geologic layer in the disposal system. In order to help quantify parameters for the calculated releases, radionuclide transport experiments have been carried out using five intact-core columns obtained from the Culebra dolomite member of the Rustler Formation within the WIPP site. This presentation deals primarily with results of analyses for  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  distributions developed during transport experiments in one of these cores. All transport experiments were done using Culebra-simulant brine relevant to the core recovery location (the WIPP air-intake shaft - AIS). Hydraulic characteristics (i.e., apparent porosity and apparent dispersion coefficient) for intact-core columns were obtained via experiments using the conservative tracer  $^{22}\text{Na}$ . Elution experiments carried out over periods of a few days with tracers  $^{232}\text{U}$  and  $^{239}\text{Np}$  indicated that these tracers were weakly retarded as indicated by delayed elution of the species. Elution experiments with tracers  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  were attempted, but no elution of either species was observed in any flow experiment to date, including experiments of many months' duration. In order to quantify retardation of the non-eluted species  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  after a period of brine flow, non-destructive and destructive analyses of one intact-core column were carried out to determine distribution of these actinides in the rock. Analytical results indicate that the majority of the  $^{241}\text{Am}$  remained very near the injection surface of the core (possibly as a precipitate), and that the majority of the  $^{241}\text{Pu}$  was dispersed with a very high apparent retardation value. The  $^{241}\text{Pu}$  distribution is interpreted using a single-porosity advection-dispersion model, and an approximate retardation value is reported.

## THE BEHAVIOUR OF $^{241}\text{Am}$ - $^{14}\text{C}$ -LABELLED ORGANIC MATTER COMPLEXES IN INTACT BOOM CLAY CORES

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In Belgium, the Boom Clay is studied as a candidate host formation for the geological disposal of radioactive waste. Organic matter represents up to 5 % of the total dry weight of the clay, of which a tiny fraction (< 0.1 %) is mobile. Because of its strong complexation properties for trivalent lanthanides and actinides, organic matter is expected to influence the migration behaviour of these radionuclides. The behaviour of Am-organic matter complexes when in contact with intact Boom Clay was studied and conclusions for performance assessment were formulated.

The mobile fraction of organic matter present in clay water is concentrated and labelled with  $^{14}\text{C}$ . This material is then contacted with  $^{241}\text{Am}$  and it is predicted that about 80% of americium will be complexed by organic matter. The mixture is injected into an intact Boom Clay core and americium is monitored in the outlet concentration. After a first peak in the outlet, outlet concentrations were observed varying from  $10^{-12}$  M to  $3 \cdot 10^{-12}$  M after a first peak. After a sufficiently long percolation time, the clay core is sliced and monitored for  $^{241}\text{Am}$  activity. From the experiments it is concluded that the initial Am-organic matter complex dissociates, and that americium is being re-solubilised by non-labelled organic matter. It also became clear that americium in the clay core is not distributing between mobile and immobile organic matter according to equilibrium constants. As such, a quasi-equilibrium approach for modelling the americium transport in clay cannot be applied.

This observation and the concentration in the percolate form the basis for performance assessment (PA) conclusions. To be conservative, it is stated that americium could migrate as unretarded species and an operational solubility range for americium in the Boom Clay, varying from  $10^{-14}$  to  $10^{-11}$  M, is proposed. Depending on the results of PA calculations, it will be decided if more studies are necessary.

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## THE MIGRATION BEHAVIOR OF NEPTUNIUM(V) IN SANDY SOIL AND GRANITE MEDIA

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Migration behavior of neptunium(V) in sandy soil and granite media was studied in the presence of humic substances using a column method. The sandy soil with mean grain size of 0.151mm was sampled at the Chalk River Laboratories of AECL. The granite was sampled at the Underground Research Laboratory of AECL and was crushed to a mean grain size of 0.121mm. Two kinds of naturally occurring fulvics were isolated from groundwater collected at the Chalk River Laboratories of AECL(hereafter, CRL-fulvics) and at the Underground Research Laboratory of AECL(hereafter, URL-fulvics). The commercial humics from Aldrich Co.(hereafter, Aldrich-humics) was also used to compare the influence of humics from different origin on the migration behavior of neptunium(V). The dominant molecular size of these humic substances was under 5,000 daltons for the fulvics, and in the range from 30,000 to 100,000 daltons for Aldrich-humics. An enhanced elution of neptunium(V) from the sandy soil column under coexistence of CRL-fulvics at 20 mg/L was observed in comparison with the studies in the absence of humic substances. On the other hand, neptunium(V) under coexistence of Aldrich-humics was retarded. The difference in the effects of the humic substances on the migration behavior of neptunium(V) may be caused by the difference in the molecular size distribution of the humic substances. That is, the CRL-fulvics, being smaller in size, has lower sorption ability on the sandy soil than the Aldrich-humics, and thereby Np-fulvics complexes may be able to easily migrate through the sandy soil column. In the case of granite column experiments, again an enhanced elution of neptunium(V) under the coexistence of URL-fulvics was found and this observation was similar to that found with the CRL-fulvics. From these observations, it is likely that the migration behavior of neptunium(V) is influenced by the presence of humic substances.

## ROCK MATRIX DIFFUSIVITY DETERMINATIONS BY *IN-SITU* ELECTRICAL CONDUCTIVITY MEASUREMENTS.

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A fast method to determine rock matrix diffusion properties directly in the bedrock would be valuable in the investigation of a possible site for disposal of nuclear waste. An "effective diffusivity borehole log" would provide important information on the variability of this entity over the area studied. As opposed to traditional matrix diffusion laboratory experiments, *electrical conductivity measurements* are fast, inexpensive and also easy to carry out *in-situ*. The relation between electrical conductivity and the diffusion coefficient in liquid phase is well known and also the rock porosity can be related to the measured conductivity (e.g. Archie's relation).

In this study electrical resistivity data from borehole logging as well as from measurements on the actual core is evaluated with the purpose of extracting matrix diffusivity data. The influence of migration of ions in the electrical double layer at the pore walls has earlier been studied in laboratory experiments. This transport process can be of great importance in low ionic strength pore water, for ions that sorb mainly by coulombic attraction to the negatively charged pore surfaces. The influence of this *surface conductivity* has to be taken into account in evaluating the *in-situ* data to accurately determine the diffusivity. Since the influence is large for low ionic strength pore water, good knowledge on the ground water composition is of importance.

The *in-situ* data compare fairly well to those measured in the rock core. To obtain diffusion coefficients from conductivity data, the influence of surface conductivity was considered. Surface conductivity was found to contribute to the ionic transport up to about 100 times over that of only pore water conductivity.

## **COLLOID FACILITATED ACTINIDE MIGRATION: NEW EXPERIMENTAL APPROACHES TO ITS APPRAISAL**

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The role of aquatic colloids on the actinide migration has been attracted much attention in the last two decades, nonetheless a controversial discussion is persistent on whether or not the subject is intrinsically significant for the long-term performance assessment of a given nuclear repository. A variety of laboratory experiments have often corroborated the colloid-borne actinide migration but the main question still remains on what extent they are applicable to natural systems of wide space and long time scale. This contention can be clarified by sound knowledge on the provenance of omnipresent aquatic colloids in different geochemical surroundings, their size and population, the chemical interaction with actinide ions, the long-term stability of actinide-bound colloids and their migration behaviour. The appraisal of all these calls for proper experimental approaches that lead to sound bases for straightforward conclusions.

The present paper deals with an overview on noble experimental approaches that are being developed and applied to the investigation of the colloid-borne actinide migration in natural aquifer systems. Quantification of aquatic colloids, the major part of which is known to be less than 50 nm in diameter, is recently attended by laser-induced breakdown detection (LIBD) that is many orders of magnitude more sensitive than conventional light scattering methods for this particle size range. A combination of this method with flow-field flow fractionation (FFFF) can accomplish the colloid size fractionation and quantification. Chemical composition of aquatic colloids is characterized by ICP-MS or neutron activation analysis (NAA). The nanoscopic chemical interaction of actinide ions, e.g. tri-valent oxidation state, onto aquatic colloids is speciated by time-resolved laser fluorescence spectroscopy (TRLFS). Together with the information from sorption isotherms the identified surface species are implemented into a surface complexation model for inorganic colloids and into a complexation model for humic colloids. Kinetic effects on the generation of colloid-borne actinides (so called pseudo-colloids) and on their migration behaviour are examined by a dynamic column experiment to ascertain how the reversible or irreversible generation of pseudo-colloids takes place. As a supporting experiment, the behaviour of natural homologues of actinide ions, that are present in aquatic colloids, is also investigated.

# MIGRATION '99

Program # B5-02

## IDENTIFICATION OF GROUNDWATER COLLOIDS FROM THE NEVADA TEST SITE

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We are continuing our identification of the colloids associated with the transport of plutonium (Pu) and other radionuclides in groundwaters collected from 2 wells, down-gradient from an underground nuclear test at the Nevada Test Site (NTS). The Pu detected was associated with the colloidal fraction of the groundwater and may have migrated as either Pu oxide colloids (radio-colloids) or sorbed onto naturally-occurring colloids (pseudo-colloids) (Kersting et al., 1999). This work is part of a larger effort to determine the geochemical mechanisms controlling radionuclide transport in groundwater.

The colloidal material was filtered and characterized using XRD, SEM and TEM techniques. Colloidal material in both wells was dominantly composed of zeolites (mordenite, clinoptiolite), clays (illite) and cristobablite, although the concentrations of the minerals varied in the different samples. Side-wall cores and rock cuttings taken of the aquifer units were analyzed and compared to the colloidal minerals identified in the groundwater. The colloid minerals are consistent with those minerals found in the host rock.

The identification of mineral colloids will help guide sorption experiments involving the colloids most likely to sorb radionuclides. These data coupled with size and concentration of the colloids will help determine the maximum amount of Pu that may be transported under these groundwater conditions.

A.B. Kersting, D.W. Efurud, D.L. Finnegan, D.J. Rokop, D.K. Smith, and J.L. Thompson (1999)  
Migration of Plutonium in Groundwater at the Nevada Test Site. *Nature*, 397:56-59.

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## COLLOID-BORNE URANIUM AND OTHER HEAVY METALS IN THE WATER OF A MINING DRAINAGE GALLERY

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The abandoned Freiberg mine in Saxony (Germany) has a depth of 721.5 m. This mine is now flooded; the water-level is at a depth of 227 m. The mine is drained by a drainage gallery named Rothschoenberger Stolln. In the southern shafts of the mine the relatively cold surface waters sink down to the floors. They move through the galleries, warm up and rise in a northern shaft toward the drainage gallery. The rising water is relatively acidic, rich in minerals and poor in oxygen. When this water enters the drainage gallery and mixes with oxic and neutral surface waters there, secondary minerals are precipitated. Thus, the entrance of the shaft water to the drainage gallery forms a large 'geochemical colloid generator'. The drainage gallery flows into a tributary of the River Elbe at a distance of about 20 km. At its mouth, the water of the gallery (pH = 7.2) contains about 1 mg/L of colloidal particles with a size of 75 to 300 nm. These particles were investigated by photon correlation spectroscopy, filtration, centrifugation, scanning electron microscopy, ICP-MS, and AAS. The colloidal particles consist primarily of iron and aluminum oxyhydroxide. However, they also carry trace elements such as Pb, As, Cu, Y, and La. The toxicants Pb and As, for instance, are almost completely bound to the colloids. Other toxicants, as e.g. the cadmium, are primarily ionogenic. Uranium exhibits a special behavior. In the original drainage water the uranium is non-colloidal (really dissolved). This is probably attributable to carbonate complexes of the uranyl(VI) ion that are not adsorbed to colloids. Decreasing the pH to 6 or 5, which destroys the uranyl carbonate complexes, makes the uranium increasingly particulate. About 50 mass % of the uranium are attached to the colloids at pH = 5. Further acidification (pH # 4) leads to an increase of the really dissolved uranium fraction again. At such low pH values also the uncomplexed uranyl ions are not adsorbed onto the iron/aluminum oxyhydroxide particles. Thermodynamic calculations with the geochemical program EQ6 agree, at first glance, only poorly with the experimental results. The discrepancies between the experiment and the calculations, however, can easily be explained. They result from an insufficient consideration of the kinetics in the chemical model. This refers especially to the elements Si, Mn, and Sn. The experiment demonstrates how EQ6 calculations applied to a real geochemical problem can be made more realistic.

## LABORATORY MIGRATION EXPERIMENTS WITH RADIONUCLIDES AND NATURAL COLLOIDS IN A GRANITE FRACTURE

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Natural colloids in groundwater could facilitate radionuclide transport, provided that colloids are mobile, are present in sufficient concentrations and can adsorb radionuclides. This paper describes the results of a laboratory migration study carried out with combinations of radionuclides and natural colloids within a fracture in a large granite block to experimentally determine the impact of colloids on radionuclide transport. The natural colloids used in this study were isolated from granite groundwater from Canada's URL, and consisted of mostly 1 to 10 nm organic colloids, along with lesser amounts of 10 to 450 nm colloids (organics and aluminosilicates) and suspended particles > 450 nm (carbonate, aluminosilicates, organics, and Fe oxide). The measured coefficients for radionuclide sorption onto these colloids were between  $3 \times 10^2$  and  $1 \times 10^3$  mL/g for  $^{85}\text{Sr}$ , and between  $7 \times 10^4$  and  $7 \times 10^5$  mg/L for  $^{241}\text{Am}$ . The  $^{85}\text{Sr}$  and  $^{241}\text{Am}$  sorption on the natural colloids appeared to be reversible. Migration experiments in the granite block were carried out by establishing a flow field between two boreholes (out of a total of nine) intersecting a main horizontal fracture. These experiments showed that dissolved  $^{85}\text{Sr}$  behaved as a moderately sorbing tracer, while dissolved  $^{241}\text{Am}$  was completely adsorbed by the fracture surfaces and showed no evidence of transport. However, when natural colloids were injected together with dissolved  $^{241}\text{Am}$ , a small amount of  $^{241}\text{Am}$  transport was observed, demonstrating the ability of natural colloids to facilitate the transport of radionuclides with low solubility. Natural colloids had only a minor effect on the transport of  $^{85}\text{Sr}$ . In a separate experiment to test the effect of higher colloid concentrations on  $^{85}\text{Sr}$  migration, synthetic colloids were produced from Avonlea bentonite. The introduction of a relatively high concentration of bentonite colloids actually reduced  $^{85}\text{Sr}$  transport because the bentonite colloids were less mobile than the natural colloids and they sorbed  $^{85}\text{Sr}$  more strongly than natural colloids.

## COMPLEX FORMATION OF Np(V) WITH HUMIC ACID AND POLYACRYLIC ACID

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By using  $^{239}\text{Np}$  and/or  $^{237}\text{Np}$ , the complexation of Np(V) with Aldrich humic acid and polyacrylic acid has been studied at the concentration of Np(V) from  $10^{-12}$  to  $10^{-4}$  M by the solvent extraction method using TTA and 1,10-phenanthroline in isoamyl alcohol. By defining the apparent formation constant as  $\beta_{\alpha} = [\text{ML}]/([\text{M}][\text{R}])$ , where [R] denotes the concentration of dissociated functional group, [M] and [ML] denote the concentration of free and bound  $\text{NpO}^{2+}$  (L consists of one or several R), the values of  $\log\beta_{\alpha}$  have been obtained at pH 5-7 in 0.1 and 1.0 M  $\text{NaClO}_4$ . For both humate and polyacrylate,  $\log\beta_{\alpha}$  increased with pH or the degree of dissociation. The increase in the ionic strength from 0.1 to 1.0 M slightly decreased the  $\log\beta_{\alpha}$  of polyacrylate, but it did not give any appreciable difference for those of humate. While the variation of Np(V) concentration had no appreciable influence on the  $\log\beta_{\alpha}$  of polyacrylate (ranging from 1.8 to 2.7 depending on pH and ionic strength), the values of  $\log\beta_{\alpha}$  of humate obtained at  $10^{-12}$  M (ranging from 4.6 to 5.3 depending on pH) were around 2 larger than those at  $10^{-4}$  M (ranging from 3.0 to 3.3 depending on pH), indicating the coexistence of strong and weak binding sites in the humic acid.

## COMPLEXATION OF THE TETRAVALENT NP ION WITH FULVIC ACID

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For the appraisal of the fulvic acid facilitated migration of a given tetravalent actinide ion under reducing conditions of aquifer systems, in this work, the  $\text{Np}^{4+}$  ion is chosen for the spectroscopic study of its fulvate complexation behaviour. Fulvic acid is taken for the reason of its solubility at the lower pH ( $< 2$ ), at which the  $\text{Np}^{4+}$  ion undergoes minimal hydrolysis and no carbonate complexation. Two sets of experiments are carried out by spectroscopic speciation. Firstly, the  $\text{Np}^{4+}$  ion concentration is varied from  $4.3 \times 10^{-6}$  M to  $7 \times 10^{-5}$  M while the fulvic acid concentration was maintained constant at  $8.2 \times 10^{-4}$  eq/l. Secondly, the  $\text{Np}^{4+}$  ion concentration was kept constant at  $6 \times 10^{-5}$  M while varying the fulvic acid concentration from  $2.1 \times 10^{-4}$  eq/l to  $8 \times 10^{-3}$  eq/l. The spectroscopic speciation is made for the  $\text{Np}^{4+}$  ion by the absorption maximum at 960 nm with a full width of half maximum (FWHM) of 6 nm and the  $\text{Np(IV)}$  fulvate at 968 nm with a FWHM of 12.4 nm. The complexation constant is evaluated by the metal ion charge neutralisation model by taking into account the loading capacity (LC), which is determined also by spectroscopy to be 15 % for the  $\text{Np}^{4+}$  ion at pH 1. With increasing pH a gradual change in spectrum is observed as expected by hydrolysis of the  $\text{Np}^{4+}$  ion. The initially binary species converts to a ternary complex of the possible form:  $\text{Np(OH)}_{4-x}\text{FA}_{(x)}$ , in which the value of x changes presumably from 4 to 1 with increasing pH.

## THE COMPLEXATION OF Th(IV) BY $\alpha$ -ISOSACCHARINIC ACID AT ALKALINE pH

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In the planned repository for low and intermediate level waste in Switzerland substantial amounts of organic waste are cellulosic. Under the alkaline conditions of the cementitious repository, cellulose degrades rapidly via a peeling off reaction. The main degradation products are the *erythro*- and *threo*-form of 2,4,5-trihydroxy-2-hydroxymethyl-pentanoic acid, called  $\alpha$ -isosaccharinic acid and  $\beta$ -isosaccharinic acid, respectively. Isosaccharinic acid belongs to the class of polyhydroxy ligands. These are known to form stable complexes with various metal cations, especially under alkaline conditions. The formation of water soluble radionuclide complexes with isosaccharinic acid in a repository might therefore enhance the release of radionuclides to the geo- and biosphere.

As part of the study on the influence of cellulose degradation on the mobility of radionuclides, the authors present results on the complexation of Th(IV) by  $\alpha$ -isosaccharinic acid in the pH range 10.7 - 13.3. Th(IV) is an ideal representative for safety-relevant tetravalent actinides such as Pu(IV) or U(IV). The evidence of complexes between Th(IV) and  $\alpha$ -isosaccharinic acid is directly demonstrated. The experiments are performed under repository conditions and, therefore, the influence of  $\text{Ca}^{2+}$  on the complexation between Th(IV) and  $\alpha$ -isosaccharinic acid is studied. It is found that  $\text{Ca}^{2+}$  stabilises the complex under investigation by participating in the complexation reaction. Conditional stability constants for the complexation of Th(IV) with  $\alpha$ -isosaccharinic acid, in the presence and absence of  $\text{Ca}^{2+}$ , are given. The dependence of the conditional stability constants on pH and  $\text{Ca}^{2+}$  concentration is discussed.

## INVESTIGATION OF HUMIC ACID COMPLEXATION BEHAVIOR WITH $\text{UO}_2^{2+}$ IONS USING MODIFIED SYNTHETIC AND NATURAL HUMIC ACIDS

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Humic acids influence the speciation and migration behavior of actinide ions in the environment. Due to their complex and heterogeneous nature, a thermodynamically based description of their complexation behavior with metal ions is difficult. Numerous uncertainties exist in the description of the complexation process, e.g., the kind and number of complexing functional groups is uncertain.

We are investigating the influence of different functional groups on the complexation behavior of humic acids to improve the understanding of the humic acid - metal ion interaction. Such information is very important for a more precise modeling of geochemical processes in the presence of humic acids. We synthesized and characterized synthetic and natural humic acids with blocked phenolic hydroxyl groups. With these humic acids, we investigate the influence of phenolic hydroxyl groups on the complexation behavior of humic acids with  $\text{UO}_2^{2+}$  ions. The investigations were carried out by laser-induced fluorescence spectroscopy and FTIR spectroscopy.

For the first time, we compared the complexation behavior of a modified and non-modified synthetic humic acid with  $\text{UO}_2^{2+}$  ions at pH 4 by laser-induced fluorescence spectroscopy. The spectroscopic results show that the blocking of the phenolic hydroxyl groups changes the interaction behavior between the humic acid and the  $\text{UO}_2^{2+}$  ion.

## SOLUTION COORDINATION CHEMISTRY OF URANIUM IN THE BINARY $\text{UO}_2^{2+}$ - $\text{SO}_4^{2-}$ AND THE TERNARY $\text{UO}_2^{2+}$ - $\text{SO}_4^{2-}$ - $\text{OH}^-$ SYSTEM

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This study deals with the chemistry of uranium(VI) in aqueous sulfate solutions. The main objectives will be on the formation and characterization of binary uranyl sulfate and polynuclear ternary uranyl sulfate hydroxide complexes. There is very little information especially on the structure and reaction dynamics of such species. On the other hand, the occurrence of uranium ( $10^{-5}$  M) and sulfate ( $3 \times 10^{-2}$  M) in some ground and surface waters indicates that there are good reasons to assume that these species can be important for the uranium speciation. The presented study is focused on the fundamental chemistry of uranium(VI), but nevertheless the information obtained is highly relevant for the understanding of uranium(VI) in complex aquatic systems in nature.

A variety of methods were used to investigate the solution coordination chemistry, the reaction dynamics and the structure of uranium species in the aqueous systems outlined above. The results obtained with potentiometric titrations,  $^{17}\text{O}$ -NMR, and EXAFS will be presented.

## THE SPECIATION OF Tc(IV) IN CHLORIDE SOLUTIONS

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The speciation of the aqueous soluble Tc(IV) complexes is still a subject of uncertainties, because the nature of the Tc(IV) aquo ions lacks quantitative information. In strong complexing media and for sufficiently high acidities one deals with complexes of the  $Tc^{4+}$  ion; for example  $TcCl_6^{2-}$  is well characterized in concentrated HCl solutions. When the acidity decreases, it has been claimed that Tc(IV) exists as complexes of the  $TcO^{2+}$  or  $Tc(OH)_2^{2+}$  moieties. This work has addressed this problem in acidic chloride media. Several techniques of speciation have been used to solve this problem: UV-visible and Raman spectrometries, EXAFS (Extended X-ray Absorption Fine Structure) and polarography, each of them partially answering the questions.  $K_2TcCl_6$  was used as the starting material and was dissolved into solutions with various pH and  $Cl^-$  concentrations. The UV-visible spectrum of  $TcCl_6^{2-}$  does not change with time in 6 M HCl. In 1 M HCl, the molar extinction coefficient decreases with a blue shift of the main absorption band from 338 to 320 nm. The slow spectral changes show slow kinetics of  $Cl^-$  substitution by the ligands coming from water :  $H_2O$ ,  $OH^-$  or  $O^{2-}$ . The Raman spectrum of Tc(IV) in 1 M HCl displays bands at 300 and 900  $cm^{-1}$ . In comparison with the bands of the pure  $TcCl_6^{2-}$  ion (322-344  $cm^{-1}$ ) and  $TcO_4^-$  ion (325 and 912  $cm^{-1}$ ), these bands may be attributed to the Tc-Cl and Tc=O stretches. A band at 400  $cm^{-1}$  may be attributed to the Tc-O( $H_2O$ ) stretch. EXAFS results show two types of Tc(IV) first neighbours: Cl at 2.35 and 2.54 Å, O at 1.65 and 1.95 Å. The half-wave potentials of the reversible Tc(IV)/Tc(III) couple are shifted versus pH to lower potentials for solutions with constant chloride concentrations. All these results indicate that the chemical formula of these complexes is :  $TcOCl_p(H_2O)_q^{(2-p)+}$ , with  $p+q = 5$ . The charge of the complexes, not already determined, may give the value of p and q.

## THE HYDROLYSIS OF URANIUM(VI) IN SULFATE MEDIA

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Acid mine drainage is a problem occurring at many mine sites throughout the world. Acid mine drainage from many uranium mines worldwide has resulted in severe environmental impacts. The oxidation of sulfidic minerals in waste rock dumps produces sulfuric acid which, in turn, can leach metals present in other minerals in the dumps, such as uranium. The presence of high concentrations of sulfate in solution will have a large effect on the stability of metal complexes. However, very few studies have measured stability constants of metal complexes in sulfate media. As such, we have investigated the hydrolysis of the uranium(VI) ion in a  $\text{Na}_2\text{SO}_4$  medium ( $1.0 \text{ mol L}^{-1}$ ). Previous studies on uranium(VI) hydrolysis have generally indicated that the dominant polymeric species are  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  and  $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ .<sup>(1)</sup> A recent study<sup>(2)</sup> of uranium(VI) in sulfate/perchlorate media, however, suggested that the latter of these two species does not appear to form in the presence of sulfate, with the species  $(\text{UO}_2)_3\text{O}(\text{OH})_2^{2+}$  forming instead. The results of the present study also indicate that  $(\text{UO}_2)_3\text{O}(\text{OH})_2^{2+}$  forms in preference to  $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ . The study in sulfate/perchlorate media<sup>(2)</sup> also suggested the presence of the  $(\text{UO}_2)_5\text{O}_3(\text{OH})_2^{2+}$  species. The presence of this latter species was not supported by data from the present study, with evidence being found for the  $(\text{UO}_2)_4\text{O}_2(\text{OH})_3^+$  species, a species which has also been postulated in other media.

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## INFLUENCE OF HUMIC ACID SIZE ON ACTINIDE COMPLEXATION

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The effect of the molecular size of humic fractions on the nature and the stability of the complexes formed has been studied. Ultrafiltration was used to obtain five different size fractions of nominal molecular size which were used in metal binding studies. Two models representing quite different approaches to the analysis of data on metal-humic interaction were evaluated, the Charge Neutralization Model (CNM) and the Polyelectrolyte Model (PM). For the data analyzed by the Polyelectrolyte Model, solvent extraction was used to obtain the binding constants of  $^{241}\text{Am(III)}$  and two fractions of humic acid (LBHAF300kD and LBHAF10kD) at two pH values (pH 4.0 and pH 6.0). The stability constants for the larger size fraction were found to be greater. In the Charge Neutralization Model, ultrafiltration was used to determine the loading capacity and the binding constant between Eu(III) at macro concentrations and two size fractions of humic acid (LBHAF300kD and LBHAF10kD) at pH 4.0 and 6.0. A significant difference - one to two orders of magnitude - was found in the calculated binding constants from the two models for trivalent actinides and the same size fractions of humic acids at pH 4.0 and 6.0. A study of Eu  $^5\text{D}_0 - ^7\text{F}_0$  excitation spectra as a function of time and loading of humic was conducted to determine the type of sites bound to the metal. The shift in wavenumbers of the peak maximum obtained after equilibrium showed that Eu(III) has a different coordination environment at the two different pH values. Such a difference of coordination environment can be explained by a difference in the number of functional groups of the humic acid bound to the metal ion.

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## IDENTIFICATION OF THE LIMITING SPECIES IN THE PLUTONIUM(IV) CARBONATE SYSTEM. SOLID STATE AND SOLUTION MOLECULAR STRUCTURE OF THE $[\text{Pu}(\text{CO}_3)_5]^{6-}$ ION

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The carbonate anion is a common ligand in nearly all natural water environments and carbonate complexation in aqueous solution is known to affect the solubilities of actinide ions through formation of anionic complexes. This is especially true for Pu(IV) which forms strong complexes with hard O donor ligands. Over the last decade, there have been many studies focused on determination of the identities of the chemical species present in the Pu(IV) carbonate system, and there has been some disagreement in the literature regarding the identity of the solution complexes. We report here our experiments to determine the nature of both the limiting Pu(IV) carbonate species under high carbonate concentrations, and the solution species present under near-neutral pH conditions. Single crystals of  $[\text{Na}_6\text{Pu}(\text{CO}_3)_5]_2 \cdot \text{Na}_2\text{CO}_3 \cdot 33\text{H}_2\text{O}$  were obtained from a 0.15M solution of Pu(IV) in 2.6M  $\text{Na}_2\text{CO}_3$ . The asymmetric unit contains a complex network consisting of  $[\text{Pu}(\text{CO}_3)_5]^{6-}$  anions and  $\text{Na}^+$  cations linked through interactions with  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{O}$  ligands. EXAFS data for Pu(IV) in 2.5M  $\text{Na}_2\text{CO}_3$  solution collected at the Pu  $L_{\text{III}}$  edge are also consistent with the presence of  $[\text{Pu}(\text{CO}_3)_5]^{6-}$  anions, giving nearly identical structural parameters to those found in the solid state. The UV-Vis diffuse reflectance spectrum of a single crystal is nearly identical to the solution absorption spectrum of the limiting Pu(IV) carbonate complex in 2.5 M  $\text{Na}_2\text{CO}_3$  solution. The peak by peak correspondence by position and relative absorption strengths, along with solution EXAFS data, suggest that the Pu(IV) chromophore is the same in both cases. EXAFS data for Pu(IV) in 0.5M  $\text{NaHCO}_3$  solution at pH 7 is consistent with a different Pu(IV) species in solution, and the data for the new species will be presented.

## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MOLECULAR ACTINYL(VI) CHLORIDE COMPLEXES OF U, Np, Pu.

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Due to the high chloride concentrations expected under some nuclear waste repositories, there is a renewed interest in the chloride complexation of actinide ions. Plutonium(VI) for example, though generally unstable to reduction via alpha particle induced radiolysis, is stabilized in brine solutions by strong chloride ion complexation. As part of our ongoing structural studies of high valent actinide ions, we have determined the solid state structures of a series of hexavalent actinyl(VI) tetrachloride complexes. We have found that the use of bulky complex cations such as  $\text{K}(18\text{-Crown-6})^+$  in HCl solutions of  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , or  $\text{PuO}_2^{2+}$  ions affords a convenient method for growing single crystals of hexavalent actinide salts of general formula  $(\text{K-18-Crown-6})_2\text{AnO}_2\text{Cl}_4$ . Single crystal x-ray diffraction analysis reveals that all three compounds are isostructural, and contain discrete pseudo-octahedral  $\text{AnO}_2\text{Cl}_4^{2-}$  ions. This isostructural series affords a unique opportunity to compare structural and spectroscopic trends of light actinide ions across the series U, Np, Pu. Axial  $\text{An}=\text{O}$  bond lengths decrease smoothly from 1.768(3)Å for U to 1.737(3)Å for Pu, while equatorial  $\text{An}-\text{Cl}$  distances reveal a relatively narrow and statistically insignificant variation in bond lengths between 2.674(1)Å for U and 2.655(1)Å for Pu. Trends in vibrational frequencies and calculation of ionic radii will be presented. By employing mixtures of aqueous and nonaqueous solvents, we have also been able to characterize the dichloro complexes. The structures of these new compounds will also be presented.

## COMPLEXATION OF CM AND EU WITH FULVIC ACID: COMPARISON WITH EXPECTED TRENDS

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Trivalent actinide ions ( $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ) in groundwater at the Oak Ridge National Laboratory are known to migrate rapidly. The expected actinide inorganic species should strongly adsorb to the shale saprolite but are not observed. From groundwater anion exchange chromatography, the transport of the actinides results from complexation by fulvic acid. Estimates of the trivalent actinide-fulvic acid stability constants were used to evaluate the geochemical speciation. The calculations agreed with environmental observations. This work presents laboratory measurements to determine the trivalent actinide-fulvic acid stability constant. The complexation of Cm and Eu with isolated fulvic acid from the Oak Ridge site is examined at pH 4-6 in 0.1 M  $\text{NaClO}_4$ . The fulvic acid is purified from groundwater. The proton exchange capacity is measured by titration. The metal ion concentration is varied from nanomolar to micromolar. Ultrafiltration, ion exchange, and time resolved laser fluorescence spectroscopy are used to determine metal ion complexation. The metal ion charge neutralization model is used to evaluate fulvic acid concentration, loading capacity, and the stability constant. The value for the stability constant is similar to expected trends.

## THE RATES AND MECHANISMS OF WATER EXCHANGE OF ACTINIDE AQUO IONS: A VARIABLE TEMPERATURE $^{17}\text{O}$ NMR STUDY OF $\text{U}^{4+}$ , $\text{Th}^{4+}$ AND $\text{UO}_2^{2+}$

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The rate of exchange of water between the first coordination sphere and the second sphere, in practice the bulk, has been studied and provides important information for the deduction of the intimate mechanisms of most ligand substitution processes in metal complexes. We have used  $^{17}\text{O}$  NMR relaxation to determine the rates, activation parameters, and mechanisms of water exchange between  $\text{U}^{4+}(\text{aq})$ ,  $\text{Th}^{4+}(\text{aq})$  and  $\text{UO}_2^{2+}(\text{aq})$  and solvent water. For the paramagnetic  $\text{U}^{4+}(\text{aq})$  with a coordination number of 10 we obtained  $(6.0 \pm 0.1) 10^6 \text{ s}^{-1}$  for the water exchange rate constant at room temperature,  $39 \pm 0.6 \text{ kJ/mol}$  for the value of  $\Delta H^\ddagger$  and  $16 \pm 2 \text{ J/mol/K}$  as  $\Delta S^\ddagger$ . Based on the coordination number and value of the activation entropy we suggest a mechanism of  $\text{I}_d$  type. In order to study the water exchange of the diamagnetic  $\text{UO}_2^{2+}(\text{aq})$  ion we used a chemical shift reagent (the paramagnetic  $\text{Tb}^{3+}$ ) to extend the time domain. The results using 5 as a coordination number are  $(1.4 \pm 0.1) 10^6 \text{ s}^{-1}$  for  $k_{\text{ex}}$  at 298 K,  $29.5 \pm 2 \text{ kJ/mol}$  for  $\Delta H^\ddagger$ , and  $-28 \pm 7 \text{ J/mol/K}$  as  $\Delta S^\ddagger$ . Despite the low negative value for the activation entropy the mechanism of the water exchange is probable also in this case dissociatively activated. We studied the water exchange for diamagnetic  $\text{Th}^{4+}(\text{aq})$  using the same method as for  $\text{UO}_2^{2+}(\text{aq})$ . We found that the water exchange rate for this ion is too fast to be determined by this way. We can give a lower limit for the value of the rate constant of the  $\text{Th}^{4+}$  water exchange:  $> 5 \times 10^7 \text{ s}^{-1}$ .

## Tc CHEMISTRY : Tc(IV) CHLORIDE/SULPHATE COMPLEXES RELATIVE STABILITY

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Chloride and sulphate are common and available ligands in natural media. The comparison of the affinity of the chloride and the sulphate ligands for a metallic ion give one information about its place in the hard soft acidity scale (HSAB). The chemistry of Tc is mostly known in its heptavalent state and Tc(IV) aqueous chemistry which is supposed to play a major role for Tc migration in reducing natural media is not well understood. So, this work deals with the evaluation of the relative stability of the chloride to sulphate complexes of Tc(IV) based on the two ways substitution  $\text{Cl}^- \rightleftharpoons \text{SO}_4^{2-}$  in the first coordination sphere of Tc(IV). The reactions were followed by UV-visible spectrophotometrie and capillary electrophoresis. The substitution reactions were slow and spectra were registered during 15 days. The main results showed :

- Without  $\text{SO}_4^{2-}$ ,  $\text{TcCl}_6^{2-}$  is rapidly transformed into insoluble  $\text{TcO}_2$  above pH3.
- With  $\text{SO}_4^{2-}$ ,  $\text{TcCl}_6^{2-}$  is partially transformed in soluble sulphate species between pH 2.5 and 4.3, some  $\text{TcO}_2$ , a brown precipitate, is also observed.
- Under pH 2.5 only soluble chloride or sulphate species were observed.

In all these experiments, carried out in the presence of air, the oxidation of Tc(IV) into Tc(VII) ( $\text{TcO}_4^-$ ) was limited to % of initial Tc(IV).

The substitution of chloride by sulphate was not achieved for solutions 4 M in  $\text{Cl}^-$  and 0.25 M in  $\text{SO}_4^{2-}$  and no chloride Tc(IV) complexes were left in 0.5 M  $\text{Cl}^-$  and 0.01 M  $\text{SO}_4^{2-}$  solutions. These indicates clearly that the sulphate complexes are formed preferentially to the chloride ones in the solutions containing the same concentration of ligands. If we assume that the substitution reaction is :



One can evaluate the value of the equilibrium constant of this reaction  $\sim 1$ .

In conclusion one can stress that Tc(IV) can be considered as one hard or border line acid. The formula of the sulphate complexes, if confirmed indicate the sulphate species can play a more important role than chloride in dissolution of some  $\text{TcO}_2$  in media with moderately high pH (3 to 6).

## INFRA RED STUDY OF URANIUM(VI) COMPLEXATION WITH NATURAL AND SYNTHETIC HUMIC ACIDS

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Solid uranyl complexes with natural and synthetic humic acids were compared by infra-red spectroscopy in middle and far infra red in the range of  $4000\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ . Two natural humic acids were studied. One was collected from bog site "Kleiner Kranichsee", near the uranium mining site of Johanngeorgenstadt (Saxony/Germany) and the second one was commercial Aldrich® humic acid. The synthetic humic acids were two selected melanoidine fractions and a polymerisation product of 3,4,5 trihydroxybenzoic acid (gallic acid). IR-spectra of both natural humic complexes agreed with those of the synthetic humic acids. The asymmetric  $\text{UO}_2$  stretching vibration in middle infra red region below  $930\text{ cm}^{-1}$  shifts to higher wavenumbers with decreasing aromatic character. In contrast, the  $\text{UO}_2$  bending frequencies in far infra red above  $255\text{ cm}^{-1}$  shifts to lower wavenumbers with decreasing aromatic character of the humic acids. Shifts of the significant vibrations are attributed to the influence of aromaticity. However, the uranium coordination in all humic acids studied was not affected by changing the aromaticity. The study confirms once more the suitability of synthetic humic acids as model substances for environmental basic research on humic acids.

## COMPLEX FORMATION IN THE TERNARY $\text{UO}_2^{2+}$ - $\text{F}^-$ - $\text{SO}_4^{2-}$ SYSTEM STUDIED BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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Chemical species of actinide ions in ground and surface water systems will depend on pH and the presence of other ligands, e.g., carbonate, fluoride, sulfate and organic substances. For uranyl(VI) ion, the chemical form of the species in aqueous solution is interesting from the viewpoints of not only the speciation under environmental conditions but also the coordination structure and bonding. The complex formation of  $\text{UO}_2^{2+}$  in the binary systems has been extensively investigated, however the formation of the ternary complexes is not known well. In this study, the complex formation in the ternary  $\text{UO}_2^{2+}$ - $\text{F}^-$ - $\text{SO}_4^{2-}$  system was investigated in 1.0 M  $\text{NaClO}_4$  at 25 °C by Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS).

Fluorescence spectra and lifetimes of U(VI) in the ternary  $\text{UO}_2^{2+}$ - $\text{F}^-$ - $\text{SO}_4^{2-}$  system and in the binary  $\text{UO}_2^{2+}$ - $\text{F}^-$  and  $\text{UO}_2^{2+}$ - $\text{SO}_4^{2-}$  systems were measured in the pH range of which no hydrolysed and carbonate complexes were formed. At lower  $\text{F}^-$  concentration in  $\text{UO}_2^{2+}$ - $\text{F}^-$  systems in the presence or absence of  $\text{SO}_4^{2-}$ , the fluorescence lifetimes of U(VI) indicated contributions of two species owing to equilibria between  $\text{UO}_2\text{F}^+$  and  $\text{UO}_2\text{SO}_4^0$  or  $\text{UO}_2^{2+}$ , respectively. At higher  $\text{SO}_4^{2-}$  concentration in  $\text{UO}_2^{2+}$ - $\text{SO}_4^{2-}$  system in the presence of  $\text{F}^-$ , the fluorescence lifetimes of U(VI) also showed two components, suggesting equilibria between  $\text{UO}_2(\text{SO}_4)_n^{2-2n}$  ( $n=1-3$ ) and  $\text{UO}_2\text{F}_n^{2-n}$  ( $n=1$  or  $2$ ). It was difficult to find an unambiguous evidence of the ternary complexes, since the effect of fluoride relative to that of sulfate was a dominant factor in the fluorescence properties of U(VI) complexes. Further works on numerical analyses of the fluorescence spectra are in progress for the quantitative evaluation of the complex formation in the binary and ternary systems and for in-depth understanding of the relationships among the spectroscopic properties, coordination structure and stability of the U(VI) complexes.

## COMPLEX FORMATION OF Eu(III) WITH POLYACRYLIC ACID

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For the quantitative description of the interaction of metal ions with humic substances, it is necessary to clarify the effects of both polyelectrolyte and heterogeneous nature of humic substances. To estimate the polyelectrolyte effect separately, polyacrylic acid ( $[-\text{CH}_2\text{CH}(\text{COOH})-]_n$ , MW=90,000) has been selected as a representative of well-defined, homogeneous polymeric weak acids, and its interaction with Eu(III) has investigated by a solvent extraction method using 152Eu with TTA and TBP in xylene. By defining the apparent complex formation constant as  $\beta_\alpha = [\text{ML}]/([\text{M}][\text{R}])$ , where  $[\text{M}] = [\text{Eu}^{3+}]$ ,  $[\text{ML}]$  is the concentration of Eu(III) associated with polyacrylic acid and  $[\text{R}] = C_{R\alpha}$  ( $C_R$  is a proton exchange capacity and  $\alpha$  is a degree of dissociation determined by potentiometric titration), the apparent constants have been obtained at several  $pC_H$  and ionic strength (0.1 M and 1.0 M  $\text{NaClO}_4$ ). The constants increased with  $pC_H$  and decreased with an increase of ionic strength, that is, the values of  $\log\beta_\alpha$  varied from 6.1 (at  $pC_H = 4.74$ ) to 7.6 ( $pC_H = 5.53$ ) at 0.1 M  $\text{NaClO}_4$  and from 4.8 ( $pC_H = 4.46$ ) to 6.5 ( $pC_H = 5.39$ ) at 1.0M. The plots of  $\log\beta_\alpha$  versus  $\log\alpha$  revealed almost linear relationship both at 0.1 and 1.0 M  $\text{NaClO}_4$ .

## **DETERMINATION OF STABILITY CONSTANTS IN AQUEOUS METAL-HUMIC ACID SYSTEMS AT HIGH IONIC STRENGTHS BY SOLVENT EXTRACTION**

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The stability constants of Ni(II) and Co(II) with humic acid have been investigated. Two different pH, values, 4.0 and 6.0 respectively, have been studied. The solutions had various ionic strengths ranging from 0.1 to 5.0 molal NaCl. Solvent extraction was used as the method to determine the stability constant values. HDEHP in toluene or heptane solutions were utilized as the organic extractant. Radioactive tracers were used to determine the distribution ratios of the metal, between the organic and aqueous phases. Data from these experiments were used to develop a model for performance assessment of the Waste Isolation Pilot Plant (WIPP) project.

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## **FLUORESCENCE QUENCHING AND METAL ION COMPLEXATION FOR THREE MOLECULAR WEIGHT FRACTIONS OF A FULVIC ACID EXTRACTED FROM KOREAN SOIL**

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Fluorescence in intensities and lifetimes of fractionated fulvic acid has been studied by the synchronous fluorescence spectroscopy and time-resolved fluorescence spectroscopy as a function of pH and metal ion concentrations. The fulvic acid samples isolated from different soil depth of a Korean volcanic soil were divided into three fractions of different molecular weight ranges (F1: less than 500, F2: 500 - 3,000, F3: 3,000 - 10,000) by gel filtration chromatography. The fluorescence quenching techniques were employed for determining the binding characteristics and the conditional stability parameters of metal complexation with the three fractions of fulvic acids. The quenching spectra of fulvic acid of different molecular size groups complexed with tri-, and di-valent metal ions showed that the high molecular weight fraction has a stronger affinity for the metal ions than the low molecular weight fraction. The quenching process of the fulvic acid by the metal ion complexation was evaluated using the lifetime data obtained by time-resolved photon counting method. It was found that the combined synchronous fluorescence quenching spectroscopy and lifetime measurements result in a very useful method in identifying the characteristics of the metal ion interactions with fulvic acid.

## ANALYSIS OF TH(IV)-HUMATE BY XPS

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The tetravalent actinide humate complexation is investigated for types of bonding between Th(IV) and humic acid. The Th(IV)-humate was prepared in solution, separated by ultrafiltration and analyzed directly on the filter by X-ray photoelectron spectroscopy (XPS). On drying the sample and transferring it into the vacuum for XPS analysis, significant changes of the Th(IV)-humate may be expected. However, extended X-ray absorption fine structure (EXAFS) studies reveal that the Th(IV) coordination in the Th(IV)-humate does not change on drying. High resolution XPS spectra of the elemental lines are recorded during long-term irradiation of the Th(IV)-humate to determine its stability against X-ray induced degradation. The spectra do not change significantly during the X-ray exposure. The Th  $4f_{7/2}$  line is well fit by one Gauß-Lorentz curve, indicating that one type of bonding is involved in the Th(IV)-humate complexation. The binding energy of the Th  $4f_{7/2}$  line and its satellite in the Th(IV)-humate spectrum are compared to those from other Th(IV) compounds of varying bonding partners. Chemical shifts and satellite features for Th(IV)-humates are found to be similar to Th(IV) complexes with an ion exchanger containing only carboxylic functional groups. This corroborates interpretation of previous EXAFS results. The present XPS study indicates that Th(IV) is predominantly bound to carboxylic groups of humic acid and demonstrates the applicability of the XPS technique for the characterization of humate complexes.

## ELECTROMIGRATION OF Eu AND ITS COMPLEXES WITH HUMIC ACID

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The interaction of Eu with purified/protonized Aldrich humic acid (HA) was studied by the free liquid moving boundary electrophoresis and by ultrafiltration as a complementary method, both techniques used in combination with the radiotracer method. Introductory experiments were carried out to test electrophoretic behavior of Eu in HA-free solutions, and to determine mobility of  $\text{Eu}^{3+}$  cation. At trace concentrations of Eu, a steep decrease of Eu cathodic mobility with increasing pH was observed, starting already at pH 3 while significant anodic mobilities occurred at pH 6. This probably indicated presence of Eu pseudocolloids formed by Eu sorption on the impurities present in solution, as hydrolysis and/or formation of carbonate complexes should play only a minor role in Eu speciation below pH 6. To get the data for evaluation of parameters describing Eu binding to HA, batch titrations of HA (10 mg/L) with Eu were performed in the range  $4.25 \times 10^{-8}$  -  $1 \times 10^{-3}$  M of Eu total concentration at pH 3, 4, 5 and 6 and 0.01 M ionic strength ( $\text{NaClO}_4$ ). In the experiments, the degree of Eu complexation with HA was determined from  $^{152/154}\text{Eu}$  electromigration to cathode. The experimental data have been curve-fitted, and the conditional binding constants together with corresponding site capacities calculated using two models - a discrete site model (Scatchard plot-like model with two types of sites) and a continuous distribution model (based on the complexation plot of the former model processed by the Gaussian distribution function). An additional information on the charge characteristics of the Eu-HA complexes has been obtained from the anodic mobilities determined besides measuring activity of the migrated  $^{152/154}\text{Eu}$  also from UV/VIS absorption of the migrated HA/Eu-HA. Results are discussed in terms of thermodynamic and kinetic stability of the Eu-HA complexes.

## DISSOCIATION CONSTANTS OF EDTA, DTPA AND NTA AND COMPLEXATION WITH SOME LANTHANIDES (III) AND ACTINIDES (III) IN HIGH IONIC STRENGTH NaClO<sub>4</sub> AQUEOUS SOLUTIONS: SIT AND PITZER MODELING

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The dissociation constants of EDTA, DTPA and NTA in aqueous solutions of various ionic strengths (NaClO<sub>4</sub> medium) in the literature have been complemented by measurements of pK<sub>a</sub> value at higher ionic strengths using potentiometric titration. The variation of the pK<sub>a</sub> values with the ionic strength has been analyzed by the Specific Interaction Theory and the Pitzer model to obtain parameters for modeling the protonation at all ionic strengths.

The stability constants of complexes of lanthanides (e.g. Nd<sup>3+</sup> and Eu<sup>3+</sup>) and actinides (e.g. Cm<sup>3+</sup> and Am<sup>3+</sup>) with these ligands in NaClO<sub>4</sub> solutions of high ionic strengths have been investigated. UV-visible absorption spectroscopy involving Arsenazo (III) as a ligand competitor was used for the determination of the stability constants for the lanthanide complexes. For the actinide complexes, solvent extraction combined with a competition with Nd<sup>3+</sup> and Eu<sup>3+</sup> using the data previously gathered has been performed. The stability constants over a range of ionic strengths (0.1m to 5m) have been modeled by the SIT and the Pitzer method.

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## EXAFS STRUCTURAL ANALYSIS OF AQUEOUS URANIUM(VI) COMPLEXES WITH WOOD DEGRADATION PRODUCTS

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To study the role of carboxylic and phenolic hydroxyl groups in the complexation of phenolic wood degradation products with uranium(VI) in aqueous solution, we prepared 1 mMol/L U(VI) complexes with the following simple model compounds at two pH ranges, i.e., 4-5 and 8-10: protocatechuic acid (3,4-dihydroxybenzenecarboxylic acid), catechol (1,2-dihydroxybenzene), pyrogallol (1,2,3-trihydroxybenzene), and vanillic acid (4-hydroxy-3-methoxybenzenecarboxylic acid). The structural parameters of the uranium near-neighbor surrounding in these complexes were measured by uranium  $L_{III}$ -edge extended x-ray absorption fine structure (EXAFS) spectroscopy.

In acid solutions containing 1:1 complexes with ligands having both carboxylic and hydroxyl groups, the uranium is surrounded by 5 equatorial oxygen ( $O_{eq}$ ) at a distance of 2.44 Å for vanillic acid and 2.46 Å for protocatechuic acid, respectively. This relatively long U- $O_{eq}$  bond distance is characteristic for bidentate coordination of the carboxylic group to the uranyl cation /Denecke et al., J. Phys. IV France 7, C2-637 (1997)/. If the ligands have only neighboring hydroxyl groups, i.e., catechol and pyrogallol, the uranium is surrounded by 5-6 oxygen atoms at a shorter U- $O_{eq}$  distance of 2.39 Å. This shows that in the pH range of 4-5, the coordination behavior of the acids is dominated by the carboxylic groups and not the hydroxyl groups. In the pH range of 8-10, the neighboring phenolic hydroxyl groups dominate the complexation. This is in agreement with the observed similarities in the EXAFS structural parameters of the corresponding 1:2 and 1:3 complexes. In all these complexes the measured U- $O_{eq}$  bond distance is 2.38 Å. It can be concluded that this relatively short U- $O_{eq}$  bond distance is characteristic for the complexation of the uranyl group with two or three ligands containing neighboring phenolic hydroxyl groups.

## THE EFFECT OF CHLORIDE ON ACTINYL(VI) SOLUBILITY AND SPECIATION

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Structural and thermodynamic properties of actinide(VI) compounds in aquatic systems are essential to predict speciation in waters intrinsic to geologic salt formations which have been proposed as nuclear waste repositories, e.g. the Waste Isolation Pilot Plant. Modeled release scenarios involve trace actinides in the presence of concentrated NaCl (or MgCl<sub>2</sub>); thus, parameterization for dilute actinides in solutions similar to natural brines is needed. We investigated the solubility and speciation of uranium(VI) and plutonium(VI) in concentrated chloride solutions. We applied spectroscopic techniques, including Raman, FTIR, UV-Vis, laser-induced fluorescence, and EXAFS, and powder and single crystal X-ray diffraction to investigate the composition and structure of An(VI) compounds and to determine significant species' formation constants and solubility products. The stability of monomeric and polymeric hydroxo  $(\text{AnO}_2)_m(\text{OH})_n^{2m-n}$ , carbonato complexes,  $(\text{AnO}_2)_m(\text{CO}_3)_n^{2m-2n}$ , and chloro complexes,  $\text{AnO}_2\text{Cl}_n^{2-n}$ , was investigated as a function of pH, chloride, and carbonate concentration. Specifically, the chloride complexation of U(VI) and Pu(VI) was studied spectroscopically, and the apparent stability constants of the inner-sphere An(VI) chloro complexes were determined for each NaCl concentration. The effect of chloride on the stability of An(VI) hydroxo and carbonato complexes and the potential formation of mixed complexes was studied. We prepared relevant An(VI) hydroxide and carbonate solid phases measured their solubility in NaCl solution as a function of pH and ionic strength. Results from solution thermodynamic (spectrophotometric titrations and solubility measurements) and solid state characterization (XAS and X-ray diffraction) studies will be presented.

# MIGRATION '99

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## A STUDY OF POLYOXOMETALATE COMPLEXATION OF Eu(III), Cm(III), AND UO<sub>2</sub><sup>2+</sup> BY TIME-RESOLVED LASER INDUCED FLUORESCENCE

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It has been proposed that polyoxometalates can be used to model the actinide-colloid interaction that occurs in natural water systems since the polyoxometalate has similar characteristics to a colloid. Polyoxometalates have also been used in the synthesis, in the presence of a pillaring agent, of pillared clays. The interaction between polyoxometalates and actinide cations has been limited to thorium and uranium while the lanthanide-polyoxometalate interaction has been more fully studied. Although there has been some recent literature published reporting stability constants between Cm(III) and two lacunary polyoxometalates (PW<sub>11</sub>O<sub>39</sub><sup>7-</sup> and SiW<sub>11</sub>O<sub>39</sub><sup>8-</sup>), there is an interest in comparing the Eu(III)-polyoxometalate and the Cm(III)-polyoxometalate time-resolved laser induced fluorescence spectra. Differences in binding tendencies between the 4f and 5f could be attributed to the increased covalency of the actinide cations in relation to the lanthanides. Eu(III) and Cm(III) are chosen to model the trivalent lanthanides and actinides due to their fluorescence spectroscopic intensity. The uranyl cation, UO<sub>2</sub><sup>2+</sup>, is chosen to model the di-oxo actinyl cation interaction with the polyoxometalate systems of interest.

In this work, analogous *plenary* and *lacunary* polyoxometalate structures (P<sub>2</sub>W<sub>18</sub>O<sub>62</sub><sup>6-</sup> and P<sub>2</sub>W<sub>17</sub>O<sub>61</sub><sup>10-</sup>) were studied to look exclusively at the structural differences in the preferred binding sites between the two ligands. We also looked at the complexation of Cm(III) and UO<sub>2</sub><sup>2+</sup> with P<sub>8</sub>W<sub>48</sub>O<sub>184</sub><sup>40-</sup>, a large tetrameric species of P<sub>2</sub>W<sub>12</sub> with multiple binding sites both inside and outside of the taurus shaped ligand. Using the equations of Kimura and Choppin for Cm(III) and Eu(III), respectively, we determined the hydration number for each cation complexed to the polyoxometalate. We also determined the thermodynamic stability constants for each system.

## THERMODYNAMIC MODELING OF METAL-LIGAND INTERACTIONS IN HIGH IONIC STRENGTH NaCl SOLUTIONS: THE Co<sup>2+</sup>-OXALATE SYSTEM

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Some of the organic ligands contained in nuclear wastes have relatively strong binding capacity with actinides and other metals. The effect of organic ligand complexation with actinides and other metals in repository must be quantified for performance assessment of the WIPP. Oxalate has been identified as an organic ligand present in the wastes. The complexation of Co<sup>2+</sup> by oxalate in 0.3 to 5 m NaCl solutions at pH ~7 has been investigated. The stability constants for Co<sup>2+</sup> with oxalate complexation were measured as a function of NaCl concentration using a solvent extraction method with HDEHP in toluene. The stability constants for this complex decreased with increasing NaCl concentrations up to 5 m. These data will be modeled using the ion-interaction formalism developed by Pitzer. The dimensionless standard chemical potential, binary interaction parameters:  $\beta^{(0)}$  and  $C^{\circ}$  will be calculated. Because of limited data, the  $\beta^{(1)}$  value is fixed at an average value of 0.29, which was obtained by averaging 1-1 interactions for other carboxylic acid salts. Higher order interaction parameters will be not required to model the data.

## FLUORESCENT STABILITY CONSTANT DETERMINATION OF MIXED $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$ COMPLEX AT DIFFERENT IONIC STRENGTHS.

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The possibility of formation of a mixed complex between  $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$  was reported earlier but little study has been given to this complex despite its possible environmental significance.

In this work the stability constant of the soluble  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  complex was determined at the pH of 8.0 in sodium perchlorate media at different ionic strengths (0.1, 0.7, 1 and 3 M). The formation of the complex was studied by fluorescent spectroscopy and the stability constant determined by the series of fluorescent titrations in which  $\text{UO}_2^{2+}/\text{CO}_3^{2-}$  was titrated by  $\text{Ca}^{2+}$  and  $\text{Ca}^{2+}/\text{UO}_2^{2+}$  by the  $\text{CO}_3^{2-}$  (in an  $\text{N}_2$  atmosphere). The ratio of  $\text{Ca}^{2+}$  to  $\text{UO}_2^{2+}$  in the complex was found to be 2:1. The number of  $\text{CO}_3^{2-}$  groups present is discussed based on speciation data of  $\text{UO}_2^{2+}$  at different  $\text{CO}_3^{2-}$  concentrations.

The speciation diagram of  $\text{UO}_2^{2+}$  was calculated over the pH range of 5-9 and is discussed, taking into account the formation of the  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  complex.

This research, conducted through the Waste Isolation Pilot Plant project was supported by the USDOE under contract DE-AC04-94AL85000 to Sandia National Laboratories and Subcontract AT 8740 to The Florida State University.

## THE ORIGIN OF COLLOIDS FROM HIGH LEVEL WASTE GLASS CORROSION

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The corrosion of a high level radioactive waste (HLW) glass under oxidative unsaturated aqueous conditions is examined in detail to explore the origin of radionuclide-bearing colloids. The HLW glass considered is a West Valley Demonstration Project (WVDP) type, where the reacted glass surfaces and solution colloids have been extensively characterized by analytical transmission electron microscopy. Smectite clay alteration layers form on the corroding glass, along with an assemblage of distinct actinide-bearing phases. The alteration phases formed from the corrosion of WVDP glass include brockite (ideally  $[\text{Ca, REE, Th}]\text{PO}_4$ ), iron oxyhydroxides, iron silicates, and thorium-iron titanate, each of which is known to either directly incorporate actinide elements, or to sorb them efficiently. As the clay layer grows in thickness, mechanical stress sloughs colloid-sized fragments to solution, many of which bear the radionuclide phases. These colloids may be important in mobilizing insoluble radionuclides that would otherwise be retained in the alteration layer.

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## THE FORMATION AND STABILITY OF GLASS WASTE FORM COLLOIDS

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The formation and stability of radionuclide-bearing colloids in solution due to the reaction of a DWPF glass under repository relevant conditions is presented. Corrosion tests were performed on an actinide-doped borosilicate waste glass (SRL 131A) in equilibrated water from the J-13 well at Yucca Mountain at a surface area-to-volume ratio of  $2000 \text{ m}^{-1}$ . The leachate samples were examined as a function of glass corrosion using dynamic light scattering to determine the particle size distribution and concentration of bulk colloids in solution. Sequential filtration and alpha spectroscopy results indicated a colloidal, actinide fraction between 6 and 450 nm for corrosion of the SRL 131A glass [W. L. Ebert and J. K. Bates, Nuclear Technology, 104, 372 (1993)]. Under the reaction kinetics of these tests, stable colloids were observed in low ionic strength leachates. However, as the ionic strength increased during the glass corrosion, aggregation of the colloidal species occurred. The mineralogical composition of the colloids, as determined by transmission electron microscopy, was important for understanding and predicting the stability of the colloids [E. C. Buck and J. K. Bates, Appl. Geochem., 14, (1999)]. Results from these tests monitored colloid formation and determined that the plutonium was associated with the bulk colloids observed in solution.

## CHARACTERIZATION OF Pu COLLOIDAL AND AQUEOUS SPECIES IN YUCCA MOUNTAIN GROUNDWATER SURROGATE

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Radionuclide speciation and groundwater composition are among the factors affecting the transport of radionuclides in groundwater. The migration of radionuclide-bearing colloids is a potential mechanism for the release of actinides from an underground nuclear waste repository. Recent studies in Nevada revealed that a colloidal form of Pu was apparently transported kilometer-scale distances through fractured volcanic rock on a timescale of decades. In this work the speciation and formation of Pu intrinsic colloids from an initial solution of Pu(V) were studied at pH 1, pH 3, pH 6, pH 8, and pH 11. The medium was the surrogate Yucca Mountain groundwater from well J-13 under air atmosphere. The solutions were monitored for several months. Samples were analyzed using liquid scintillation counting, ultra filtration, solvent extraction, light scattering and laser-induced photo-acoustic breakdown spectroscopy. Redox potentials were measured periodically. The time dependencies of soluble and colloidal Pu concentrations are reported. The size and concentration of Pu colloid particles were estimated.

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## INTERACTION OF WASTE GLASS COLLOIDS WITH IRON OXIDE SOLID

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Colloidal particles are formed during simulated weathering (leach tests) of nuclear waste glasses. A significant fraction of the Pu and Am released from the glass is associated with the colloidal particles. Previous work has indicated the colloids are derived from secondary silicate phases formed at the glass surface during leaching. We are investigating the interaction of waste-glass colloids with  $\text{Fe}_2\text{O}_3$  as a model compound for corrosion products in a nuclear waste repository. Colloidal suspensions were prepared by reacting a radionuclide-doped borosilicate glass sample (SRL131A produced at Savannah River) with dilute aqueous solution at  $90^\circ\text{C}$ . Solution composition is representative of near-field water composition expected for a repository at Yucca Mountain, Nevada, and consists primarily of  $\text{NaHCO}_3$  and dissolved silica with an initial pH of 8. The suspensions were equilibrated with  $\text{Fe}_2\text{O}_3$  powders of well-defined particle size at pH 7-11, and the distribution of Pu and Am among the bulk solid, colloidal and dissolved components was determined. By comparing results of batch sorption experiments conducted under similar conditions, but in the absence of waste glass colloids, we hope to separate the effects of reversible and irreversible adsorption in the colloid experiments.

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## APPLICATION OF LASER-INDUCED BREAKDOWN DETECTION METHOD FOR THE QUANTIFICATION OF Th(IV)-COLLOID FORMATION

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The laser-induced breakdown detection (LIBD) method developed in our laboratory provides the possibility of quantifying aquatic colloids of the lower nm size range, for which it is highly sensitive, more than one million times than a light scattering method. The LIBD method is applied in this work to determine the Th(IV)-colloid formation and therefrom the solubility product of Th(OH)<sub>4</sub>(am).

Experiment is started with  $1 \times 10^{-5}$  mol/L Th in 0.1 M HNO<sub>3</sub> and pH is varied gradually from 1 to 10, while measuring breakdown events at each given pH. The colloid generation via hydrolysis is observed starting from pH 3 and reached a near saturation at pH 5. Based on the pH value of starting colloid generation, the calculated solubility product of Th(OH)<sub>4</sub>(am) appears to be  $\log K_{sp}^0 = -52.6 \pm 0.7$ , which agrees with the value determined by another independent method:  $\log K_{sp}^0 = -52.3 \pm 0.9$ . A comparative experiment is conducted in the presence or absence of CO<sub>2</sub> and the characteristics of colloid generation in the two systems are quantified. An average size of colloids is found to remain at  $15 \pm 5$  nm diameter at all investigated pH. Discussion is extended to the application of the method for the quantification of various colloids in general.

## EFFECTS OF pH AND TEMPERATURE ON SORPTION AND DIFFUSION OF Sr AND Cs IN BENTONITE

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This study deals with the diffusion and sorption mechanisms of  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  in clay, which can be considered as a kind of better buffer material in radwaste disposal. Preventing the groundwater intrusion and possessing excellent sorption capability of nuclides are the two important criteria for an ideal buffer material. In this study, Jishin soil and Wyoming bentonite (MX-80) were selected as candidate buffer materials. The sorption parameters of radionuclide were determined by batch experiment. The diffusivities of  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  were performed by steady state method in the clay thin-layer diffusion column, with a compacted dry density of  $1.8 \text{ g cm}^{-3}$ . According to the results of zeta potential measurement, sorption data in batch method were compared with in order to understand the variable electrostatic forces between charged surfaces and nuclide species. The adsorption coefficients of strontium are more dependent on pH values than that of cesium in the same condition. The adsorption of strontium on bentonite increases in the same pH region and in a similar manner as the zeta potential indicating an electrostatic binding of solvated  $\text{Sr}^{2+}$  ions which are placed in the diffusive double layer to negative surface groups. The mechanism for nuclide diffusion is discussed in both pore water diffusion and surface diffusion. In this experiment, it was found that surface diffusion is an important factor in MX-80 bentonite than Jishin soil. The dependence of the diffusion of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  on the sorption intensity is accommodated by a model encompassing diffusion of the sorbed cations within the electrical double layer next to the mineral surface in addition to diffusion in the pore water. Because of the sorption character of  $\text{Sr}^{2+}$ , one can find greater surface diffusion in MX-80 bentonite. It is believed that to find the different sorption and diffusion behaviors and their parameters for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  nuclides in MX-80 bentonite and Jishin is useful for disposal assessment.

## **RADON EMANATION FROM CRUSHED MINERAL. INFLUENCE OF PORE SIZE AND HUMIDITY**

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Radon and its progeny represent the main cause of radiation exposure. The risk is due to the possible accumulation of excessive levels of this gas in buildings and dwellings. The radon problem also concerns the nuclear waste management. Indeed mining and purifying produce the largest amount of radioactive residues. Unused radioelements like radium, concentrated in these residues, may constitute a strong radon source.

This work deals only with the migration of radon atom from the crystals where they are formed to the pore space defined by the compacting of the residues. The radon emanation is modelled considering the alpha recoil phenomenon. Indeed during the decay of radium-226, the newly formed radon atom achieves a kinetic energy of about 86 KeV. This recoil energy enables the radon atom to have ranges of motion in crystals amounting to several tens of nanometres and then to escape the mineral phase.

The modelling is done considering that radium is either homogeneously distributed in the mineral phase or adsorbed at the mineral surface. Co-precipitation phases relate to a particular case of an homogeneous distribution. The pores are considered as parallelograms. The model is first solved for the two limiting cases where the pore space is either filled with air or saturated by water. Results show that radon emanation becomes maximum beginning at nanometre size pore when the pore is filled with water. When the pore is filled with air, the maximum of emanation is reached only for pores in the micrometre scale.

This modelling has been applied to a reference sample (dolomite) containing  $38.6 \text{ Bq.g}^{-1}$  of radium 226. The radon emanation coefficient of this sample has been theoretically calculated both in dry and water saturated conditions on the basis of its pore size distribution, as obtained by mercury porosimetry. Experimental emanation coefficients and predicted values show a good agreement. To conclude, this model is used to estimate the influence of increasing moisture in the case of pore size of micrometre scale. Assumption is made that water forms a continuous film at the grain surface. This simple assumption could then explain some tendencies observed in the literature.

## CRUSHED-ROCK COLUMN TRANSPORT EXPERIMENTS TO DETERMINE PARAMETERS FOR A MULTIRATE MASS TRANSFER MODEL FOR THE CULEBRA DOLOMITE AT THE WIPP SITE, NEW MEXICO

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A series of single-well and multiple-well tracer tests have recently been conducted in the Culebra dolomite at the Waste Isolation Pilot Plant (WIPP) site. Data interpretation suggests that a multirate mass transfer model provides the best description of the transport of nonsorbing tracers for length scales of a few meters to tens of meters. The application of the model to adsorbing species in the fractured dolomite, however, has been limited by lack of data for relevant apparent diffusion rates into the rock matrix. Crushed-rock column transport experiments are currently being carried out at Sandia to constrain actinide diffusion rates and sorption parameters (retardation factors and partition coefficients) in the Culebra with and without organic complexants. Experiments have been run at two flow rates, using two different sieve fractions of crushed Culebra dolomite (mean grain diameters, 0.23 and 0.65 mm) and using both nonsorbing and sorbing tracers ( $^{22}\text{Na}$  and  $^{232}\text{U}$ , respectively). Tracer concentrations in the effluent are measured by liquid scintillation, with a detection limit  $\sim 5$  orders of magnitude below the initial concentration. Breakthrough curves and eluted tails for square tracer pulses are fitted using STAMMT-L, a linear multirate transport code (Haggerty and Reeves, 1998), assuming a lognormal distribution of diffusion rate coefficients ( $D_a/a^2$ ). Five parameters are used to fit each data set; the mean and standard deviation of  $\ln(D_a/a^2)$ , the capacity coefficient ( $\beta$ ), the retardation factor in the mobile zone ( $R_m$ ), and the Peclet number. To test the robustness of the multirate model, diffusion rates and capacity coefficients derived from separate columns, each with a single size fraction of dolomite particles, will be used to predict the behavior of a column containing a mixture of both size fractions.

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## Rn-222 DIFFUSION IN CRETACEOUS LIMESTONES AQUIFER

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The diffusion of the Rn-222 was studied in waters of high salinity and temperature. This natural aquifer system is developed in geological behavior integrated by cretaceous limestone. This area is located in the part north-center of the Cuban Island. Ra, Rn, Cl, Na, SH<sub>2</sub>, Br and Sr are elements present in this water type.

Track-etch method was used for detection of the Rn-222 in drill hole and surface. The cellulose nitrate plastic detector used, were the LR-115 and CR-39.

The aqueous Rn-222 concentration showed an increasing with depth, until 200000 Bequerels per cubic meter, at 300 meter under surface. In the surface the Rn-222 concentration showed high levels of contamination in water and soils, however, there is a decrease until 95000 Bequerels per cubic meter. Beside that in the surface, was determinated the presence up to 1575 ppm of Ra-226 in nonconsolidated sediment. This higher concentration of Ra-226 in surface increases the gamma ray intensity up to 1200 microrentgen per hour and more. The zone was monitored during 30 days, and showed high level of pollution from natural sources.

The Rn-222 and Ra-226 upward to the surface in a vertical flow from depth, the first in microbubbles of different gas flows and the second inside of interstices of Ca molecules. These waters ascend through microfractures, fractures and fault systems, by hydrostatic pressure.

Finally, when the radon measurements were compared with the diffusional model of radon transport, we found that the results disagree significantly. A model, which includes diffusion and upward flow transport, is necessary to explain the results.

## THE EFFECT OF SHORT TERM AGING ON THE TRANSPORT OF SELECTED ACTINIDES IN SEDIMENTARY SOILS

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Laboratory column studies were performed to investigate the retardation of actinides by sedimentary soil from the Snake River Plain. The objectives of these experiments were to characterize the transport of selected actinides in simulated perched water, to isolate the conditions under which high mobility fractions are observed, and to suggest mechanisms that may be responsible for high mobility fractions. In the column tests, spikes of simulated perched water containing a variety of ligands were introduced into the columns as a finite step of approximately one pore volume. Two sets of experiments were performed – one with a spike which was allowed to age for 24 hours following addition of the actinide and one which was not aged. Experiments were conducted with thorium, uranium, neptunium, plutonium, and americium. Tritium was used as a non-partitioning tracer to evaluate column dynamics and to check for channeling. Column effluent was collected in discrete fractions, and samples were analyzed by liquid scintillation. The resulting breakthrough curves were analyzed by the method of moments to determine retardation factors of peaks appearing in the effluent. For freshly prepared spikes of thorium, neptunium, plutonium, and americium breakthrough curves were generally characterized by a high mobility fraction that ranged from 0.1% to 1% and a moderate mobility fraction that ranged from 4% to 60%. The moderate mobility fraction was largely due to the presence of EDTA and/or colloidal species less than 20 nm. For uranium, the breakthrough curves were characterized by a high mobility fraction of near 100%. In spikes that had aged for 24 hours, americium and thorium breakthrough was reduced to near zero. Uranium breakthrough showed little change. In addition, batch filtration experiments were conducted to verify thermodynamic predictions of insoluble species and to measure the rate at which filterable (> 20 nm) colloids are generated in the spikes. In these experiments, the fraction of the actinide in a colloidal form (> 20 nm) was measured as a function of aging time.

## DANGER OF PLUTONIUM MIGRATION IN ATMOSPHERE IN THE FORM OF VOLATILE OXIDES PuO<sub>3</sub> AND PuO<sub>4</sub> FORMED IN OXIDATION OF DISPERSED Pu IN THE GAS PHASE

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The results of experiments are presented, which were aimed at the preparation of plutonium in the highest oxidation state and evaluation of the possibility of migration of its oxidation products in the atmosphere after nuclear tests and accidents at nuclear power plants. By using a thermochromatographic technique, behaviour of volatile compounds, formed under the heating of trace quantities of <sup>238</sup>Pu and <sup>239</sup>Pu in a stream of helium and oxygen mixture, was studied. The quartz apparatus was used. The concentration of the reagent was changed between 50 and <math>10^{-8}</math> %. The deposition zones were measured using an  $\alpha$ -spectrometer. It was found that under certain conditions plutonium forms three adsorption zones with the centres at  $450 \pm 25^\circ\text{C}$ ,  $250 \pm 25^\circ\text{C}$  and  $-105 \pm 25^\circ\text{C}$ . For interpretation of the obtained results a series of model experiments with carrier-free radioisotopes of <sup>185</sup>Os, <sup>183</sup>Re, <sup>97</sup>Ru and <sup>96</sup>Tc was performed. It was shown that in a stream of helium with a negligible touch of oxygen they were adsorbed at  $450-500^\circ\text{C}$  and at  $250-300^\circ\text{C}$  in the forms of dioxides and trioxides, respectively. Similar results were obtained in the experiments with trace quantities of uranium. Basing on these data we assume that the first adsorption zone ( $450 \pm 25^\circ\text{C}$ ) appears due to formation of PuO<sub>2</sub> and the second one appears due to formation of PuO<sub>3</sub>. Comparison of the <sup>185</sup>OsO<sub>4</sub> and <sup>97</sup>RuO<sub>4</sub> adsorption zones with the third adsorption zone ( $-105 \pm 25^\circ\text{C}$ ) indicates their similarity. It is shown that low concentration of O<sub>2</sub> in the carrier-gas leads to formation of the lower plutonium oxides only, which is also characteristic of Ru and Os. We can make a conclusion that octovalent plutonium has been produced, which in a form of very volatile PuO<sub>4</sub> deposits at a negative temperature. It was concluded that the volatility of PuO<sub>3</sub> is not sufficiently high and it can migrate in the atmosphere only by means of the aerosol transport, while PuO<sub>4</sub> owing to a very high volatility can be transferred in the atmosphere by airflow.

## SOLUTE TRANSPORT PROPERTIES OF COMPACTED Ca-BENTONITE USED IN FEBEX PROJECT

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The present concept of a deep geological high level waste repository includes an engineered clay barrier around the canister. The clay presents a very high sorption capability for radionuclides and a very small hydraulic conductivity, so that the migration process of solutes is limited by sorption and diffusion processes. Therefore, diffusion and distribution coefficients are the main parameters to be obtained in order to characterise solute transport which could be produced after the canister breakdown.

Through-diffusion and in-diffusion experiments with HTO, Sr, Cs and Se were carried out using compacted FEBEX bentonite, which is the reference material for the Spanish concept of radioactive repository. Diffusion and distribution coefficients were simultaneously determined by means of numerical modelling with the CORE\_LE code (Samper et al., 1998). Contrary to the use of analytical solutions for the interpretation of the experiments, automatic parameter estimation using numerical tools allows us to account for the role of synters as well as time-varying boundary conditions. Experimental results show that diffusion coefficients decrease with increasing clay dry density. Distribution coefficients obtained with these experiments are significantly smaller than those obtained from batch experiments. Anion exclusion effects, which can be responsible for the low diffusion coefficients found for  $\text{SeO}_3^-$ , have been also investigated.

## STUDY OF THE INTERACTION OF Pu(IV) AND Np(IV,V,VI) WITH Fe AND SOME OTHER METAL HYDROXIDES TO PREDICT THE BEHAVIOR OF ACTINIDES IN ENVIRONMENTAL MEDIA

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Natural aquatic systems and radioactive waste sludge generally contain high Fe and Al concentrations. Compounds of Fe(III) also are widely used to coprecipitate radioactive elements. Therefore, study of An(IV,V,VI) interactions with multivalent metal hydroxides in neutral and basic aqueous media is useful to understand the behavior of actinides entering soils as alkaline radioactive waste solution by tank leaks.

A Mössbauer effect method was used to study the formation of mixed hydroxides in the alkaline coprecipitation of Pu(IV) or Np(IV) with Fe(III). The Mössbauer spectra of mixed  $^{239}\text{Pu(IV)-Fe(III)}$  and  $^{237}\text{Np(IV)-Fe(III)}$  hydroxide samples differ from that of pure  $\alpha\text{-FeO(OH)}$  formed in aqueous basic solutions. The Mössbauer spectra of Pu(IV) hydroxide and Fe(III) hydroxide samples, precipitated separately and then mixed in water or NaOH solutions with five hours of agitation, also produce spectra differing from the pure  $\alpha\text{-FeO(OH)}$  spectrum but are almost the same as those of the coprecipitated samples. This difference may be explained by the lower symmetry of the oxygen environment of Fe(III) ions in the mixed hydroxides compared with that of pure  $\alpha\text{-FeO(OH)}$  caused by the presence of Pu and Np in the Fe compound structure.

The Pu(IV)-Fe(III) hydroxide results were confirmed by IR spectroscopy and sedimentation. Similar tests of Pu(IV)-Al(III) and Pu(IV)-Cr(III) hydroxides also were performed.

Alkaline coprecipitation of Np(V) or Np(VI) with Fe(III) hydroxides does not produce the mixed hydroxides shown by Pu(IV) or Np(IV) with Fe(III). The general Mössbauer spectral parameters of the Np(V),(VI)-Fe(III) hydroxides are similar to those of pure  $\alpha\text{-FeO(OH)}$ . At liquid nitrogen temperature, however, the spectra of the mixed Np(V) and Fe(III) hydroxides display hyperfine magnetic splitting; the inner magnetic field, 360 kOersted, is much lower than 520 kOersted of pure  $\alpha\text{-FeO(OH)}$  at 110 K. The difference may be caused by the influence of  $\text{NpO}_2^+$  ions' magnetic moment on  $\text{Fe}^{3+}$  ions caused by the very close proximity of these ions. Therefore, though Np(V) and Np(VI) hydroxides adsorb on the Fe(III) hydroxide surface without forming mixed compounds, strong bonding between the ions probably occurs.

In summary, the interaction of actinides with environmental solid phases containing iron or other metal hydroxides seems to depend on the formation of mixed hydroxides or the adsorption of actinides on the metal hydroxide surface. Such interactions can capture actinides from alkaline waste solutions on bulk metal hydroxides and inhibit their further migration into natural aquatic systems.

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## THE EFFECT OF pH ON PLUTONIUM(V) TRANSPORT THROUGH A SANDY ATLANTIC COASTAL SOIL IN A LOW CARBONATE ENVIRONMENT

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Laboratory column tests were conducted to determine the effect of solution pH on the transport of plutonium through a sandy coastal soil from the Savannah River Site. A plutonium spike (as <sup>238</sup>Pu(V)) of approximately one displaced pore volume was introduced into 1.5 cm diameter by 8.3 cm long columns packed with the 250 – 420 mm soil size fraction. The tests were conducted with low-carbonate aqueous solutions of 0.02 M NaClO<sub>4</sub> at pH 3, pH 5, and pH 8. Following each spike, the columns were eluted with the unspiked solution for 10 – 600 pore volumes at a mean linear velocity of 0.008 cm/s, and plutonium concentrations were measured as a function of time in the effluent. Filtration analyses and oxidation state analyses were performed on selected effluent fractions. At the end of each test, the spatial distribution of plutonium remaining in the column was also measured. At each pH, multiple forms of plutonium, each with a distinct mobility, were observed. The breakthrough curves were all characterized by a well defined peak in which the average retardation factor, R, and the fractional breakthrough varied with pH. At pH 3, 90% of the plutonium emerged with a retardation factor of 1.4; at pH 5, 75% emerged with a retardation factor of 8.4; and at pH 8, 38% emerged with a retardation factor of 38. The experimental breakthrough curves were compared to predictions of the coupled transport/equilibrium speciation code BLTEC. In the code, sorption was based on a diffuse layer surface complexation model, and three approaches were evaluated for approximating the reactive mineral surfaces. In the first, the reactive was kaolinite, in the second it was iron (oxy) hydroxide, and in the third it was a mixture of kaolinite and iron (oxy) hydroxide.

## MIGRATION OF PLUTONIUM IN PRESENCE OF EDTA

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Subsurface contamination due to the mixed wastes is a problem at many DOE sites such as Hanford and Savannah River sites. Mixed wastes usually consist of radionuclides such as plutonium, cesium, strontium and organic chelating agents like NTA, EDTA and DTPA.

The nature of interactions between contaminants and soil has a major impact on contaminant migration in the subsurface. It is well known that EDTA forms stable and highly soluble complexes with plutonium; for example Pu(III)-EDTA, Pu(IV)-EDTA, Pu(V)-EDTA, Pu(VI)-EDTA have stability constants  $\log K$  estimated to 18.2, 25.6, 12.9 and 16.39, respectively. These high stability constants make the Pu-EDTA very mobile in the environment.

To better understand the effect of EDTA on the fate, transport and remediation of plutonium in DOE sites, laboratory experiments have been performed. The contaminant systems we selected are Pu(III) and Pu(IV)-EDTA to investigate how the presence of EDTA will affect the transport of Pu through soils.

The sorption experiments have been carried out in batch-series as a function of the soil mass. The concentration of Pu was kept constant at  $10^{-6}$  M and the pH was adjusted to 5. The ratio of Pu to EDTA was 1:1.

The diffusion study was carried out using a diaphragm cell at atmospheric pressure and temperature and at pH ~5. The initial Pu concentration was  $10^{-6}$  M. The ratio of Pu to EDTA was also 1:1. This study was carried out as a function of time until all systems reached steady-state conditions.

Measurements from the sorption and diffusion studies allow us to evaluate the distribution coefficient  $K_d$  and diffusion coefficients  $D$  for the selected systems.

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## LABORATORY SCALE APPROACHES FOR MEASURING RADIONUCLIDE RETARDATION ON CRYSTALLINE ROCK

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In transport models, radionuclide retardation has been usually taken into account by the  $K_d$  concept, in which a retardation factor is used to apply the distribution ratio to radionuclide transport. Determination of the retardation factor by the means of fracture flow experiments is a direct approach to application of the effects of sorption in radionuclide transport models. However, different static and dynamic approaches for measuring the interaction between radionuclides and rock matrix are needed in order to test the compatibility of experimental retardation parameters and transport models used in assessing the safety of the underground repositories for the spent nuclear fuel. In this work transport and retardation of sodium ( $^{22}\text{Na}$ ), calcium ( $^{45}\text{Ca}$ ), strontium ( $^{85}\text{Sr}$ ) and cesium ( $^{134}\text{Cs}$ ) was studied in rock fracture columns and in crushed rock columns with different fraction sizes. The rock samples representing different rock features and porosities were mica gneiss, unaltered, moderately altered and strongly altered tonalite taken from hole SY-KR7 drilled in the Syyry area in Sievi in western Finland. Radionuclide retardation in column experiments was estimated by use of retardation factor which was determined as the ratio of tracer velocity to groundwater velocity. Flow conditions in the columns were determined using tritiated water and chloride ( $\text{HTO}$ ,  $^{36}\text{Cl}$ ) as non-sorbing tracers. The mass distribution ratio values for each fraction have been determined earlier using the static batch and thin section methods. The sorption of tracers onto different minerals was observed using rock thin sections and autoradiographic methods. In this paper mass distribution ratio values determined from dynamic fracture and crushed rock column experiments and static batch and thin section experiments are summarized.

## LOT -*IN SITU* DIFFUSION TESTS USING RADIOACTIVE TRACERS

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An experiment series at Äspö Hard Rock Laboratory, called "Long Term Test of Buffer Material", LOT, was carried out at Äspö Hard Rock Laboratory to validate models of clay buffer performance at standard KBS-3 repository conditions, and to quantify clay buffer alteration processes at adverse conditions. In conjunction with the tests of the bentonite, cation diffusion tests using cesium and cobalt were performed.

38 cylindrical blocks of bentonite clay with a hole in the middle were placed around a copper rod in a vertical hole at a depth of 450 meters. Four identical cylindrical bentonite plugs were doped with 1 MBq  $^{57}\text{Co}$  and  $^{134}\text{Cs}$ , respectively, and inserted in the fifth block from the bottom. The system was left to be saturated with ground water before heating of the central copper rod started to simulate the thermal activity of radioactive waste.

The experiment continued for 14 months before the bentonite blocks were drilled out using over-core drilling technique. The lowest blocks were cut up, sparsely in the outer layer, and in cubic centimeters big samples closer to where the activity was inserted. All samples were analyzed using a gamma spectrometer to get a three dimensional picture of the activity distribution. The system was then fitted to a diffusion model to obtain apparent diffusivities for the two cations.

The apparent diffusivity for cobalt agrees well with those obtained in other *in situ* experiments and in laboratory studies, while the value for cesium is lower than expected. This can be due to that the clay was not fully water saturated during the experiment.

## EXPERIMENTAL INVESTIGATION AND MODELING OF CITRIC ACID EFFECTS ON ACTINIDE SPECIATION AND TRANSPORT

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The transport of radionuclides in saturated porous media is governed by element speciation and the processes that act to transport those species. Dissolved organic matter constitutes an important actinide complexing ligand pool in natural water systems, yet its effects on actinide speciation and transport are still not fully understood. Using citric acid as an organic matter surrogate in batch equilibrium experiments and column experiments, we examine the role organic ligands play on actinide speciation and transport.

The sorption of Th(IV) to hematite and U(VI) to hematite and quartz sand in the absence and presence of citric acid was studied as a function of pH, ionic strength, ligand concentration and solid/solution ratio in a series of batch equilibrium experiments. The sorption of citric acid to hematite and quartz sand as a function of pH was also examined over a range of ligand/mineral ratios. Surface complexation modeling (SCM) techniques were employed to evaluate these systems and to provide insights into actinide speciation and actinide/ligand/mineral interactions.

In the column experiments, solutions containing U(VI) and citric acid were introduced to columns packed with a quartz sand. Our experimental results show that U(VI) transport may be enhanced by the presence of citric acid, depending on system conditions such as pH and U(VI)/citric acid ratio. Employing SCM results from the batch experiments, U(VI) transport simulations were obtained using a reactive transport code which incorporates an SCM with transport equations. The coupled SCM/transport model improved our ability to accurately simulate the effects of uranium/citrate complexes on U(VI) transport relative to the use of distribution coefficients or isotherms to quantify actinide/sorbent partitioning.

## THE INFLUENCE OF GRAVEL ON SEDIMENT DISTRIBUTION COEFFICIENTS AND RETARDATION FACTORS

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Standard measurements of solute sorption to sediments are typically made on the <2-mm fraction of a sediment. This fraction is used by researchers to standardize the method, and to ease experimental protocol, whereby large labware would not be required to accommodate the gravel (>2-mm particles). Because sorption is a phenomenon directly related to surface area, it is likely that sorption measurements [i.e., Kd values] based on the <2-mm fraction would overestimate whole sediment values, especially for sediments containing large proportions of gravel. This is a problem for groundwater contaminant transport modelers who attempt to use laboratory-derived sorption values, typically expressed as a distribution coefficient (Kd), to calculate the retardation factor (Rf), a parameter that accounts for solute-sediment interactions. The objectives of this study were to determine: 1) the effect of gravel on Kd and Rf values, and 2) the best method to calculate gravel-corrected Kd values (Kdgc). One experiment involved measuring Sr Kd values for various size fractions of eight gravel-containing sediments. The second experiment involved measuring Sr sorption to sediments amended with varying amounts of gravel. Three calculated Kdgc concepts were evaluated: a correction based on surface area (Kdgc-s), a correction based on the assumption that the gravel had no sorption capacity and simply diluted the Kd<2mm (Kdgc-g=0), and a correction based on the assumption that the Kd of the intact sediment (Kdt) was a composite of the Kd<2mm and the Kd>2mm (Kdgc-g=x). On average, Kd<2mm tended to overestimate Kdt by 25%, whereas Kdgc-g=x overestimated Kdt by only 5%, and Kdgc-g=0 underestimated Kdt by only 10%. Similar comparisons of Rft to Rf values calculated using the various Kdgc values and their respective bulk density and porosity values followed similar trends. In summary, the Kd values and Rf values based on the sorption of the <2-mm and gravel fractions (Kdgc-g=x) provided the best estimate of actual values (Kdt). However, a slightly less accurate, but much more readily available correction, is to assume that the gravel has no sorption capacity (Kdgc-g=0). This correction would be an improvement over traditional estimates based on the Kd<2mm and would provide, unlike the Kd<2mm, a conservative estimate with respect to risk assessment calculations. This work has significant implications regarding the traditional approach to modeling contaminant transport using Kd<2mm values because such calculations may not be truly conservative and may overestimate the ability of sediments to retard contaminant migration.

## APPARENT DIFFUSION COEFFICIENTS AND CHEMICAL SPECIES OF NEPTUNIUM (V) IN COMPACTED NA-MONTMORILLONITE

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Diffusion of neptunium (V) in compacted Na-montmorillonite was studied by the non-steady state diffusion method. In this study, two experimental attempts were carried out to discuss the diffusion mechanism of neptunium. One was the determination of the activation energy for the diffusion. The activation energy was used to discuss the diffusion process in the montmorillonite. The other was the estimation of the chemical species of neptunium in the montmorillonite by a sequential batch extraction treatment.

In the diffusion experiments, purified Na-montmorillonite was compacted and saturated with deionized water in a cell. Then, a 10  $\mu\text{l}$  tracer solution ( $^{237}\text{NpO}_2^+$  in 2M  $\text{HNO}_3$ ) was applied to the montmorillonite. The cell was kept at a constant temperature between 288 and 323 K under the atmosphere. After a prescribed period, the montmorillonite was cut into 0.5 mm-thick-slices. They were mainly used to determine the apparent diffusion coefficients. Some of the slices picked up at a certain interval of the distance from the diffusion source were subjected to a sequential extraction treatment. The montmorillonite slices were contacted with deionized water for extracting the solubilized neptunium species in pore water of the montmorillonite, with 1M KCl for extracting the  $\text{NpO}_2^+$  adsorbed on the montmorillonite, and with 1M HCl for extracting the residual species of neptunium.

The apparent diffusion coefficients of neptunium in the montmorillonite at dry density of  $1.0 \text{ Mg m}^{-3}$  were  $3.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  at 288 K to  $9.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  at 323 K. The activation energy for the neptunium diffusion at dry density of  $1.0 \text{ Mg m}^{-3}$  was  $17.8 \text{ kJ mol}^{-1}$ ; this value is similar to those reported for diffusion of other ions in free water (e.g.  $18.4 \text{ kJ mol}^{-1}$  for  $\text{Na}^+$  and  $17.4 \text{ kJ mol}^{-1}$  for Cl). The fractions of the neptunium in the montmorillonite slices obtained by the sequential treatment were similar to each other and independent of the distance from the diffusion source. Approximately 15% of the neptunium was extracted with deionized water, approximately 75% with 1M KCl, and the remainder with 1M HCl. Diffusivity and chemical species of neptunium (V) in compacted Na-montmorillonite will be discussed from both kinetic and thermodynamic data obtained in diffusion and desorption experiments, respectively.

## DIFFUSION MECHANISM OF CHLORIDE IONS IN SODIUM MONTMORILLONITE

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For safety assessment of the geological disposal of HLW, it is necessary to study diffusion mechanism of radionuclides in compacted bentonite. Activation energy is an important parameter to clarify the diffusion mechanism of radionuclides; e.g. the activation energy must be constant and also be almost equal to that in free water if diffusion in liquid phase is predominant in the system.

In the previous study[1], we reported that the activation energy for diffusion of chloride ions in compacted Na-montmorillonite increased from 13.5 to 25.1 kJ mol<sup>-1</sup> as the dry density of montmorillonite increased from 1.0 to 1.8 Mg m<sup>-3</sup>. These findings suggested that other diffusion mechanisms than the liquid phase diffusion were predominant for chloride ions in compacted montmorillonite. However, diffusion mechanism was not discussed in detail there.

Here we therefore discuss the diffusion mechanism of chloride ions in compacted Na-montmorillonite with new experimental data on the activation energy at lower dry densities. The activation energies obtained here were 17.4, 15.0, 15.2 and 15.6 kJ mol<sup>-1</sup> at dry densities of 0.7, 0.8, 0.9 and 1.1 Mg m<sup>-3</sup>, respectively. From the results in both the previous and present studies, the activation energy was found to be minimum at dry density of 1.0 Mg m<sup>-3</sup>; it decreased from 17.4 to 13.5 kJ mol<sup>-1</sup> as the dry density increased from 0.7 to 1.0 Mg m<sup>-3</sup>, while it increased at dry densities above 1.0 Mg m<sup>-3</sup>. Similar change in activation energy was also found for diffusion of Na<sup>+</sup> ions[2].

The basal spacing of water-saturated montmorillonite was determined by X-ray diffraction method. The basal spacing of 1.88 nm, corresponding to three-water layer hydrate state, was not observed until the dry densities increased up to 1.0 Mg m<sup>-3</sup> where the minimum activation energy was obtained. According to the conventional diffusion model for ions in compacted clay, chloride ions have been considered to diffuse predominantly in liquid phase since chloride ions were excluded by electrostatic forces from clay surfaces where negatively charged. These findings, however, indicate that the diffusion of chloride ions cannot be explained only by the diffusion in liquid phase, and also suggest that close relationship between the activation energy and the basal spacing. In this study, diffusion mechanism will be discussed in detail from the viewpoint of unique changes in the activation energy and basal spacing of montmorillonite, with dry density of montmorillonite.

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## THE INFLUENCE OF HUMIC SUBSTANCES ON THE MIGRATION OF RADIONUCLIDES $^{85}\text{Sr}$ , $^{237}\text{Np}$ and $^{238}\text{Pu}$ IN A SHALLOW UNCONFINED AQUIFER, A FIELD COLUMN EXPERIMENT

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The influence of humic substances on the migration of radionuclides in geological formations has been well recognized and a considerable amount of laboratory experiments has been conducted focusing on the complexing reactions of radionuclides with humic/fulvic acid and the adsorption behavior of radionuclides under the existence of humic substances, while scarce data of field experiments has been reported. Generally, the influence of humic substances on the migration of radionuclides in geological formations depends highly on the chemical composition of the corresponding media, however field experiments would provide useful site specific data to explain the real situation. In this paper, the result of a field column experiment investigating the influence of humic substances on the migration of radionuclides  $^{85}\text{Sr}$ ,  $^{237}\text{Np}$  and  $^{238}\text{Pu}$  in a shallow unconfined aquifer is described. Radionuclides with and without humic substance (different layers) were introduced at the center of two-section undisturbed aquifer columns and the columns were installed horizontally into an unconfined aquifer. The aquifer water flows naturally through the columns for 1.5 years and the columns are sliced to determine the distribution of these radionuclides in the columns.

## DETERMINATION OF THE MIGRATION PARAMETERS OF RADIONUCLIDES IN CLAYEY SOILS BY ELECTROMIGRATION

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Studies of the migration behaviour of radionuclides are essential for the performance assessment studies of a geological disposal of HLW. In Belgium, the Boom Clay is studied because of its excellent properties to restrain radionuclides of migrating into the biosphere.

For low permeability soils (clays), diffusion experiments are often time consuming. To reduce the experimental time, an electrical field is used as a very effective force to accelerate the migration of ionic species. The apparent molecular diffusion coefficient can be calculated from the apparent dispersion coefficient and the total apparent convection velocity obtained from an electromigration experiment.

From the velocity of the migrating species, corrected for electroosmotic flow, the apparent molecular diffusion coefficient can be calculated according to the relation of Einstein. But also from the linear relationship between the apparent dispersion coefficient and the total apparent convection velocity the apparent molecular diffusion coefficient can be calculated. The main advantage of electromigration is that by the time reduction, more experiments can be performed in a shorter time increasing considerably the statistic reliability. The tests are run at different electrical fields, covering a wide range of convection velocities. Because of the linear relationship between the total apparent convection velocity (or electrical field) and the apparent dispersion coefficient, we have a third independent way to obtain the apparent molecular diffusion coefficient as the intercept of the curve.

Apparent molecular diffusion coefficients are determined for  $^{85}\text{Sr}^{2+}$  ( $0.8 \times 10^{-11} \text{ m}^2/\text{s}$ ),  $^{131}\text{I}^-$  ( $14 \times 10^{-11} \text{ m}^2/\text{s}$ ), HTO ( $24 \times 10^{-11} \text{ m}^2/\text{s}$ ),  $^{22}\text{Na}^+$  ( $6.5 \times 10^{-11} \text{ m}^2/\text{s}$ ),  $^{45}\text{Ca}^{2+}$  ( $0.8 \times 10^{-11} \text{ m}^2/\text{s}$ ),  $^{137}\text{Cs}^+$  ( $0.01 \times 10^{-11} \text{ m}^2/\text{s}$ ),  $^{14}\text{CH}_3\text{NH}_3^+$  ( $1.3 \times 10^{-11} \text{ m}^2/\text{s}$ ) and  $^{14}\text{C}$ -labelled Dissolved Organic Matter ( $0.5\text{-}3.3 \times 10^{-11} \text{ m}^2/\text{s}$  depending on the size and charge of the organic material fraction).

The results clearly demonstrate the wide applicability (cationic, anionic, neutral and colloidal radionuclides) of the technique for the determination of migration parameters in clayey soils.

## IODIDE DIFFUSION THROUGH CLAYSTONES. ANIONIC EXCLUSION

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The iodide (I<sup>-</sup>) diffusive behaviour is studied in host claystones which may be used for the geological disposal of radioactive waste. We use a radiotracer process (Na<sup>125</sup>I + NaI) with the throughout diffusion cell method in order to determine the effective diffusion coefficient ( $D_e$ ) and the accessible porosity ( $\epsilon$ ). These techniques are based on the acquisition of flux data and the resolution of the Fick's first law. The main experimental conditions are : constant temperature, representative synthetic water, either oxic or anoxic atmosphere. Different experiments were run with various iodide concentrations between  $10^{-8}$  and  $10^{-1}$  mol/l. A tritiated water diffusion (HTO) was also realized for each sample.

We are investigating the iodide behaviour in two types of indurated argillaceous formations (siltites from Gard site, France; shales from East site, France). In each location, diffusion coefficient and accessible porosity of water and iodide are given from several core samples.

The iodide effective diffusion coefficient are lower than those of water. The negative charge on the surface of the clay platelets linked with the small size of pores reduce the iodide flux by anionic exclusion. We have also to take into account the size of the I<sup>-</sup> ion.

The effective diffusion coefficient does not vary linearly with the iodide concentration. But the general observed tendency is an increase of the effective diffusion coefficient with the increase of the concentration. A large part of this effect is due to an increase of the accessible porosity which may be explained by a decrease of the thickness of the double layer in high concentration of NaI.

## DIFFUSIVE-CONVECTIONAL Cs<sup>137</sup> TRANSFER IN POROUS MEDIA

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Local failures and cracks (pores) degrading containers and concrete disposal facilities shielding result in contamination of the ground water with dissolved radionuclides which can migrate over large distances far from repository. In many cases radionuclides transport is mainly restricted by the convection, and intensity of convection can be significantly reduced when micro porous materials are applied as the retardation buffer layers (clay, loam) in the interior of the repository and out of the disposal facility. If pores diameters are less than 1mm the convection process contribution to total nuclides flow is comparable with diffusion transfer and the mass transport is restricted by diffusion process in subporous media. The main parameter to characterise the diffusive-convectional transport is effective diffusion coefficient  $D_{\text{eff}}$  equal to the sum of molecular (real) diffusion coefficient  $D_0$  and so called convective diffusion coefficient  $D_c$ . The technique of molecular diffusion coefficient analysis in water solutions of Cs\*Cl was developed. This technique is based on <sup>137</sup>Cs distribution measurements along the capillary cell by Ge (Li) detector  $\gamma$ -spectrometer.  $D_0$  was determined to be in 11 – 42 C temperature interval with values in range from  $1.24 \cdot 10^{-5}$  (cm<sup>2</sup>/c) to  $3.08 \cdot 10^{-5}$  (nm<sup>2</sup>/c). Accounting liquid flow velocity (Darcy) definition and values the convective diffusion coefficient  $D_c$  and  $D_{\text{eff}}$  can be estimated. The obtained results permit to predict the nuclides migration in porous geological medium.

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## ADVECTIVE DIFFUSION EXPERIMENT USING I, Se, AND Cs IN FRACTURED ROCKS

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Advective diffusion of I, Se, and Cs in fractured rock was experimentally determined. As a fracture, 100  $\mu$  m-gap was artificially made between two granite blocks (2 $\times$ 4 $\times$ 20cm). Distilled water was injected through the fracture at a rate of 100~300  $\mu$  l/hr for a month. After stabilizing the flow rate, solutions containing non-sorbing tracer (inactive I and Se), and sorbing tracer (Cs-134) were injected into the fracture at the same flow rate. The inlet concentration was 1000 mg/l for I, and Se. For Cs, 1 mg/l of inactive Cs containing about 130 Bq/cc of Cs-134. The effluent solutions at the outlet were collected and analyzed for determining the concentration of these tracers. The period of the tracer injection was about a half month. After the injection period, the granite blocks were separated. The blocks were cut off perpendicularly to the fracture surface. The distribution profiles of Se and I on the cutting section were analyzed by ion micro analyzer (IMA). The Cs-134 activity distribution along the fracture was measured by  $\gamma$ -spectrometry. The breakthrough curves showed that Cs was more retarded than I and Se due to the sorption of Cs on the fracture surface. From the profiles of Se and I, these tracers penetrated into the granite to the depth of more than 10<sup>-1</sup>m. This implied that matrix diffusion occurred during the experiment. The diffusion and sorption properties of these tracers were estimated by a model including advection, diffusion, dispersion, sorption and matrix diffusion. The apparent diffusion coefficients in the rock matrix were evaluated 4.3 $\times$ 10<sup>-11</sup>, 1.5 $\times$ 10<sup>-11</sup>, and 3.1 $\times$ 10<sup>-14</sup> m<sup>2</sup>/sec for Se, I, and Cs, respectively. The distribution coefficients estimated from the apparent diffusion coefficients were nearly zero for Se, and I, and about 10<sup>-2</sup> m<sup>3</sup>/kg for Cs, respectively. These results indicated that the effect of matrix diffusion is important for transport of I and Se in fractured rocks.

## EXPERIMENTAL AND MODELING STUDIES ON SORPTION AND DIFFUSION OF RADIUM IN BENTONITE

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It is necessary to understand sorption and diffusion behavior of radionuclides in compacted bentonite for the performance assessment of geological disposal of high-level radioactive waste. Here, sorption and diffusion behavior in bentonite of  $^{226}\text{Ra}$  identified as one of the most hazardous radionuclides was studied by batch sorption and in-diffusion experiments. Results were interpreted by using the relevant sorption and diffusion models.

Sorption experiments of radium on sodium bentonite(Kunigel V1<sup>®</sup>) and purified sodium smectite were carried out by batch method over a wide range of conditions in which pH, ionic strength of solution and liquid to solid ratio were varied. Radium was contacted with these solids in distilled water and 0.1M-NaCl solution for about 30 days in an argon glove-box at room temperature. Liquid to solid ratios were 500 and 50 ml g<sup>-1</sup> and pH of solutions was controlled in the range of 7-11. Sequential desorption experiments with 1M-KCl and HCl solutions were also conducted after the sorption experiments. The distribution coefficients(Kd) obtained for both solids were in the range of 10<sup>2</sup> to 10<sup>4</sup> ml g<sup>-1</sup>. The tendency of parameter effects on Kd values was the same for both solids, pH and liquid to solid ratio had little effect, ionic strength had significant effect. The desorption experiments indicated that most of sorbed radium was extracted by 1M-KCl. The results for purified sodium smectite were interpreted by using a model considering ion exchange and surface complexation reaction, and reaction constants between radium and smectite were obtained. The model considering the presence of impurities in addition to the above reactions interpreted the results for bentonite. The experimental and modeling results suggested that sorption behavior of radium existing mainly as Ra<sup>2+</sup> ion was dominated by ion exchange reaction with layer cations in smectite.

Diffusion experiments of radium in compacted bentonite were carried out by in-diffusion method under aerobic condition at room temperature. Bentonite was compacted to dry densities of 1.4 and 1.8 g cm<sup>-3</sup> and saturated with distilled water and 3%-NaCl solution. The apparent diffusion coefficients (Da) were in the range of 1.7–9.0 x 10<sup>-12</sup> m<sup>2</sup> s<sup>-1</sup> and decreased with increasing dry density. The Da values obtained in bentonite saturated with NaCl solution were lower than those in bentonite saturated with distilled water. The Kd values in compacted bentonite were derived from measured Da and effective diffusion coefficients (De) calculated by the diffusion model taking into account to electro-chemical interaction between smectite surface and aqueous chemical species. The sorption behavior in compacted bentonite was discussed by comparison with the application of the above sorption model.

## **RADIONUCLIDES IN GROUNDWATER: A STUDY OF THE 1976 NUCLEAR TEST CHESHIRE**

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The Nevada Test Site (NTS) situated in southern Nevada provides a unique location to study radionuclides in an underground environment. After a nuclear test, radioactive material remains incorporated in melt glass, deposited on rock surfaces, dissolved in groundwater and even present in the gaseous state. Once groundwater has filled the cavity produced by the explosion, dissolution, sorption and desorption, precipitation and colloid formation reactions may take place. We are particularly interested in observing those processes that may lead to transport of radionuclides via groundwater. In February 1976 the Cheshire nuclear test was conducted at a depth of 1167 m, about 540 m below the standing water level, in bedded rhyolite tuffs and fractured lavas at the NTS. We began studying the radionuclide distribution at this site four months later and since then have been periodically sampling the water from the level of the explosion cavity as well as higher in the overlying collapse chimney. In 1983-85 we pumped over 104 m<sup>3</sup> of water from the cavity horizon; in 1985-87 a like amount of water was pumped from a transmissive horizon in the chimney 400 m above the cavity. In 1987-8 we pumped several hundred m<sup>3</sup> of groundwater from an exploratory well drilled some 300 m down gradient from the Cheshire test which intercepted the upper transmissive horizon. We have measured a variety of gaseous, refractory and soluble radionuclides in the pumped groundwaters. Notably, Cheshire was the first site at the NTS where colloid transport of radionuclides was documented. In 1998, we revisited this site to investigate the speciation of longer-lived radionuclides identifiable after 20 years. We observed significant differences in the concentrations and characteristics of radionuclides between the cavity and chimney horizons considered earlier. Studies at the Cheshire site provide a unique opportunity to document the distribution of radionuclides within and adjacent to large, deep underground nuclear tests conducted in permeable rock. These data are vital to efforts to both develop and validate models of radionuclide migration in groundwater.

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## ESTIMATION OF RETARDATION PARAMETERS FOR RADIONUCLIDES THROUGH CLAY CORE PERCOLATION EXPERIMENTS IN BOOM CLAY

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We report the results of long term (1~10 years) percolation experiments under both in situ and laboratory conditions in Boom Clay cores for the following radioisotopes:  $^{75}\text{Se}$ ,  $^{99}\text{Tc}$ ,  $^{233}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ , and  $^{238}\text{Pu}$ . The significant observation is that the measured concentrations at the outlet of the percolation cells reached steady values for most of the radioisotopes after short time. According to these outlet concentrations, we can categorise the studied radionuclides into three groups: (1) Se and Tc with an outlet concentration of  $\sim 10^{-8}$  mol/l; (2) U and Np with an outlet concentration of  $\sim 10^{-10}$  mol/l; and (3) Am, Cm, and Pu with an outlet concentration of  $\sim 10^{-13}$  to  $10^{-14}$  mol/l. In combination with solubility and speciation calculations, this can be interpreted as: (1) Se and Tc are respectively present in Boom Clay as anions and neutral species without sorption onto clay surfaces so that their outlet concentrations are solubility limited; (2) U(IV/VI) and Np(IV) seem weakly sorbed and/or solubility limited; (3) Am, Cm and Pu are trivalent and strongly complexed with natural organics on clay surfaces so that their outlet concentrations are extremely low. The observed outlet concentrations are very useful information for a performance assessment (PA) because these are the concentrations at which radionuclides migrate to the far field. We therefore applied a  $K_d$  concept for a column experiment to define a range of retardation factors,  $R$ , using the information of the outlet concentrations and the solubilities. We concluded that a conservative approach for PA is to consider all radionuclides as non-retarded species, *i.e.*,  $R = 1$  with an operational solubility which equals the outlet concentration. The advantage of this approach is that we could reduce the uncertainties of migration parameters by means of these high quality, reproducible, long term lab. and *in situ* measurements. The results of this study also demonstrated that in an organic rich clay formation like Boom Clay, organic matter plays an advantageous role, instead of a disadvantageous role as it is generally accepted, for retarding radionuclides migration.

## DIFFUSION OF STRONTIUM IN BENTONITE IN THE PRESENCE OF HUMIC COLLOIDS

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Diffusion of radionuclides in compacted bentonite is studied extensively today. Groundwater saturating the bentonite surrounding the copper canisters capsulating the spent fuel contain dissolved organic carbon(DOC). Humic acid is a major part of the DOC and can form colloids with high specific surfaces with high negative charge in neutral pH. Consequently the humic colloids are potentially strong complexing agents for radionuclides. Humic acid is also known to facilitate for redox reactions and change the radionuclides speciation. The diffusion behavior and mobility of radionuclides can therefore change in the presence of humic acid.

Diffusion of strontium in bentonite in the presence of humic colloids has been studied. This study was setup to determine the effect of complexation with humic colloids on strontium mobility. A series with diffusion experiments through compacted bentonite has been performed in different environments. The experiments were carried out with a factorial design by varying the pH, the Sr and humic concentration. An experimental domain was stretched out where complexation between Sr and humic colloids is realistic and where the environment is imitating a natural environment in a deep bedrock repository for spent nuclear fuel. Sixteen diffusion cells were coupled to an inlet and an outlet reservoir. All inlet solutions contain 0.1 M NaClO<sub>4</sub> within pH range 7-8, Sr within concentration range 10<sup>-6</sup>-10<sup>-4</sup> M and humic acid within concentration range 0-0.2 g/l. Initially the outlet solutions contained 0.1 M NaClO<sub>4</sub>. The breakthrough of strontium was studied by monitoring the strontium activity in the outlet by  $\gamma$ -spectrometry using a germanium detector and multi-channel analyzer. The fluxes and time lag through the bentonite plugs were analyzed to:

- determine if the complexation of radionuclides with humic colloids change the mobility.
- determine if the complexation is favored by high strontium or humic concentration.
- determine the influence of pH on the mobility of complexes through bentonite.

## A POSITIVE CORRELATION BETWEEN THE EFFECTIVE DIFFUSIVITY OF Ba<sup>2+</sup> IN GRANITE MATRIX AND ITS SORPTIVITY

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Contribution of the surface diffusion or diffusion in the sorbed state has been mentioned occasionally to explain unexpectedly high diffusivity of cations in water-saturated geological media. In order to provide new evidence to support the hypothesis of the surface diffusion, a series of through-diffusion experiments have been performed for Ba<sup>2+</sup> in a granite from Inada, Ibaraki, eastern Japan.

A 5-mm thick, 40-mm diameter granite disk was sealed into an acrylic diffusion cell with a silicone gasket to eliminate any gap between the rock disk and the acrylic cell surface. The granite disk was soaked in deionized water under vacuum to remove all air from the interconnected pores. The diffusion cell was filled with a working solution (10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup> or 10<sup>-4</sup> mol/dm<sup>3</sup> BaCl<sub>2</sub> solution) under atmospheric pressure to pre-condition the disks for the solution for 30 d. A source solution containing <sup>133</sup>Ba<sup>2+</sup> and <sup>125</sup>I was prepared and was placed in the source reservoir to start the diffusion experiment. The diffusion experiments were performed in triplicate for each BaCl<sub>2</sub> concentration at 25 °C in a water bath.

In the diffusion experiments using the 10<sup>-2</sup> mol/dm<sup>3</sup> BaCl<sub>2</sub> solution, the effective diffusivity (D<sub>e</sub>) of (1.95-0.21) × 10<sup>-13</sup> m<sup>2</sup>/s and the rock capacity factor (ε+ρK<sub>d</sub>) of 0.210-0.018 were obtained. The 10<sup>-3</sup> mol/dm<sup>3</sup> BaCl<sub>2</sub> solution produced the larger D<sub>e</sub> and the larger (ε+ρK<sub>d</sub>) of (2.58-0.38) × 10<sup>-13</sup> m<sup>2</sup>/s and 0.56-0.07, respectively. We obtained the largest D<sub>e</sub>, (6.6-0.7) × 10<sup>-13</sup> m<sup>2</sup>/s, and the largest (ε+ρK<sub>d</sub>), 1.26-0.08, for the 10<sup>-4</sup> mol/dm<sup>3</sup> BaCl<sub>2</sub> solution. The D<sub>e</sub> values obtained for the most concentrated solution of BaCl<sub>2</sub>, 10<sup>-1</sup> mol/dm<sup>3</sup>, were largely scattered between the triplicate run, and further discussion was not made. The effective diffusivity of I, non-sorbing species, was not affected by BaCl<sub>2</sub> concentrations; (6.1-0.8) × 10<sup>-13</sup>, (8.4-1.4) × 10<sup>-13</sup> and (6.7-2.5) × 10<sup>-13</sup> m<sup>2</sup>/s for 10<sup>-2</sup>, 10<sup>-3</sup> and 10<sup>-4</sup> mol/dm<sup>3</sup> BaCl<sub>2</sub> solution, respectively. The results for I show that the physical property of the pore structure was almost the same between the experiments, and accordingly the variation in D<sub>e</sub> of Ba<sup>2+</sup> was not physically caused.

The effective diffusivity of sorbing species increased as the sorptivity (ρK<sub>d</sub>) increased in our experiment. This fact is strongly indicative of surface diffusion.

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## MIGRATION AND SORPTION BEHAVIOUR OF URANIUM IN THE BOOM CLAY

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Performance assessment studies on the direct disposal of spent fuels in a clay formation have clearly indicated that uranium isotopes and their daughters would be the main contributors to the total dose at very long term. So, it is particularly important to correctly understand and to predict in a reliable way the migration behaviour of uranium in the Boom Clay Formation, the main barrier of the disposal system presently studied in Belgium.

A main concern arises from the dual behaviour of uranium under the reducing conditions prevailing *in situ* in the Boom Clay. Both tetravalent and hexavalent oxidation states of uranium might coexist according to the large uncertainties in the thermodynamical data of uranium and in the true value of  $E_h$  in Boom Clay (measurements between -250 mV and -400 mV). On one hand, U(VI) complexed by carbonate is very soluble and able to migrate in Boom Clay as the large, but unretarded, anion  $UO_2(CO_3)_3^{4-}$ . On the other hand, U(IV) solubility could be controlled by both crystalline  $UO_2$  ( $\sim 10^{-10}$  M) or amorphous  $U(OH)_4$  ( $\sim 10^{-4}$  M), while the resulting soluble neutral species  $U(OH)_4$  could be only slightly retarded if the complexation of U(IV) with the organic matter immobilized at the clay minerals surface should play a minor role.

Percolation experiments on undisturbed clay cores indicate a permanent leaching of uranium at concentrations increasing progressively from  $10^{-11}$  M to  $10^{-10}$  M. Up to now, to explain this behaviour, we cannot distinguish between a poorly soluble but unretarded species and a more soluble but retarded species. A combination of a low solubility and a small retardation factor has been selected to estimate realistic, but still conservative, migration parameters needed for new performance assessment calculations (Wang et al., this issue).

To address the problems of solubility and sorption of uranium at the critical ratio of U(IV) / U(VI) prevailing under *in situ*  $E_h$  conditions, various reduction techniques have been used to prepare tetravalent uranium: dithionite, Walden and Jones reductants, and electroreduction at a controlled potential. The solubility values vary from  $5 \cdot 10^{-6}$  to  $5 \cdot 10^{-4}$  M and strongly depend on the reduction technique. Batch sorption tests with U(IV) and U(VI) were also performed with  $^{232}U$  and  $^{233}U$  both on Boom Clay and pure pyrite, the main sink expected for uranium in Boom Clay beside apatite.  $K_d$  of U(VI) on Boom Clay increases with solid to liquid (S/L) ratio and with organic matter concentration, a behaviour opposite to this of trivalent europium in Boom Clay.

## EXPERIMENTAL INVESTIGATION OF RADIONUCLIDE TRANSPORT THROUGH FRACTURED, HYDROTHERMALLY ALTERED CONCRETE

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Transport of <sup>233</sup>U and <sup>237</sup>Np through fractured, hydrothermally altered concrete was examined to assess the feasibility of locating a high level waste facility at Yucca Mountain, NV. Pulses of radionuclide and colloid-bearing solutions were eluted through a concrete core. To prepare the core for the experiments, a fracture was induced and the core was reacted at 200 °C for 8 months in 3 mM NaHCO<sub>3</sub>. We identified the mineralogy of the altered core to assist in interpretation of the transport experiment data. Major phases in the altered core include calcite, dolomite, and quartz; minor phases include the calcium silicate hydrate minerals scawtite, tobermorite, and xonotlite, and layer silicate clays tentatively identified as smectite and serpentine.

Fractions of effluent from the transport experiments were analyzed for radionuclides, colloids, iodide, and other dissolved constituent concentrations. We used a combination of analytical techniques, including liquid scintillation counting, laser breakdown spectroscopy, fluorimetry, an ion selective electrode, ion chromatography, inductively coupled plasma spectroscopy, potentiometric pH measurement, and acid/base titration. Following the transport experiments, the core was removed and examined using SEM, SIMS, and alpha-autoradiography.

No radionuclides, and very low levels of colloids, were detected in the effluent. Effluent [U] may be limited by the low solubility of CaUO<sub>4</sub>; Np may be sorbed onto calcite. Colloids may be trapped in the core by fibrous mineral structures observed on the fracture surface. The complex alteration of the fracture surface and the colloid blockage suggest that fractures in hydrothermally altered concrete may be self-sealing. Our results indicate that concrete of this mineralogy is an effective sink for U and Np, even when fractured.

## U-SERIES DISEQUILIBRIA IN A GROUNDWATER FLOW ROUTE AS AN INDICATOR OF URANIUM MIGRATION PROCESSES

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Uranium concentration and isotopic activity ratios ( $^{234}\text{U}/^{238}\text{U}$  and  $^{230}\text{Th}/^{234}\text{U}$ ) in groundwater and adjoining rock matrix along a groundwater flow route were studied to obtain information of U migration processes. The flow route is situated in fractured granitic rock, in near surface environment (0-150 m) and in the vicinity of U deposit. Groundwater samples were taken from packered sections in five drill holes along the proposed flow route. Most samples show clearly oxidic conditions (200 to 400 mV) whereas the deepest ones display redox potentials close to zero. The pH varied from near surface values 6.5-7.5 to over 8 deeper in the flow route. Fracture coatings (mainly calcites) and bulk rock samples, taken from the corresponding drill cores, were studied to obtain information of the processes in the long-term. Although the relatively fast groundwater transport time through the flow route is indicated, the results show two generations of dissolved U. In the whole rock samples, taken as a function of distance from fracture face into the rock, intense and very recent U leaching is indicated by the U concentration and the Th-230/U-234 activity profiles. Deeper in the flow route considerable preferential leaching of U-234 from both calcites and the whole rock can be observed, suggesting a very long-term continuous U removal. In the studied flow route net U leaching in the long-term can be indicated.

## CONTRIBUTION OF BIOSORPTION IN THE BEHAVIOUR OF RADIONUCLIDES IN THE ENVIRONMENT

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Micro-organisms, in particular bacteria, have a significant influence on the speciation and migration of radionuclides and toxic metals in both aquatic and terrestrial ecosystems by the way of several physico-chemical and biological mechanisms. One of them is biosorption. The aim of this presentation is the study of the contribution of bacteria in the behaviour of radionuclides in the near field of a nuclear waste storage located at surface or in subsurface sites.

We chose to determine the biosorption of uranium (VI), nickel, technetium (VII) and caesium, by *Pseudomonas aeruginosa* (PA), *Thiobacillus intermedius* (TI) and a mixed population of micro-organisms represented by an activated sludge (AS). The strains of pure cultures are representative of populations isolated from a variety of borehold laboratories in the world.

The aqueous media selected were deionized water at pH 7, 8 and 13, clay water and cement water.

The results of the experiments with the pure strains at pH 7 showed that PA fixes up to 344 nmol U per mg of dried biomass but only up to 34 nmol Ni, under the same conditions. Uranium shows a stronger affinity for the parietal layer of PA than nickel. The same phenomenon is observed in the case of TI with respectively 465 nmol U mg<sup>-1</sup> and 5 nmol Ni mg<sup>-1</sup>. Moreover, TI adsorbs more uranium than PA but in the case of the Ni we found the opposite. These studies point out that biosorption is function of the cation chemistry and of the composition the structure and the nature of the bacterial layers. We do not found any biosorption for technetium and caesium under these conditions.

In clay water, we show a significant inhibition effect of the carbonate and sulphate ions on, respectively, the uranium and nickel biosorption. The aerobic or anaerobic AS are principally used in the case of the biosorption studies at pH 13 in deionized water and cement water. These experiments point out the favourable effect of the presence of cations from the IA and IIA column for the fixation of uranium species: the biosorption capacity varied by a factor 5.

Finally, the presence of soluble biopolymers influence the biosorption, two washing steps of the AS lead to a factor 2 of increase in the fixation capacity.

For the caesium we have study the bioaccumulation capacity for mix population in a dynamic system, represented by a biofilm growth of glass beads.

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# MIGRATION '99

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## THE ROLE OF SUBTERRANEAN MICROBES AS BIOCOLLOIDS IN THE TRANSPORT OF ACTINIDES AT THE WASTE ISOLATION PILOT PLANT AND GRIMSEL TEST SITE

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Microorganisms may affect the long-term stability and mobility of radionuclides disposed of in deep geological formations. Of particular concern is the association of radionuclides with microbial cells and transport of radionuclides as biocolloids by subterranean microorganisms. We examined the total and respiring microbial populations in two groundwater samples: one from the Culebra dolomite member of the Rustler Formation at the Waste Isolation Pilot Plant (WIPP), NM and the other from the granitic formation at the Grimsel Test Site (GTS), Switzerland. Transuranic waste is slated for disposal in the deep (658 m below land surface) geologic salt formation at the WIPP. The GTS is a research facility for the European radioactive waste disposal concept. Groundwaters from the Culebra dolomite formation, ~200 m below land surface, and the GTS, ~450 m below land surface, were collected using sterile techniques. Bacterial populations were enumerated by epifluorescence microscopy and bacterial cell size by microscopy and image analysis. The response of the microbial populations to nutrient addition (carbon and nitrogen) was also determined. Culebra groundwater (ionic strength 2.8 M, pH 7) contained  $1.02 \pm 0.49 \times 10^5$  cells ml<sup>-1</sup>, with a mean cell length of  $0.82 \pm 0.14$  μm and width of  $0.66 \pm 0.14$  μm. In contrast, low ionic strength groundwater (0.001 M, pH 9) from GTS contained  $3.97 \pm 0.37 \times 10^3$  cells ml<sup>-1</sup>, with a mean cell length of  $1.50 \pm 0.16$  μm and width of  $0.37 \pm 0.13$  μm. The addition of appropriate nutrients to the groundwaters stimulated the growth of aerobic, facultative (denitrifying), fermenting, and sulfate reducing microorganisms. The cell surface functional groups that may be involved in actinide complexation were determined by potentiometric titration. Actinide biosorption studies with two isolates, a denitrifier from the Culebra and an anaerobic culture (*Acetobacterium* sp.) from GTS showed that under optimum conditions at pH 5, and a cell density of 108 cells ml<sup>-1</sup>, the cultures biosorbed  $180 \pm 10$  and  $70 \pm 2$  mg uranium g<sup>-1</sup> dry weight of cells, respectively. These results suggest that the bacteria in the groundwater at the repository sites are capable of bioaccumulating actinides to varying degrees and therefore the potential exists for the biocolloidal transport of actinides in the subsurface.

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## THE IMPORTANCE OF HUMIC SUBSTANCES AND THEIR CHARACTERISATION IN ENVIRONMENTAL GEOCHEMISTRY : IMPLICATIONS FOR ACTINIDE MOBILITY

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Much previous work has demonstrated the importance of humic substances for actinide binding in both soils and sediments. It is now increasingly recognised, however, that the more traditional mode of investigation via strong base/strong acid extraction may be too extreme and hence unrealistic. In contrast with such approaches, an important part of our studies has been to develop softer chemical isolation procedures and to investigate interactions of actinides with fractions of humic material rather than a bulk extract. This approach has the potential, therefore, to provide more detailed information about the nature and environmental behaviour of the humic molecules involved in binding.

Our previous work has shown that gel electrophoresis can effect simultaneous extraction and fractionation of humic substances from aqueous suspensions of soils. These extracts comprise relatively hydrophilic humic molecules but fractionation also indicates a range of size/charge/shape. In view of the potential importance of humic-actinide binding for actinide mobility, this work has focused on U, Pu and Np associations with electrophoretically separated fractions of soil humic substances.

Soil blocks (30 cm x 30 cm x 30 cm) were excavated from two forests (one deciduous and one coniferous) and were cut into 1-cm slices. Selected samples were suspended in aqueous buffer (0.050 M Tris-HCl; pH 8.5), placed in electrophoresis wells and humic substances extracted and fractionated under identical conditions (agarose gel (1% w/v); 0.045 M Tris-borate running buffer (pH 8.5); 75 V; 1 h). Each gel was subdivided, using a custom made stainless steel cutter, into 10 slices. The humic extracts (in triplicate for each sample) were obtained by centrifugation after freeze-thaw treatment of the gel. This procedure has been repeated with soil samples pre-equilibrated with <sup>236</sup>U, <sup>242</sup>Pu and <sup>237</sup>Np, respectively, at pH values close to that of the soil solution (~4). All fractions were prepared for analysis by ICP-MS (2% HNO<sub>3</sub>; VG PQ3 with S-option). The distribution of natural and spike U, Pu and Np will be compared.

The analytical work has also included a multi-technique approach (CHN, UV/vis, FTIR, alkalimetric titration, ultrafiltration/size exclusion etc.) to characterisation of the humic fractions obtained either by gel chromatographic or electrophoretic separation in order to establish key features of important fractions.

## INFLUENCE OF CELLULOSE DEGRADATION PRODUCTS ON THE SORPTION OF URANIUM AND EUROPIUM TO A SANDY COASTAL PLAIN SOIL

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The presence of natural organic matter (OM) has been known to affect the speciation and mobility of metals and radionuclides in the subsurface. The degradation of cellulosic material (e.g., paper and wood products) leads to the formation of natural OM. Therefore, co-disposal of cellulosic material with radionuclides in near-surface burial trenches can significantly influence transport of the radionuclides from these facilities.

A series of laboratory studies were initiated to investigate the influence of cellulosic degradation products (CDP) on europium and uranium sorption to a sandy coastal plain soil and kaolinite respectively. CDP are a complex mixture of many organic compounds and previous studies have only been able to identify several percent of the total organic carbon as easily identifiable compounds. Because of these complexities and the obvious analogies between burial trench degradation of cellulosic materials and those found in forested ecosystems, naturally occurring dissolved OM isolated from the Suwannee River was used as a surrogate for CDP expected in near-surface burial trenches.

The approach of using lanthanides or rare earth elements as chemical surrogates for the trivalent actinides ( $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ , and  $\text{Cm}^{3+}$ ) is well established. Use of the divalent ( $\text{UO}_2^{2+}$ ) and trivalent ( $\text{Eu}^{3+}$ ) species provides insight into the influence of valence on nuclide behavior.

Uranium (as  $\text{UO}_2^{2+}$  at  $10^{-6}$  M) sorption studies were completed using Suwannee River OM (0-30 mg C/L) and kaolinite (3.3 g/L). Europium (as  $\text{Eu}^{3+}$  at  $10^{-6}$  M) sorption studies were completed using the same OM (0-500 mg C/L) and soil collected in Aiken, South Carolina (1g clay/L). Kaolinite is the major type of clay in the Aiken soil.

Results show that both pH and organic matter have a significant influence on Eu and U sorption in this study. In the case of U, an OM concentration of 10mg C/L enhanced the sorption by 65% at pH 4 as compared to no OM. In both cases, maximum sorption was 100% above pH 5.5. Increasing the OM concentration to 30 mg C/L also enhanced sorption below pH 4.5. Above that pH, sorption was decreased by up to 50%. In the case of Eu, a steep sorption edge occurred between pH 3 and 4 in the absence of OM. Maximum sorption was 100%. In the presence of 500 mg C/L, the sorption of Eu was slightly enhanced at pH 3, and was decreased by up to 60% at pH 6.

In order to validate the dissolved OM surrogate method, actual CDP were generated in the laboratory. Identical tests using the CDP, soil, and Eu were performed. Results from these tests will be discussed.

## MODELING THE SORPTION OF URANIUM (VI) TO GRAM-NEGATIVE BACTERIA

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The transport of metal ions through water saturated soil or rock is often dominated by the sorption of the metal ions to surfaces. A potentially important, but neglected, surface in this type of system is bacterial cells. This study focuses on modeling the sorption of uranium (VI) to the surface of *Desulfovibrio vulgaris*, a gram-negative sulfate reducing soil bacterium. Gram-negative bacteria differ from the more commonly modeled gram-positive bacteria in that along with sorption of metal ions to the outer membrane, ions can diffuse through porins into the periplasmic space of gram-negative bacteria. Traditional techniques used to model the sorption of metal ions to charged surfaces combine complexation chemistry with an electric double layer model to account for the electrostatic charge of the surface. An assumption in electric double layer models is that the surface is a flat, non-porous plane; however, bacterial surfaces consist of a porous three-dimensional matrix of polysaccharides and proteins, which contain a variety of functional moieties. To model bacterial surfaces we have invoked the Donnan model, which treats the cell as a separate phase from the bulk and accounts for the presence of inert electrolyte ions in the porous matrix of charged functional groups in a physically realistic manner. The time dependent behavior of acid/base titrations of live bacteria is analyzed to estimate the quantity and character of functional groups present and to quantify the diffusion of ions into the cell. Uranium sorption edges and sorption kinetic data were generated and modeled by first correcting sorption and titration data for diffusion and then using surface complexation modeling coupled with the Donnan model. The sorption of uranium (VI) to gram-negative bacteria is highly dependent on pH and carbonate concentration. Uranium sorption increases with increasing pH until a sorption maximum is reached at ca. pH 6 and then decreases with increasing pH as non-sorbing uranium-carbonato species start to dominate the solution chemistry.

## SPECIATION OF IODIDE IN NATURAL WATERS: ROLE OF ORGANIC MATTER

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The presence of organic matter such as humic substances (humic and fulvic acids) in natural waters may affect the behavior of radiotoxic elements in the geosphere. Indeed these organic substances possess important complexation properties towards the metallic elements and present an affinity for the mineral surfaces. Moreover, due to their colloidal form, they can contribute to the migration of the radioelements. Numerous results obtained in our laboratory concerning different humic substances, have evidenced their strong affinity for trace elements. In particular, our recent results obtained using neutron activation analysis and X-ray emission, have reported non negligible iodine concentrations in natural humic substances. Iodine is an important element since the <sup>129</sup>I is a long-life fission product of <sup>235</sup>U, and because it is principally under the I<sup>-</sup> form (so potentially mobile) in natural waters. Our work is devoted to the understanding of the associations between the humic substances and iodine (role of the organic matter, nature of the interaction mechanisms). The effect of the presence of humic acids on the iodine retention on a mineral surface is followed, considering a ternary system (silica/iodine/humic acid). The nature of functional groups of the humic substances able to trap the iodine is also researched. Nuclear microanalysis techniques permit to quantify the thickness of the organic matter and the concentrations of the associated trace elements. X-ray Photoelectron Spectroscopy (XPS) can evidence the chemical environment of the trace elements. Our results obtained by XPS on model molecules containing iodine (aromatic and aliphatic compounds, potassium iodide) have displayed that it is possible to determine the chemical environment of iodine and particularly to discriminate ionic from covalent bonds. These preliminary data are actually applied to the analysis of various humic substances containing different iodine contents.

## ACCUMULATION OF URANIUM BY ARTHROBACTER SIMPLEX AND BACILLUS SABTILIS

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Standard strains of *Arthrobacter simplex* and *Bacillus subtilis* were examined for their ability to accumulate uranium from solutions. The batch equilibrium metal sorption studies used 20-mg (dry-basis) of wet cell samples resuspended in 25 ml of uranium-bearing solution of ionic strength 0.1 M (NaCl) and known initial metal concentration. The pH of the reaction mixtures were adjusted to 4 or 6 and were controlled within  $\pm 0.1$ .

Both microorganisms showed similar sorption characteristics. The uptake of uranium by these microorganisms was rapid, reaching equilibrium within 12 hours. Uranium was effectively removed from the solution at initial uranium concentrations up to several hundreds  $\mu\text{M}$ . Further, it was found that the sorption was affected by pH. The uranium sorption isotherm at pH 4 was compatible with a Langmuir isotherm and a sorption capacity of around 500  $\mu\text{M/g}$  was obtained. At pH 6, on the other hand, no definite saturation was observed within the solubility limit of uranium and, the sorption isotherm was compatible with a Freundlich isotherm. In addition, at low uranium concentration, the uranium uptake at pH 4 was higher than that at pH 6 indicating that low molecular weight organic ligands, released from the cell, may have a significant role in stabilization of uranyl ions in aqueous phase. The role of such extra-cellular ligands becomes less significant at higher uranium concentrations.

## COLLOIDAL PARTICLES PRODUCED BY SULFATE-REDUCING BACTERIA AND SULFIDE-OXIDIZING BACTERIA: TEM/AEM STUDY

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Selenium ( $^{79}\text{Se}$ ) is a fission product of nuclear fuel with a half-life time of 65000 years. Oxidative alteration of spent nuclear fuel will result in the formation of selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ) oxy-anions together with uranyl oxy-cation in solution. Sorption of the anions on clays and other minerals are extremely low. Because they are chemically and radiologically toxic, it is important to immobilize the aqueous selenium and uranyl species.

Sulfate-reducing bacteria are able to reduce sulfate and other oxidized oxy-anions such as selenate, selenite, and uranyl ( $\text{UO}_2^{2+}$ ) etc. In general, the reduction potentials of redox pairs (at pH 7) utilized by bacteria are within the range of -0.7 eV to +1.36 eV. Transmission electron microscopy (TEM) results from the systems containing selenate and selenite with a sulfate-reducing bacteria of *Desulfovibrio desulfuricans* show that yellow spherical (Se,S) sub-micro crystals precipitated outside the cell. Amorphous-like Se-rich spherical particles may also occur inside the bacteria cell. The bacteria is more active in the solution containing selenite than in the solution containing selenate. It is proposed that the Se-rich particles are at the periplasmic region between outer membrane and plasma membrane (Tomei et al., 1995). Similar features (U-oxide nano-crystals) also occur in the *Desulfovibrio desulfuricans* bacteria that have reduced uranyl ions (Barton et al., 1995).

Photoautotrophs *Chromatium* spp. are able to oxidize sulfide ( $\text{S}^{2-}$ ) by using light. The bacteria grown in sulfide- and selenide-bearing system show amorphous-like (S,Se) globules inside the cell. The position of the (S,Se) globules is same as that of Se-rich particles inside the *Desulfovibrio desulfuricans* bacteria. Compositional zonation in the (S,Se) globules occur in *Chromatium* spp. collected from a selenate-bearing pond.  $\text{S}^{2-}$  may be from the products of sulfate-reducing bacteria. It is proposed that the S-rich zones formed during day (bacteria active) time, and the Se-rich zones formed during night (less active) time. The *Chromatium* bacteria prefer S more than Se. It is proposed that both *Desulfovibrio desulfuricans* and *Chromatium* bacteria are able to immobilize and collect the oxidized selenium (either selenate and/or selenite) and uranyl in the forms of elemental selenium and reduced U-compound.

## BIOTRANSFORMATION OF URANIUM IN BRINE BY A DENITRIFYING HALOPHILIC BACTERIUM UNDER ANAEROBIC CONDITIONS

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Biotransformations of ionic, and inorganic and organic complexes of uranium were investigated under anaerobic (denitrifying) conditions, using nitrate as an electron acceptor, by a halophilic bacterium (*Halomonas* sp.) isolated from the Waste Isolation Pilot Plant (WIPP) repository environment in order to assess the role of microbes in the colloidal transport of actinides at WIPP. The WIPP repository is a US Department of Energy facility designed to demonstrate the safe, permanent disposal of transuranic waste from defense-related activities. The addition of uranyl nitrate, uranyl citrate, or uranyl ethylenediaminetetraacetate (EDTA) to bacterial growth medium (succinate, nitrate, phosphate, and yeast extract in 4M NaCl) resulted in the precipitation of uranium. Characterization of the precipitate by extended X-ray absorption fine structure (EXAFS) analysis at the U L<sub>III</sub> edge showed the formation of predominantly uranyl phosphate species. The bacterium metabolized citrate released from the complex, but not the released EDTA. Complexed U-citrate was not metabolized by the bacterium. Dissolution of the U precipitate occurred concomitant with an increase in bacterial growth. Characterization of the solubilized U in the culture medium by UV-vis spectrophotometry and by EXAFS showed the formation of uranyl carbonate species due to production of CO<sub>2</sub> from bacterial metabolism. Addition of uranyl carbonate to the growth medium did not result in precipitation of U. The bacterium neither biosorbed nor bioaccumulated the uranyl carbonate species in solution because of the neutral or anionic nature of the complex. These results show that microbial activity can affect actinide solubility, but the association of actinides with suspended bacteria, and the formation of actinide-biocolloids, is determined by the speciation and bioavailability of the actinide.

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## MIGRATION OF LONG-LIVED RADIONUCLIDES IN SOIL

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The main objects of studies were  $^{137}\text{Cs}$  normally produced in nuclear explosions and in the core of nuclear reactors and cobalt radionuclides which are priority objects of studies in the Uzbekistan nuclear research center, located near Tashkent.

Determined: distribution coefficient defined as the ratio of the equilibrium radionuclide concentration in solid phase to that in solution; fraction of the total amount of the adsorbed radionuclide in soil; the state of radionuclides in the soil studied; the rate of convective transfer of radionuclides by moisture; diffusion coefficients.

Distribution coefficient for radionuclides in the soil, of the average loamy greyish type have been found to be in the range of 100-120  $\text{cm}^3/\text{g}$  for Cs, 180-210  $\text{cm}^3/\text{g}$  for Co. Measurements were carried out at normal humidity.

It was shown that 97% of cesium in soil is in adsorbed state, of this ~70% is in inexchangeable, and ~25% in exchangeable states and 5% in the state soluble in water. Cobalt radionuclides (~28%) are in adsorbed state, being basically in exchangeable and (5%) in water soluble forms.

We have studied spatial and time distribution of radionuclides in soil and have developed a model of their migration in soil of arbitrary profile in time after a single event of surface pollution.

## THE LONG-LIVED ARTIFICIAL RADIONUCLIDES IN THE LITTORAL AQUATORIUMS OF THE FAR EAST AND NEAR NOVAYA ZEMLYA

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The man-made radiation sources connected with the atomic navy were investigated in three regions. Concentrations of artificial radionuclides  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  were studied in sediments from Ussuriskiy Golf where at 10.08.1985 an accident on atomic U-boat take place. Concentration of  $^{137}\text{Cs}$  up to 50 Bk/kg of dry sediments was measured. In 3 samples of sediments  $^{60}\text{Co}$  with concentration up to 14 Bk/kg was found.

The average concentration of  $^{137}\text{Cs}$  for samples (they were sampled in 1989 and 1993 years) is  $22 \pm 4$  Bk/kg. The concentration is significant more then the average concentration of  $^{137}\text{Cs}$  (about 7 Bk/kg) in sediments of Baltic Sea. It may be compared also with the radionuclide inventories in the Seto Inland Sea where the average concentration of Cs-137 is  $\sim 4$  Bk/kg. Two probes were analyzed on the concentration of  $^{239}\text{Pu}$ .

The measurement for 5 samples of sediments (sampled in 1993 year) from Kalashnikov Bay (Kamchatka peninsula) demonstrated about the same concentrations of  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ . The significant concentration of  $^{60}\text{Co}$  denotes the permanent source of the man made radionuclides in both aquatoriums. In connection with our estimations radioecological significant may be only  $^{60}\text{Co}$ .

The third region is St. Anna Trough near Novaya Zemlya. Several probes from the trough were sampled in 1994 and investigate mainly for the measurements of the concentration of  $^{239}\text{Pu}$  and  $^{238}\text{Pu}$ . In one place the very intensive line of  $^{238}\text{Pu}$  was found. The high relative concentration of  $^{238}\text{Pu}$  may show that the source is not the atmospheric nuclear testing. The average concentration of  $^{137}\text{Cs}$  in the sediments is 2 - 3 Bk/kg. This is normal for the region. The radioecological problems may arise if the source of  $^{238}\text{Pu}$  (and  $^{239}\text{Pu}$ , of course) will be accelerating the activity.

## DISTRIBUTION OF $^{226}\text{Ra}$ , $^{210}\text{Pb}$ AND $^{210}\text{Po}$ IN THE VENICE LAGOON (ITALY)

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Phosphogypsum is the by-product resulting from phosphoric acid or phosphate fertilizer production. The phosphate ore used in these chemical processes contains the naturally occurring radioactive material U and all its subsequent decay products.

Large volumes of solid waste products were discharged from phosphoric acid production plant at the margin of the Venice lagoon (Italy). Dissolved and particulate  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in this aquatic environment show different distribution and patterns.

Water, suspended matter and biota were monitored in the Venice lagoon and in the Adriatic Sea, because these environments would be considered the final reception areas of radionuclides transported from inland. This monitoring activity allowed to identify different areas in the lagoon: the inner part characterized by fine sediments and enriched in  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  concentration; the outer part nearby the lagoon inlet, where marine water exchanges prevail, characterized by sandy sediments and low  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  contamination.  $^{226}\text{Ra}$  from eroded particles dissolves in the lagoon and contributes to increased concentrations of dissolved  $^{226}\text{Ra}$  in the brackish water.

As a results of these processes, the brackish water flowing into the coastal sea contains enhanced concentrations of  $^{226}\text{Ra}$ , but it depleted in dissolved  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  due to the rapid sorption of these radionuclides on the settling particles. Bottom sediments in the lagoon represent a sink for  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  from the industrial waste release.

## ENVIRONMENTAL MIGRATION OF LONG-LIVED RADIONUCLIDES FROM THE MINING AND MILLING OF URANIUM ORE

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The uranium mine and mill at Zirovski vrh (RZV), Slovenia stopped mining and milling in 1990. The facilities consist of an underground mine, a mill and several deposits of mining and hydrometallurgical wastes. During the operational period the ore was crushed and leached with sulphuric acid. The mill tailings containing about 20 % moisture were transported to the disposal site called Borst. These tailings are deposited on a sloping area and consist of sands and slimes less than 28 mesh and contain on average 8600 Bq kg<sup>-1</sup> Ra-226, 3900 Bq kg<sup>-1</sup> Th-230 and 1000 Bq kg<sup>-1</sup> U-238. The tailings dump incorporates a system of capillary or wick drainage to capture and collect maximum amounts of moisture from the tailings deposit and discharge the water via a channel to the river. Spoils and lower grade ores were disposed of on the waste pile called Jazbec. In the form of layers among the thicker layers of spoil so-called red mud is also present. The red mud comes from liming of spent liquors in the milling process and consists mainly of fine precipitates of calcium sulphate and metal oxides, containing more than 60,000 Bq kg<sup>-1</sup> Th-230 and 1500 Bq kg<sup>-1</sup> Pa-231. These radionuclides are highly radiotoxic. To divert background and underground waters, polyethylene pipelines, a drainage system and a concrete outlet channel were placed at the bottom of the pile. However, the pipes are squeezed and disconnected by the weight and the whole drainage system is damaged. Waters of the diverted Jazbec brook and possibly groundwater seep through the pile and leach its constituents, which contaminate the outflow. In this work a study of leaching and migration of the radionuclides U-238, Th-230, Pa-231, Ra-226, Pb-210 and Po-210 from the waste piles is described. For determination of radionuclides, gamma and alpha spectrometry, neutron activation analysis and liquid scintillation techniques were used. Increased activities of uranium and radium in the Jazbec brook were determined in water, while in sediment increasing activities of Th-230, Ra-226, Pb-210 and Pa-231 was obtained. The water and sediment from the Borst waste disposal recently contain higher activities of radium, uranium and Pb-210 relative to the operating period.

## EVIDENCE FOR RE-DISTRIBUTION OF ATMOSPHERICALLY DERIVED RADIONUCLIDES DEPOSITED AT NY-ALESUND (SVALBARD)

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Many pollutants of anthropic origin (e.g. trace metals, organochlorine derivatives, radionuclides) are deposited in arctic regions. To assess the extent of their possible effects on biotope it is necessary to determine their inventory as well as their accumulation rates. Direct pollutants fluxes measurements in arctic terrestrial or aquatic ecosystem are onerous and/or impractical. Therefore the study of deposition pattern on soil, vegetation and aquatic sediments could be a reasonable alternative. In particular dated sediments may allow us to examine temporal scales by measuring contaminant fluxes. However this chance could be affected by local alterations of geomorphology. The Svalbard islands geomorphology includes mountain chains, sedimentary plains, rocky areas and lowlands in which the soil layer is missing or very small. The determination of the activity and of the distribution of some natural and artificial radionuclides ( $^7\text{Be}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ ,  $^{(238, 239+240)}\text{Pu}$  and  $^{241}\text{Am}$ ), in the area under investigation, form the basis for a better understanding of the transfer of contaminants from the drainage basin to the aquatic system and make it possible a better accuracy in stratigraphic temporal reconstruction of sedimentary deposits. Other interesting related topics are the study of radionuclides diffusion mechanism, the determination of long-range transport of pollutants, the environmental persistence of organic contaminants and the transfer of pollutants along the trophic chain. Preliminary data indicate a large variability in the inventories of unsupported  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and other fall-out radionuclides. Data regarding the sampling campaign conducted during August 1997 at Ny-Alesund on the southern side of Kongsfiorden ( $78^{\circ}55'\text{N}$ ,  $11^{\circ}56'\text{E}$ ) form the basis of this paper.

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## **RADIOCAESIUM MIGRATION IN SOIL: TEMPORAL AND ENVIRONMENTAL DEPENDENCE OF DISTRIBUTION**

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The  $^{137}\text{Cs}$  distribution is studied in selected areas in Greece during 1998 in relation to the Chernobyl deposition on April 1996. The regional averages of  $^{137}\text{Cs}$  in the main land Greece during 1996 varied between 1.3 and 30 kBq m<sup>-2</sup> according to the local weather conditions and environmental parameters. Nevertheless, local maxima up to 100 kBq m<sup>-2</sup> were observed especially in Northern Greece, the area with the strongest impact of the Chernobyl radioactive cloud. Considering the concentrations of  $^{137}\text{Cs}$  in soil samples, a wide spectrum of values (4 – 210 Bq kg<sup>-1</sup>) were observed in the sampling network covered the administration regions of the Greek main land. As regards the measurements of  $^{137}\text{Cs}$  12 years later we can notice that, in general, no horizontal migration of  $^{137}\text{Cs}$  in the undisturbed regions were observed, whereas transfer of  $^{137}\text{Cs}$  through special environmental processes (e.g. soil erosion) were observed in selected areas. Considering the vertical migration of  $^{137}\text{Cs}$ , more than 80% of the  $^{137}\text{Cs}$  measured in the sediment core was distributed in the 0 - 20 centimeter layer.

## NUCLIDES MIGRATION FEATURES IN EXTERNAL NUCLEAR DISPOSAL FACILITIES REGIONS

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Theoretical model substantiating observed contamination mechanism basing the data analysis of radioactive contamination distribution in unsaturated zone in the vicinity of near surface disposal «Buryakovka» in Chernobyl exclusion zone is proposed. The model is developed taking into account the following assumptions:

1. Water movement in near field region of disposal (hosted rocks) is supposed to be anisotropic occurring mainly in zones characterized by high permeability (cracks, lithologic contacts).
2. Zones characterizing by high permeability have low absorption.

Observed alternation of non-contaminated and contaminated zones (the last are usually small if compare with the first) which are formed on sorption barriers at high permeability zones feathering-out or on local redox barriers prove the proposed assumptions.

Assessing the results obtained the conclusion was made on possible exceed of real velocity nuclides intake in ground water if compare with most conservative predictive models.

## SELECTIVE SORPTION, FIXATION AND BIOAVAILABILITY OF $^{137}\text{Cs}$ IN SOIL

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Presented are physico-chemical models of radiocaesium mobility and bioavailability in soil based on long-term laboratory and field experimental studies. Mechanisms of radiocaesium selective sorption and fixation are discussed. Experimental data on capacity of selective sorption sites and exchangeable radiocaesium interception potential ( $\text{RIP}^{\text{ex}}$ ) in soils and bottom sediments are presented. Diffusional model of radionuclide fixation in soil is proposed and tested against the experimental data. An equilibrium model of radiocaesium soil-to-plant transfer is applied to parameterise the transfer factor according to environmental characteristics. The model describes the processes of ion exchange and sorption-desorption (selective and regular) on soil, ion exchange on the root exchange complex and transfer from the root surface to other parts of the plant. It is shown that the radiocaesium soil-to-plant transfer factor is a linear function of the bioavailability factor. The latter depends on the exchangeability, the exchangeable radiocaesium interception potential ( $\text{RIP}^{\text{ex}}$ ) and the ion composition of the soil solution. The model has been tested with experimental data measured in different geographic and climatic conditions. A dynamic model of the radiocaesium soil-to-plant transfer in forests is also described. This model allows consideration of the role of fungi mycelium and mycorrhizae as mediators of the radiocaesium transfer to plants.

## SORPTION AND PARTITIONING OF I-129 IN THE NATURAL ENVIRONMENT

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Solid, low-level radioactive wastes from industrial, academic and medical applications have been stored in trenches at the Chalk River Laboratories, AECL. The trenches overlie a groundwater flow system in unconsolidated sands, glacial tills and permeable very-fine to fine-grained sands overlying bedrock which ultimately discharges into a swamp comprised of approximately 3 m of sphagnum peat and underlying sands. Groundwaters flowing through these trenches and into the aquifer have generated a contaminant plume having chemical characteristics of a dilute, sanitary landfill leachate containing C-14 (DOC, DIC), tritium (HTO) and levels of I-129 which are elevated above present-day precipitation levels of approximately  $10^7$  atoms I-129/litre water. Groundwaters sampled from several, multi-level piezometers transecting the flow system, core samples of recharge-site sands and discharge-site peats and samples of vegetation and air have been analyzed for their stable I, I-129, tritium and C-14 contents, C-13/C-12 ratios and anions/cations to characterize the general hydrochemistry of the system and to obtain information on the distribution of I and I-129 in the local environment. Recharging and discharging groundwaters within the contaminant leachate plume are tritium- and C-14 enriched and have elevated concentrations of I and I-129 up to 67 ppb and  $828 \times 10^9$  atoms I-129/litre water, respectively. Correlations are observed amongst the nuclides in the contaminant plume, particularly between tritium, I and I-129. Over the length of the flow system, there is a decrease in the concentration of I and I-129 by a factor of approximately 2 to 8 suggesting partial uptake of iodine during groundwater migration processes. Leach experiments on the recharge-area sands and discharge-area peats yield average soil/water  $K_D$  values for I-129 of approximately 10 and 285, respectively, with the bulk of the I-129, and to a smaller extent, I, loosely bound to solid coatings on aquifer solids and lesser amounts easily exchangeable with chloride-rich solutions. Measured I-129 concentrations in vegetation in the discharge areas suggest foliar uptake of a gaseous I component. The results from this study are amongst the first to provide in-situ measurements of I-129 adsorption on aquifer materials and indicate that iodine is partially volatilizing in the discharging groundwaters and sequestered by vegetation. An empirical mass balance, based on the field data, suggests that approximately 19 % of the total I-129 has been adsorbed onto the aquifer solids and up to 18% has accumulated in plants in the discharge area.

## SPECIATION OF Cs-137, Sr-90, Pu-239,240, Pu-238 AND Am-241 IN CHERNOBYL SOIL

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Migration of radionuclides depending on their chemical and physical properties was investigated. Speciation of  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{239,240}\text{Pu}$ ,  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  was determined in soil samples collected in the 30 km zone around the Chernobyl Nuclear Plant. The Chernobyl soil was sampled in December 1994 on the left bank of the Pripiat river about 15 km from Chernobyl NPP. Two soil cores (5 cm in diameter) were taken at 7 cm depth and sectioned at 1 cm. For the study of speciation, 7 layers of 1cm were used. For the investigation of radionuclides chemical forms the sequential extraction was carried out. The following extractants were used and subsequent characterisations are: 0.05  $\text{CaCl}_2$  (exchangeable and water-soluble), 0.5M  $\text{CH}_3\text{CO}_2\text{H}$  (specifically adsorbed), 0.1M  $\text{Na}_4\text{P}_2\text{O}_7$  (organically bound) 0.175M  $(\text{CO}_2\text{NH}_4)_2$ /0.1M  $(\text{CO}_2\text{H}_2)$  (oxide bound),  $\text{HF}/\text{HNO}_3$  (residual) and  $\text{H}_2\text{O}$ , (water-soluble);  $\text{MgCl}_2$ , pH 7.0, (exchangeable); 1M  $\text{NH}_4\text{Cl}$ , pH 7.0, (exchangeable); 1M  $\text{NH}_4\text{Ac}$ , pH 5 (HAc), (carbonate bound); 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% HAc, (oxide bound); 30%  $\text{H}_2\text{O}_2$  at pH 2 ( $\text{HNO}_3$ ), then 3.2 M  $\text{NH}_4\text{Ac}$  in 20%  $\text{HNO}_3$ , (organically bound); 7M  $\text{HNO}_3$ , (acid soluble); 40%  $\text{HF}$ ,  $\text{HNO}_3$  (residual).

All the supernatant was separated by filtering through 0.2  $\mu\text{m}$  membrane filters. The main part of  $^{137}\text{Cs}$  was found in residue. For  $^{90}\text{Sr}$  the presence in exchangeable form was characteristic. A relatively high percentage of all radionuclides extractable with  $\text{Na}_4\text{P}_2\text{O}_7$  can be interpreted as binding with organic matter but extracted with  $\text{H}_2\text{O}_2$  - not only as binding with organic matter, but also by the presence of fuel particles in soil samples. Moreover a considerable amount of transuranic isotopes was found associated with oxides and of  $^{241}\text{Am}$  - specifically adsorbed.

The upper layer of soil can be influenced by high temperature during forest fires or even burning of grass. In this case migration behaviour of radionuclides can change. In order to determine possible transformation of radionuclide forms a laboratory experiment was carried out. For the experiment a 0-1 cm soil layer was used. Soil was dried at room temperature, weight, and burned. Temperature was slowly raised during one hour and then samples were kept for four hours at 200, 450, 700, and 900°C.

It has been determined that speciation of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  is changed at high temperature. Heating to 200 - 700°C causes an increase in water-soluble, exchangeable, carbonate and oxide bound forms of  $^{137}\text{Cs}$ . On the other hand  $^{137}\text{Cs}$  was fixed in crystal lattice of minerals by its heating to 900°C. A different effect of soil was observed for  $^{90}\text{Sr}$ .

## STUDY OF PLUTONIUM PARTITIONING TO CONTAMINATED SEDIMENTS

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Although the seasonal cycling of Pu in warm, monomictic fresh water systems has been reported, the underlying mechanisms controlling the transfer of Pu from sediments to the water column are not well understood. Elucidation of such geochemical processes would aid in understanding and predicting Pu mobility in aquatic systems and would be useful in developing soil remediation technologies. In this work, the mechanisms of Pu release from sediments collected from Pond B of the Savannah River Site, SC are under investigation. The distribution of Pu in various soil fractions has been determined. The Pond B sediment has been fractionated into nine size fractions: >425  $\mu\text{m}$ , 425-73  $\mu\text{m}$ , and 75-53  $\mu\text{m}$  representing the course, medium and fine sands fractions; 53-20  $\mu\text{m}$ , 20-5  $\mu\text{m}$ , and 5-2  $\mu\text{m}$  representing the course, medium and fine silts; and 2-0.2  $\mu\text{m}$ , 0.2-0.08  $\mu\text{m}$  and the < 0.08  $\mu\text{m}$  fractions representing the course, medium and fine clays. We observe that the plutonium is not homogeneously distributed in the various size fractions of the sediment. Not surprisingly, the majority of the plutonium is found in the smaller fractions of the sediment. However, the nature of the Pu in the various fractions differs, although the reason for this behavior is not clear. Using fission track analysis,  $^{239}\text{Pu}$  in the various size fractions can be observed. Once particles bearing  $^{239}\text{Pu}$  are isolated, their elemental composition will be analyzed. These results will be compared to sequential extractions of the bulk sediment.

## SEDIMENT SAMPLES ALONG THE ROMANIAN SECTOR OF THE DANUBE RIVER AND THE BLACK SEA COAST AS SOURCE AND SINK OF MICROELEMENTS AND RADIONUCLIDES

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Sediments can be either a sink for efficiently scavenged radionuclides or a source of radionuclides by upward diffusion. The concentration distributions of  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in sediment samples, collected along the Romanian sector of the Danube river and the Black Sea coast during 1994-1995 indicated a differentiate accumulation of the radionuclides in the investigated samples<sup>1,2,3</sup>. The concentration distribution of microelements determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) showed the same preferential accumulation as those of the radionuclides.

The X-ray diffraction on random and oriented slides (treated with ethylene glycol, heated at 350 and 550° C and K-saturated) showed the presence of 2:1 clay minerals in the sediment sites in which the accumulation of the microelements and the radionuclides is important. The quantitative determination of the cation exchange capacity, using the method of the silver-thiourea complex  $[\text{AgTU}]^4$  in the same samples confirmed the results of the X-ray diffraction.

According to the cation retention positions of the clay minerals (reversible or irreversible sorption sites) the accumulation capacity of the sediment sites was appreciated as temporary or on a long-term. The mineralogical composition of the selected sites proves itself crucial in monitoring pollutants over a large area such as the basins of rivers and seas, sandy sites should be investigated especially for the water and the suspended matter pollution, while clay mineral sites reveal a reversible or irreversible accumulation potential.

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## DISTRIBUTION COEFFICIENT OF Cs-137, Sr-90 and Co-60 IN SOILS: STATISTICAL ANALYSIS ON EFFECTS OF SOIL PROPERTIES

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The migration of radionuclides leached from a shallow land disposal facility is one of the important paths by which the radionuclides are transported from the shallow land disposal site to the environment. Studies on the sorption characteristics of radionuclides in geological media are closely related to the safe disposal of radioactive wastes. To predict the migration of radionuclides, sorption coefficients are of importance. Soil is one of the most important components in the evaluation of radionuclide behavior in a terrestrial ecosystem. The distribution coefficient ( $K_d$ ) is a commonly used parameter to evaluate radionuclide migration in soil. In this study, the distribution coefficient values of Cs-137, Sr-90 and Co-60 in different soils has been measured in batch experiment. The sorption coefficients have been determined for these radionuclides by soil matrices collected from a number of locations in Bangladesh. The soils were collected from the surface (0-20 cm depth). One gram of dry soil sample was mixed with a solution of water containing the radionuclide in the ratio of 1:50 in a 100 ml centrifuge tube. The pH values of these mixture were adjusted to 2, 4, 6, 8, 10 and 12 using dilute hydrochloric acid and sodium hydroxide solutions. The solutions were shaken with automatic shaker for an hour at room temperature. After the required time interval the samples was centrifuged at 7000 rpm (5280 g) for 30 minutes. The solution phase was rapidly filtered through 0.45 micrometer membrane filter and analyzed immediately. A HPGe detector coupled with 4096 channel analyzer was used for Cs-137 and Co-60 analyses and a liquid scintillation counter was used for the determination of Sr-90. Distribution ratios were determined using a standard procedure. The chemical properties of soil and contact solution were determined. The relationships of  $K_d$  values with pH and EC in the supernatant, CEC, ExCa, ExK, total Ca and total K were statistically analyzed for each radionuclides. The distribution ratios for all soils decreased in the order Cs-137>Co-60>Sr-90. The results are presented and discussed in the report.

## QUANTITATIVE PARAMETERS OF RADIONUCLIDE VERTICAL MIGRATION IN THE SOILS ON DIFFERENT MEADOW TYPES

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Meadow ecosystems represent critical systems determining the major contribution to exposure dose to the population both in the first period and for a long time after a radiation accident. Meadow ecosystems are characterized by a significant variety of those parameters that define differences in rate of radionuclide migration and its contribution. As a result of the accident, meadows of different types - dry, flood plain, lowland and peat lands - were contaminated. In addition, soil cover on the meadows is represented by a wide range of soil.

The vertical migration of  $^{137}\text{Cs}$  in different types meadow is characterized by a sufficiently slow redistribution in soil depth. However, the character of the vertical distribution of radionuclides in soils profile depends on meadow type, its moisture regime, the meteorological condition and soil properties.

The two-component convective-diffusional model was used for determination of vertical migration parameters of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in meadow ecosystems and dependence from meadow type and soil properties was shown. The migration coefficients decrease in the order: peatland>lowland meadows>flood plain meadows>dry meadows. The ecological half-life in the root zone ranges from 55 to 143 y for dry meadows and from 15 to 21 y for peatlands. Analogous parameters for  $^{90}\text{Sr}$  were 30-96 and 13-18 y, respectively.

## ADSORPTION OF Cs AND U(VI) ON SOILS OF THE AUSTRALIAN ARID ZONE

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The adsorption of Cs and U on desert soils of central Australia is being studied as part of the site-selection process for a national repository for low level and short-lived intermediate level radioactive waste. The soils of the region have a distinctive chemistry, characterised by surface sodicity, and are commonly strongly alkaline. A series of batch adsorption experiments has been undertaken to measure the distribution coefficients ( $K_d$  values) for U and Cs on these soils under a range of conditions. The  $K_d$  values for trace  $^{137}\text{Cs}$  in 0.02 M NaCl were typically around  $10^4$  mL/g, indicating strong retention of this radionuclide in the soil. The pH had little effect on the  $K_d$  for Cs. However, the  $K_d$  decreased with increasing ionic strength, and was also strongly dependent on the total Cs concentration. Much lower  $K_d$  values (around  $10^2$  mL/g) were measured for systems containing 1 mmol/L total Cs in a background electrolyte of 0.1 M NaCl. The sorption behavior of U was entirely different to Cs, with  $K_d$  being strongly dependent on pH and decreasing from about  $10^3$  mL/g at pH 7 to around 10 mL/g at pH 9. The  $K_d$  decreased with increasing U concentration. The behavior of U in the system appears to be strongly influenced by the presence of carbonate derived from the soil materials.

## NATURAL AND ARTIFICIAL RADIONUCLIDES IN FOREST AND BOG SOILS: TRACERS FOR MIGRATION PROCESSES AND SOIL DEVELOPMENT

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The study presented here is concerned with gamma-spectrometric investigations on forest and bog soils from highlands in Saxony (Erzgebirge), Germany. Low concentrations of natural (U- and Th-decay series nuclides including  $^{210}\text{Pb}$ ), cosmogenic ( $^7\text{Be}$ ) and artificial ( $^{125}\text{Sb}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$ ,  $^{241}\text{Am}$ ) radioisotopes have been determined using low-level HPGe-detectors with active and passive shielding. The investigated forests and bogs were rather undisturbed concerning anthropogenic influences. Well adapted methods of sampling and preparation were applied. Forest and bog soil horizons were sub-sampled as thin slices and analyzed. In addition to the gamma-spectrometric investigations the activities of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  have been determined by a radiochemical procedure and alpha-ray spectrometry. To date the sampled bog profiles  $^{14}\text{C}$ -ages and pollen analysis results were used. The results were compared with excess  $^{210}\text{Pb}$  ages and time markers from the  $^{241}\text{Am}$  and  $^{125}\text{Sb}$  input. Stable elements investigated by ICP-AAS/-AES were used to get additional information about the geochemical situation of the bogs. The characteristic depth distributions of the above mentioned chemically different radioisotopes in well defined organic and mineral horizons will be shown and compared with existing geochemical migration predictions. Transfer processes at sub-horizon levels will be discussed. The suitability of immobile radionuclides in order to date soil horizons will be illustrated.

## SELECTIVE EXTRACTION TECHNIQUES TO INVESTIGATE THE INFLUENCE OF WATER SATURATION ON THE ENVIRONMENTAL AVAILABILITY OF RADIONUCLIDES AND HEAVY METALS.

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This project examined the partitioning and environmental availability of cadmium, cesium, lead and uranium in a sandy soil aquifer with respect to the degree of water saturation and the presence and character of reactive iron and aluminum surface coatings. For 33 years, low-activity liquid wastes from the chemical separations areas at the U.S. Department of Energy's Savannah River Site were disposed of in a series of unlined seepage basins. The affected aquifer consists of soils classified primarily as sand or loamy sand, with interspersed layers of sandy clay loam. These soils are believed to have been significantly altered by the low-pH plume released during basin operations.

Sets of soil and associated pore water samples were collected from the region downgradient of the basins using a cone penetrometer system. Sampling sites were selected to obtain the widest variance in groundwater chemistry and contaminant concentration. Additional soil samples were collected from the vadose zone sites believed to have been impacted during basin operation. A selective extraction technique involving the use of progressively more aggressive chemicals was employed to estimate contaminant availability and the quantity and character of reactive surface coatings. The eight-step extraction allowed an insight into the amount of each contaminant retained by specific operationally defined surface sites or reactive mineral coatings. When also considering the results of additional laboratory sorption/desorption experiments, prudent use of the extraction technique allowed an operational identification of the environmentally available fraction of each contaminant under a wide range of geochemical conditions.

Specifically, the availability of cadmium, cesium, lead and uranium was examined in: (1) uncontaminated background soils; (2) saturated zone soils exposed to an acidic contaminant plume; and (3) soils that are currently in vadose zone, but which in the past had been exposed to the plume. Results show distinct differences of in amount of contaminant which is easily extractable with respect to the current saturation condition. For example, statistically significant differences were observed for uranium for which vadose zone samples from impacted areas had  $29 \pm 21\%$  of their uranium easily extractable, whereas the saturated zone samples from the same regions had  $57 \pm 20\%$ . This compares with only  $19 \pm 10\%$  of the uranium being easily extractable from samples collected from regions unimpacted by basin operations. A correlation exists between the amounts of extractable amorphous iron and aluminum and the environmental availability of trace metals. Additionally, the relative amounts of crystalline and amorphous iron oxides appear to be a function of water saturation.

## LONG-TERM INVESTIGATION OF THE CHERNOBYL ORIGINATED <sup>137</sup>Cs IN DIFFERENT SOIL TYPES

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Knowledge on the behaviour of long lived radionuclides is very important for prediction of the consequences of radioactive contamination. Site-specific migration constants are necessary for the correct estimation of the internal doses originating from radionuclides transported into the human organism via the terrestrial food-chain. Remedial actions for the reduction of the food-chain transport and for the reduction of the external gamma-dose can be planned successfully only with the knowledge on the present and supposed future distribution of the radionuclides in the soil. In the project presented here, the distribution of <sup>137</sup>Cs activity concentration has been measured and analyzed over 13 years after the Chernobyl reactor accident. A considerable amount of data was collected during this period.

The study was concentrated on five representative Hungarian soils. The sampling was always performed on plane, grassy, uncultivated fields, and several layers were taken down to a depth of 20 cm. After physical treatment of the samples the <sup>137</sup>Cs content was determined by gamma-spectroscopy (Canberra).

On the basis of the experimental data a model has been developed for long-term prediction of the <sup>137</sup>Cs behaviour. By the applied diffusion-convection model the results can be well fitted, and the data can be used for long-term prediction of the <sup>137</sup>Cs distribution profile.

# MIGRATION '99

Program # PB6-20

## CONCENTRATION AND MOBILITY OF PLUTONIUM, $^{241}\text{Am}$ , $^{90}\text{Sr}$ , AND $^{137}\text{Cs}$ IN CULTIVATED AND UNCULTIVATED SOILS OF THE MARCHE REGION (ITALY)

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The concentration and the behaviour of  $^{239+240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in the first 5 cms of some cultivated and uncultivated soils near Urbino (Marche, Italy) at 450 m a.s.l. were determined. A vertical profile of these radionuclides was also obtained in a 50 cm deep core to calculate the relevant mobilities.

Gamma spectrometry was used for  $^{137}\text{Cs}$  measures;  $^{90}\text{Sr}$  was determined retaining Y-90 by extraction chromatography followed by a low background beta counting. Plutonium and americium were separated and determined by extraction chromatography, electroplating and alpha spectrometry.

For all the radionuclides the mean concentration in the uncultivated soils was greater by a factor of 4 - 8 showing a mobilization effect due to ploughing and other cultivation activities. Moreover all the concentration values in the cultivated soils were more scattered by a factor 1.5-2.5.

As far as the 50 cm deep core of an uncultivated soil is concerned, the following conclusions can be drawn. About 95% of  $^{137}\text{Cs}$ , 90% of plutonium and americium and 68% of  $^{90}\text{Sr}$  were present in the first 20 cms with peaks at 50-10 cms for plutonium, americium,  $^{90}\text{Sr}$  and at 2-5 cms for  $^{137}\text{Cs}$ , showing that the mobility of the four radionuclides is in the order:

$^{90}\text{Sr} > ^{241}\text{Am} > ^{239+240}\text{Pu} > ^{137}\text{Cs}$ . The ratio  $^{238}\text{Pu}/^{239+240}\text{Pu}$  ( $0.029 \pm 0.003$ ) was constant showing no isotopic effect in the migration and a plutonium deposition mainly due to weapon test fall out.

## Tc GETTERS IN THE NEAR SURFACE ENVIRONMENT

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Conventional performance assessments hold that radioactive  $^{99}\text{Tc}$  travels as a non-sorbing component with an effective  $K_d$  of 0. This follows from the fact that silicate surfaces commonly develop a net negative surface charge in aqueous environments and that Tc is often found as an anionic pertechnetate species ( $\text{TcO}_4^-$ ) in solution. However, several materials have been identified which may retard or permanently sequester Tc so that its entry into groundwater systems can be delayed or prevented. Three general mechanisms hold promise as the means for diminishing health risks presented by pertechnetate migration: (1) reduction of  $\text{Tc}^{7+}$  to the low solubility tetravalent metal species ( $\text{Tc}^{4+}$ ), although it may be susceptible to complexing ligands like most other tetravalent heavy metals, (2) anion exchange on those rare, but not unknown, materials which develop net positive surface charges, and (3) coprecipitation during formation of bulk phases similar to those that participate in anion exchange processes.

In assessing Tc getter performance, it is of great importance to define the environment in which it is to function. In many subsurface contaminant plumes, source term delivery rates are slow and extensive dilution occurs along the flow path. Thus, concentrations in the sub-ppb range are to be expected. Experimental data are presented demonstrating that a variety of natural materials may retard  $\text{TcO}_4^-$  in this setting, imogolite, boehmite, Cu-sulfides and oxides, goethite, sulfate-exchanged hydrotalcite, lignite and sub-bituminous coals. In contrast, near a leaking waste tank Tc may exist at ppm levels in strongly caustic, high ionic strength solutions. Data are presented demonstrating that both bone char and freshly precipitated aluminum hydroxide have the potential for retarding, if not stopping pertechnetate in these settings. It is concluded that the search for Tc getters is far from hopeless, although at this stage of development underlying sequestration mechanisms are virtually unknown. Before Tc getters are placed in service this shortcoming must be remedied.

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## DISTRIBUTION OF NATURAL RADIONUCLIDES DURING THE PROCESSING OF PHOSPHATIC ROCKS FROM ITATAIA-BRAZIL, FOR THE PRODUCTION OF PHOSPHORIC ACID AND URANIUM CONCENTRATE

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In this research we evaluated the distribution of long-lived radionuclides of the uranium and thorium natural series, in products and wastes generated during the processing of rocks from Itataia, state of Ceará, Brazil, for the production of phosphoric acid and uranium concentrate. The ore deposit of Itataia is not only important as the largest known Brazilian uranium reserve, but also for presenting unique geological characteristics in associating phosphorous and uranium in the form of uraniferous apatite. The estimated phosphatic ore reserves are approximately  $80 \times 10^6$  ton, with  $9 \times 10^6$  ton of  $P_2O_5$  and  $80 \times 10^3$  ton of  $U_3O_8$ .

The processing is composed of two steps, an acid treatment of the phosphatic rock for the production of phosphoric acid and the separation of the uranium in the produced acid, utilizing a liquid-liquid extraction. This process was simulated in a pilot plant because the Itataia project is in the economic evaluation phase before implantation. In the production of phosphoric acid via wet processing a dihydrate system was used in which produces phosphogypsum as a waste, with the ratio of phosphogypsum to phosphoric acid being 4:1. The liquid-liquid extraction of uranium uses DEHPA (di-2-ethylhexyl phosphoric acid) – TOPO (trioctyl fosfina oxide) system.

The radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$ ,  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  were analyzed and the results show that the major part of the uranium and thorium content of the phosphoric rocks was encountered in the phosphoric acid, with radium and lead being found predominantly in the phosphogypsum. The uranium extracted from the phosphoric acid was recovered as ammonium diuranate. The determination of the radionuclides contents in the phosphoric acid permits the anticipation of their contribution to the fertilizers which will be produced from this raw material.

## LEACHABILITY STUDIES OF RADIOACTIVE AND NON-RADIOACTIVE ELEMENTS FROM PHOSPHOGYPSUM

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Phosphate fertilizer is produced by chemically processing phosphatic rock with sulfuric acid. The fertilizer industry is concerned about the fact that for every ton of  $P_2O_5$  produced about 4-6 tons of phosphogypsum is generated. Besides being mainly composed of  $CaSO_4 \cdot 2H_2O$ , it contains heavy metals, trace elements, rare earth elements and naturally occurring radionuclides originating from the phosphate rock. These constituents have been identified as a potential environmental hazard related to the stockpiling of phosphogypsum, its utilization in soil amendment and as building materials. The geochemical processes that control leaching might be understood to evaluating the environmental impact of phosphogypsum. Then, to obtain more detailed information about the physicochemical availability of heavy metals and naturally-occurring radionuclides, 3 methods of leaching were applied to the material. First, the sequential extraction, an usual method for soil and sediment studies, which separated the elements in chemical forms likely to be released in solution under various environmental conditions. Five fractions were obtained: exchangeable, bound to carbonates, phases easily reducible (bound to iron and manganese oxides), bound to organic matter and residual. Second, the EPA extraction procedure for toxicity of waste; in this method, the samples were stirred 18 hr in water and filtered. If concentration of some elements in the extract is greater than the EPA maximum concentration of containment, the material possesses a toxicity characteristic. Third, the soil fertility method, which consists in the extraction of the available species through the stirring of a soil, water and ion-exchange resin, in a process that, up to a certain extent, simulates the action of the roots. Phosphogypsum samples from two different Brazilian industries were analyzed for the heavy metals Cd, Zn, Pb, Mn, Cr, Hg, As and Cu, and the radionuclides Ra-226, Ra-228, Pb-210, U-238/234 and Th-232. The results indicate that a major fraction of heavy metals and radionuclides was found in the residual phase.

## CHARACTERISTIC OF CESIUM ACCUMULATION BY EDIBLE MUSHROOM (*Pleurotus ostreatus*)

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The characteristic of the high concentration of radiocesium by the mushroom was studied by mycelia and fruit bodies of saprophytic *Pleurotus ostreatus* (Fr.) Kummer (*P. ostreatus*) Y-1 strain -one of edible mushrooms to appeal to Japanese taste- using tracers such as  $^{137}\text{Cs}$  or stable Cs. Saprophytic mushrooms are more easily cultured in the laboratory than mycorrhizal mushrooms. To evaluate the proliferation of mycelia and their  $^{137}\text{Cs}$  accumulation, mycelia of the edible mushroom *P. ostreatus* Y-1 were cultured in YMG medium containing 15 mM Cs and 10,000 Bq/kg  $^{137}\text{Cs}$ . When the mycelial dry weight after 48 h of culture was used as the reference value (1.0), the mycelial weight after 72, 96, and 120 h expressed as the weight ratio was 2.7, 2.8, and 3.1, respectively, showing constant values. The *P. ostreatus* Y-1 mycelia were found to be in the logarithmic phase until 48 h after initiation of culture but are in the stationary phase after 72 h or more. The concentration ratio ( $^{137}\text{Cs}$  concentration in the dried mycelia /  $^{137}\text{Cs}$  concentration in the wet medium) already showed about 10 after 24 h of culture, indicating early uptake. Some elements in *P. ostreatus* Y-1 mycelia in the proliferation and stationary phases were analyzed applying a scanning electron microscope (SEM)-energy dispersive X-ray microanalyzer (EDX). The ratio of stable Cs in the stationary phase to that in the proliferation phase (stationary/proliferation phase stable Cs ratio) at the mycelial root dense with mycelia formed in the early stage was about 5 times that at the mycelial tip. The stationary/logarithmic phase ratio of K or P -essential elements of mushrooms- did not markedly differ between the mycelial tip and root, though the amount of each element was slightly larger in the logarithmic phase than in the stationary phase. And, we also performed  $^{133}\text{Cs}$ -NMR studies on Cs uptake by cultured fruit bodies of *P. ostreatus* Y-1.

## EFFECTS OF AMELIORANTS ON CHANGES IN THE SOIL CHEMICAL PROPERTIES AND RADIONUCLIDE MOBILITY

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Following the Chernobyl NPP accident, different fertilisers, minerals and natural clays are being used to reduce the radionuclide mobility in the natural and agricultural ecosystems. The mechanism of their action is caused by changes in the soil properties and formation of slightly mobile compounds with radionuclides.

The application of lime on acid soils results in a reduced acidity, increased cation exchange capacity and exchangeable calcium. As a result a decrease is noted in the content of exchangeable and mobile forms of  $^{137}\text{Cs}$ , as well as a 1.5-2 fold decrease in its transfer to plants.

The application of higher rates of P fertilisers in the form of superphosphate on acid soils can lead to an increase in  $^{137}\text{Cs}$  accumulation in plants due to the acidulation of soil solution and Ca binding by phosphoric acid ions. The  $^{90}\text{Sr}$  mobility in soils with neutral reaction falls 1,3-1,8 times which is probably connected with the formation of slightly soluble compounds  $\text{SrHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Sr}_3(\text{PO}_4)_2$ .

The application of higher K rates contributed to the maximum (1.9-3.1 fold) reduction in  $^{137}\text{Cs}$  content in the available for plants form. The effect of K fertilisers is related to an increase in the content of  $^{137}\text{Cs}$  chemical analogue - potassium in soil in the exchangeable form and, consequently, to a decrease in the portion of  $^{137}\text{Cs}$  being desorbed by ammonium acetate.

The application of N fertilisers in the form of ammonia salts increased the radionuclide mobility by a factor of 1.1-1.2 which is most likely connected with the displacement of  $^{137}\text{Cs}$  by ammonium ions from the soil absorbing complex from the surfaces of clay minerals, highly selective relative to  $^{137}\text{Cs}$  (FES surfaces).

The mechanism of action of the polygorskite clay (clay mineral of the montmorillonite group) is caused by an increase in the soil CEC. In this case, the content of exchangeable  $^{137}\text{Cs}$  (displaced by  $1\text{n AcNH}_4$ ) and mobile  $^{137}\text{Cs}$  (displaced by  $1\text{n HCl}$ ) decreases on average 1.3 times and the portion of unexchangeable  $^{137}\text{Cs}$  increases from 70 to 76%.

## SORPTION OF URANYL IONS ON PHOSPHORYLATED WOOD

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The sorption of uranyl ions on phosphorylated wood in aqueous solutions was studied in relation to the phosphorus content, uranyl concentration, and pH value. Cation exchangers with a phosphorus content of up to 16.5 weight % were obtained by using original method of esterification. Taking into account that wood contains about 60% of cellulose we can conclude that the maximum possible phosphorylation degree of wood substance was attained. It has been found that in the presence of 0.02 M  $\text{UO}_2^{2+}$  the limit of uranium absorption by phosphorylated wood is reached. For the sample with 6.0 wt % phosphorus sorbent exchange capacity (SEC) is 1.0 mmol/g, and for the sample with 16.5 wt % phosphorus this value is 2.5 mmol/g. Distribution coefficient  $K_d$  ( $\text{cm}^3/\text{g}$ ) is about 4 000 for first sample and 19 000 for second one. The equilibrium of sorption is established within 1-5 min. For the sample with 6.0 wt % phosphorus pH dependence of  $K_d$  is typical of sorption on cation exchanger. The maximum sorption is observed in the range of pH from 2 to 3. A low sorption degree in acidic solutions is caused by competitive sorption of  $\text{H}^+$  ions. Decrease in sorption at  $\text{pH} > 3.5$  is due to hydrolysis of uranyl ions. In the case of the sample with 16.5 wt % phosphorus the maximum sorption is observed at  $\text{HNO}_3$  concentration of up to 0.3 M. Then the  $K_d$  decreases, remaining, however, sufficiently high even for 1-2 M  $\text{HNO}_3$ . We assume that sorption of  $\text{UO}_2^{2+}$  by phosphorylated wood is a result of ion exchange with  $-\text{P}-\text{OH}$  groups and formation of coordination bonds through  $-\text{P}=\text{O}$  groups. The contribution of the latter process increases with increasing content of phosphorus in the material. Low cost and high selectivity to uranyl ions and also to transuranium elements are the main advantages of phosphorylated wood giving a possibility of their use to prevent the migration of actinides in the geosphere.

## DESORPTION OF URANIUM (VI) FROM NATURAL SEDIMENTS - EFFECTS OF SURFACTANTS

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Given the significant health risks uranium poses, numerous Department of Energy and mine tailing sites require decontamination. Promising chemical treatments include carbonate/bicarbonate and  $\text{H}_2\text{SO}_4$ . However, these treatments suffer from serious limitations: the efficiency of carbonate is greatly reduced at low pH due to the buffering capacity of soils, and  $\text{H}_2\text{SO}_4$  dissolves large quantities of the soil matrix. As an alternative, we suggest using surface active agents (surfactants) to remediate acidic soils. Surfactant aggregates, known as micelles, have been shown to bind metal ions (e.g.,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{UO}_2^{2+}$ ) in aqueous solutions. This paper will report on uranium sorption onto natural sediments and on the efficiency of surfactants in desorbing U(VI) from contaminated soil.

Experiments with an iron oxide-coated clay-sand collected at the Melton Branch Watershed (Oak Ridge National Laboratory, TN) indicate that U(VI) sorption is strongly dependent on the pH. An adsorption edge is observed at  $2 < \text{pH} < 4$ , followed by a maximum sorption at  $4.8 < \text{pH} < 7$ . Formation of U(VI)-carbonate complexes is responsible for a desorption edge at  $\text{pH} = 8$ . Calcium concentration has only a minor influence on the amount adsorbed, indicating that U(VI) is principally sorbed onto amphoteric hydroxyl groups present in the iron oxide coating and at the edge of the clay particles.

Following contamination, several chemical treatments, including surfactants, were chosen to desorb U(VI). Artificial groundwater and sodium and calcium chloride had no significant effect on U(VI) desorption, confirming that U(VI) is tightly bound to the soil matrix. Conversely,  $\text{H}_2\text{SO}_4$  is a successful solubilizing agent, desorbing 98% of the U(VI) initially sorbed. The release of large amounts of iron, however, indicates matrix dissolution. Approximately 65% of U(VI) is recovered using bicarbonate. Unfortunately, the buffering capacity of the acidic soil and the presence of calcium severely reduce U(VI) desorption. Under similar conditions, anionic surfactants (AOK and T77) are relatively successful and desorb 68% U(VI). The surfactant treatment is less sensitive to the soil-to-liquid ratio and causes little matrix dissolution when compared to the carbonate and  $\text{H}_2\text{SO}_4$  approaches. Cation exchange in the electric double layer surrounding the micelles is the main mechanism responsible for U(VI) release. Slower diffusion into the soil matrix, a function of micelle size, is shown to decrease the initial U(VI) desorption. Other limitations associated with a surfactant treatment, such as possible competition with other cations, will also be discussed.

# MIGRATION '99

Program # PB7-04

## MIGRATION OF $^{90}\text{Sr}$ , $^{106}\text{Ru}$ , $^{137}\text{Cs}$ AND $^{144}\text{Ce}$ IN THE SOIL-TO-PLANT SYSTEM

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For the first time the connected dynamics of the basic parameters which determine biological availability of  $^{90}\text{Sr}$ ,  $^{106}\text{Ru}$ ,  $^{137}\text{Cs}$ ,  $^{144}\text{Ce}$  was experimentally investigated. The criteria for the quantitative description of processes of sorption are offered and parametrization of them is suggested on the basis of the agrochemical and physical soil parameters. It is shown that the decrease of the content of the exchangeable forms of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  and their biological availability with the time can be expressed in the terms of similarly exponential dependencies. The dynamics of accumulation of  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$  by plants differs from behaviour  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the soil-to-plant system.  $^{106}\text{Ru}$  remains available for the plants form much longer time. A close functional relationship was revealed between the processes of sorption of radionuclides in soils and dynamics of their accumulation in plants, which can be described by the regression equations. The parameters of the equations as a function of the properties of soils for each of the investigated radionuclides were evaluated. The migration ability the radionuclides in the soil-to-plant system is determined to the greatest extent for:  $^{137}\text{Cs}$  - by the content of the fine-dispersion fractions and cation exchangeable capacity;  $^{90}\text{Sr}$  - by the content of organic matter, exchangeable calcium, the fine-dispersion fractions and capacity;  $^{106}\text{Ru}$  and  $^{144}\text{Ce}$  - by  $\text{pH}_{\text{KCl}}$ ,  $\text{R}_2\text{O}_3$  content and cation exchangeable capacity. The kinetic approach suggested allows to identify the basic mechanisms which determine the behaviour of radionuclides in the soil-to-plant system and can be used as a basis for a long-term forecasting of the behaviour of radionuclides in the soil-to-plant system.

## EVALUATING THE EFFECT OF APATITE AMENDMENTS ON URANIUM AND NICKEL TOXICITY IN AGED CONTAMINATED SEDIMENTS

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As numerous sites worldwide are contaminated with radionuclides, heavy metals, and organics, it is critical to develop cost-effective management and remediation strategies which simultaneously reduce metal toxicity and mobility, facilitate bioremediation, and minimize human and ecological risks. This work evaluates the potential of hydroxylapatite (HA),  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , as a reactive *in situ* amendment for redirecting the speciation of uranium and nickel into less toxic and less mobile forms in aged contaminated sediments. These contaminated sediments are the result of decades of nuclear fuel and target fabrication activities on the Savannah River Site, a former nuclear weapons production facility near Aiken, South Carolina. Sediment concentrations of depleted U and Ni can exceed  $5000 \text{ mg kg}^{-1}$  in deposition zones along a stream channel. Sediment-porewater equilibrations, TCLP extractions, and sequential extractions indicate that apatite amendments are effective at reducing metal availability. However, the effectiveness of apatite amendments decreases with increasing organic content of sediments. SEM and TEM examination of treated and untreated sediments indicate U redistribution into poorly-ordered Al/Fe rich phosphate phases. Adsorption of U to apatite surfaces does not appear as an important mechanism for immobilization. Results from MetPLATE™ microplate toxicity assays and microbial community profiles obtained using denaturing gradient gel electrophoresis (DGGE) analysis of the V9 region of the 16s rRNA gene are used in conjunction with information from direct and indirect speciation methods to correlate chemical speciation data with biological effects.

## DEVELOPMENT AND TESTING OF RADIONUCLIDE TRANSPORT MODELS FOR FRACTURED CRYSTALLINE ROCK

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Water transport pathways in crystalline rock are inherently heterogeneous and difficult to characterise in detail. Nevertheless, over the last decade, a conceptual model representation of the key transport paths in the crystalline basement of Northern Switzerland has been developed which integrates input from structural geological studies, hydrogeological data and the geochemistry of fracture infills and deep groundwater. This conceptual model is also consistent with in-situ radionuclide transport experiments carried out in the Grimsel Test Site, within the Nagra / JNC Migration Experiment (MI). A more rigorous test is provided by the subsequent connected porosity studies and migration path excavation following injection of a cocktail of strongly sorbing radionuclides (together comprising the radionuclide retardation project RRP, also supported by JNC).

This paper will highlight the key findings of the MI / RRP projects and discuss how they influence the conceptual model of radionuclide transport developed for repository performance assessment. It will also discuss input from further ongoing and planned new projects in the GTS which will investigate radionuclide speciation, colloid transport and the development of a high pH plume in such a flow system.

## SORPTION OF Cs(I) ON BENTONITE AND ZEOLITE: APPLICATION TO EBS DESIGN

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Swelling clay-based materials have been selected by ANDRA as buffer/backfill for high level radioactive wastes. This classical choice is clearly deduced from some well-known properties of bentonite like low hydraulic conductivity, high swelling capacity and plasticity, or high sorption capacity. This last characteristic has been evaluated with regard to retardation of caesium, which is one of the more mobile ion found in the radwates. Safety requirements for caesium on argileous backfill are to obtain a quantitative decay of <sup>137</sup>Cs through the engineered barrier and to limit the rate of migration of <sup>135</sup>Cs at the interface with the geosphere. Performance assessment exercises showed that these requirements lead to a depth of the argileous barrier up to four meters. Following this observation, an optimization of the backfill material has been examined. One way could be to add zeolites to the clay on account of their high sorption capacity and selectivity for caesium. An experimental study was performed on sorption properties of bentonite, zeolite, and mixtures of both. The influences of pH, ionic strength, solid/liquid ratios, types of zeolite, have been qualified and quantified within batches experiments. Modelling of the isotherms was consistent with mechanistic sorption models previously used to describe clays surfaces (Constant Capacity Model). Results are mass action law constants, which can describe bentonite and zeolites properties. Predictive calculations performed for mixtures are in good agreement with experimental measurements. In the argileous mixtures, 5% of synthetic mordenite or 30% of natural clinoptilolite retain all the sorbed caesium, which confirm the high affinity of zeolites for caesium.

Then modelling data have been used in order to evaluate new K<sub>d</sub> values, as a function of zeolite ratios, in the argileous barrier. New performance assessment exercises have shown real gain of depth regarding caesium migration through the barrier. Diffusion measurements are being performed through several bentonite/zeolite compacted mixtures in order to confirm additives efficiency. <sup>3</sup>H diffusion have shown that zeolite mass ratio up to 40% does not affect diffusivity but grain size seems to be important. Diffusion measurements with caesium are on going.

## CALCULATIONS OF THE IMPACT OF SOIL-BASED CHEMICAL COUNTERMEASURES ON SOIL SOLUTION CHEMISTRY

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For agriculturally used areas which are contaminated by the debris from a nuclear accident, the use of chemical amendments (e.g. potassium chloride and lime) is among the most common soil based countermeasures. These countermeasures are intended to reduce the plant uptake of radionuclides (mainly Cs-137 and Sr-90) by competitive inhibition by chemically similar ions. So far, the impacts of countermeasures on soil solution composition - and thus their efficiencies - have almost exclusively been established experimentally, since they depend on mineral composition and chemical characteristics of the soil affected. In this study, the well-established code PHREEQC has been used as a geochemical model to calculate the changes in the ionic composition of soil solutions which result from the application of  $\text{CaCO}_3$  and/or  $\text{KCl}$ . The calculations were performed with four different initial soil solution compositions, corresponding to particular soil types and conditions (cambisol, podzol, aerated peat, waterlogged peat). For each soil type, the cation exchange capacity and the pH value were varied in a range that had previously been determined experimentally. Generally, the calculations showed that the concentrations of soil cations are increased, this effect being most pronounced in the case of a combined lime and  $\text{KCl}$  application. The calculations also indicate that in general the effectivity of these soil-based chemical countermeasures tends to decrease with increasing cation exchange capacity. A high Al content of solution and exchanger affects the effectivity of liming. These calculational results are in supported by experimental findings and by the experience gained after the Chernobyl accident. These results show that calculating the impacts of soil-based chemical countermeasures on soil solution chemistry using geochemical codes such as PHREEQC offers an attractive alternative to establishing these impacts by often time-consuming and site-specific experiments.

## DIFFERENCES IN MIGRATION OF $^{137}\text{Cs}$ AND $^{239,240}\text{Pu}$ IN TYPICAL SOILS OF NEAR AND FAR ZONES CONTAMINATED WITH CHERNOBYL FALLOUT

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Migration rates of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in typical soils (soddy-podzolic (**S-P**), sandy-loam (**S-L**) and peaty-boggy (**P-B**)) of near (**N**) and far (**F**) zones on the territory of Belarus contaminated by Cherbobyl fallouts have been calculated in terms of compartment model. Calculated and empirical (in brackets) values of average migration rate  $v_{av}$  (cm/y) of radionuclides in soil profiles are given in Table. The migration rate  $v_n(i)$  of  $^{239,240}\text{Pu}$  in layers of soddy-podzolic soil in various zones are presented as example. The results show that increasing migration rate of  $^{239,240}\text{Pu}$  in the far zone is remarkably larger than in case of  $^{137}\text{Cs}$ . The causes of observed behaviour of migration rates are discussed.

Soil	$^{137}\text{Cs}$			$^{239,240}\text{Pu}$		
	S-L	S-P	P-B	S-L	S-P	P-B
<b>N</b>	0.36(0.44)	0.20(0.27)	0.27(0.35)	0.29(0.27)	0.24(0.19)	0.24(0.23)
<b>F</b>	0.50(0.69)	0.35(0.42)	0.47(0.57)	0.88(0.99)	0.78(0.72)	0.90(0.78)

## **SORPTION OF RADIOACTIVE SUBSTANCES IN FRACTURED GRANITE**

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Modelling of groundwater flow and transport of solutes is a major task in the site characterization phase, for operations, and the post-operation phase for the disposal of high-level radioactive waste in hard rocks.

During the last four phases of the research work at the Grimsel Test Site (Switzerland), a numerical program system based on the finite-element method was developed to simulate flow and solute transport in fracture systems. This program system has been successfully used to study the hydraulic tests and tracer experiments in the Grimsel Rock Laboratory.

To test the suitability of these numerical programs for water-saturated rock formations, the SM2 (flow) and TM2 (transport) programs have been used to model the radially converging tracer tests and dipole tracer tests at ÄSPÖ, Sweden.

Owing to the relatively little geometric and hydrogeological information available, a simple homogenous model with two coupled fracture systems was used first. This model was calibrated with the data obtained from measurements of the natural flow system and the preliminary tracer test. To some extent, study of transport parameters, e.g., effective porosity, dispersivity, diffusion and sorption coefficients, and half-lives has eliminated uncertainties in the values of the transport parameters of the numerical model. However, the complex flow geometry could not be interpreted correctly in the first stage. It indicated that a non-homogenous model can better describe the natural fracture system and corresponding boundary conditions.

## **RADIONUCLIDE RELEASE AND TRANSPORT FROM NUCLEAR UNDERGROUND TESTS PERFORMED AT MURUROA AND FANGATAUFA - PREDICTIONS UNDER UNCERTAINTY**

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In the context of a study by IGC and IAEA on the effects of nuclear tests at the atolls of Mururoa and Fangataufa, release to the biosphere is estimated for 35 radionuclides originating from 137 underground tests. Based on relatively scarce site-specific data, a model chain was developed to conservatively estimate the radionuclide fluxes via groundwater from their sources, the explosion cavities, towards the biosphere, the ocean or lagoon.

Finite element thermo-hydraulic modeling was used to describe water flow. Parameters were calibrated by fitting a few pre-test temperature profiles in bore holes. Then the disturbance of flow by the thermal drive and mechanical impact on rock caused by the tests was considered. Estimates were made to quantify their spatial extensions and temporal evolution. Tests were categorized according to their specific properties although detailed data were missing. A base case parameter set was defined for the hydraulic conditions, for the initial radionuclide inventory of individual tests, and the nuclide partition on rubble and molten rock or in water within the test cavity. Simple models were used to describe the concentrations of radionuclides in the cavities as a function of time. Radionuclide transport from the cavities to the biosphere was described by two different approaches, a double porosity model for the fractured volcanic rock and a single porosity model for the overlaying, highly porous carbonates.

The sensitivity of the results was investigated using different models and parameters. A few measured data (concentrations in a few cavities and in the lagoons for selected radionuclides, such as  $^3\text{H}$ , Sr, Cs and Pu) were available to be compared with the calculations. In view of the lack and uncertainty of site-specific data, the comparison is of acceptable quality. The calculated radionuclide releases to the biosphere are dominated by a few tests. The peak release of non-sorbing nuclides has already occurred in the past. Sorbing long-lived nuclides will reach the biosphere far in the future at low levels, whereas sorbing short-lived nuclides will decay in the underground. We will discuss model assumptions, parameter choice and their impact on predictive results as well as the comparison with measured data.

## DEVELOPMENT OF A METHODOLOGY FOR ELICITING TIME-DEPENDENT CHEMICAL PARAMETERS

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Previous performance assessments carried out by United Kingdom Nirex Limited (Nirex) have assumed that most of the parameters used in the assessment do not vary with time. As a result of the development of the Time-Dependent Probabilistic Safety Assessment programme (TDPSA) Nirex now has the capability of modelling the time-dependent nature of certain parameters that may affect the calculated risk from the repository. Such calculations depend on the quality of the input data. For a probabilistic assessment, it is important to quantify the uncertainty associated with the particular parameter. The method adopted by Nirex includes using structured elicitation procedures to obtain parameter values from groups of experts who can share their knowledge and expertise under the guidance of a trained assessor.

The aim of the work described in this paper was the development of a methodology for eliciting time-dependent chemical parameters. It is illustrated with the near-field solubility of uranium (U) in the absence of organic complexants. The methodology comprised the following four stages:

- (i) a literature review of solubility data for uranium in the range of chemical conditions, for example pH, redox potential (Eh) and temperature, expected in the near field of a hypothetical repository;
- (ii) a series of HARPROB calculations to determine the solubility and speciation of uranium under the expected range of near-field conditions and quantify the uncertainties associated with these calculated solubilities;
- (iii) use of the results found in items (i) and (ii), and approved elicitation procedures to elicit Probability Distribution Functions (PDFs) for the near-field solubility of uranium as a function of the range of pH and Eh values that may exist during the evolution of the near-field environment;
- (iv) generation of the expected time-dependence of pH and Eh in a hypothetical repository, and the development of an appropriate approach to sample from the PDFs generated in point (iii).

## HETEROGENEOUS MATRIX DIFFUSION IN CRYSTALLINE ROCK – IMPLICATIONS TO GEOSPHERE RETARDATION OF MIGRATING RADIONUCLIDES

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Performance assessments (PA) of repositories for spent nuclear fuel include estimates of the transport of radionuclides that accidentally escape through the engineered (local) barriers. An important issue is how the interaction of various physical and geochemical processes and their spatial variability (heterogeneity) can be accounted for on a geometrical scale relevant to the PA analysis. This study focuses on the up-scaling (averaging) of the heterogeneous processes occurring on the scale of a single fracture.

In addition to generally recognised mechanisms such as advection, dispersion, matrix diffusion and sorption, radionuclide migration can depend significantly on sorption kinetics as well as the heterogeneity of matrix diffusion. As a basis for an analysis of the effect of heterogeneity on radionuclide migration, experiments to determine the geostatistics of the main properties for transport in crystalline rock have been determined for two rock types collected at the Äspö Hard Rock Laboratory, Sweden. A large number of slabs were sampled from the drill core in a certain pattern to a sufficient statistical basis for estimation of the covariances of the porosity, effective diffusivity and adsorption characteristics such as partition coefficient,  $K_d$ , and adsorption kinetics. The 'hole covariance-function' was found to provide an acceptable representation of the porosity, effective diffusivity and  $K_d$ .

Analytical solutions in one dimension for the mean values of the temporal moments of the residence time probability density function were derived using the spectral method. The analysis included adsorption kinetics and the heterogeneity in both matrix diffusion and advection velocity. The effect of sorption kinetics and heterogeneity in matrix diffusion was studied in a single fracture by decomposing the transport problem into a one-dimensional mass transfer problem and a two-dimensional flow problem by the use of a Lagrangian method of description. Monte Carlo simulations were used to simulate the flow field and to deduce the aperture statistics along the trajectory paths in the flow field.

Based on PA-specific parameter values, relative errors much larger than unity is generally introduced in the skewness of the travel time probability density by neglecting sorption kinetics and heterogeneity in matrix diffusion. The effect of heterogeneous matrix diffusion on the skewness increases markedly with the retardation factor of the system and the typical residence time for nuclides in the rock matrix. Sorption kinetics has a significant affect also on the variance of the travel time probability density.

Parameterisation of the phenomena occurring on the fracture scale in terms of a transport models applicable to a scale relevant for a PA analysis should primarily reflect the mean travel times along individual fractures or transport paths. However, higher order temporal moments of the travel time probability density are important measures for both the duration and peak level of the radioactivity in the biosphere. A method is proposed for estimation of the peak activity based on a simple transport path model. Estimation of the activity duration, however, requires more advanced flow models than employed in this study.

## NUMERICAL MODELING OF COUPLED FLUID FLOWS AND REACTIVE TRANSPORT INCLUDING FAST AND SLOW CHEMICAL REACTIONS

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Consideration of couplings among chemical reaction rates, advective and diffusive transport in fractured media or soils, and changes in hydraulic properties due to precipitation and dissolution along fractures and rock matrix may be important for nuclear waste disposal and remediation of contaminated sites. This paper describes the development and verification of a LEHGC2.0, a mechanistic-based numerical model for simulation of coupled fluid flow and reactive chemical transport, including both fast and slow reactions in variably saturated media. Theoretical bases, numerical implementation, and three numerical experiments using the model will be described. The first example is related to the potential effect of cement backfill on transport through fractured rock. It is based on the design of experiments at the Grimsel Test Site, Switzerland and illustrates the effect of precipitation-dissolution on fluid flow and matrix diffusion in a two-dimensional fractured media. Because of precipitation-dissolution and the associated decrease in diffusion of solute from the fracture into the matrix, the estimated retardation in the fractured medium is not as large as the case wherein interactions between chemical reactions and transport were not considered. The second example focuses on a complicated but realistic advective-dispersive-reactive transport problem. This example exemplifies the need for innovative numerical algorithms to solve problems involving stiff geochemical reactions. The third problem examines the potential effect that irreversible "sorption" reactions can play in supporting natural attenuation of heavy metals and radionuclides at contaminated sites. Radionuclides such as uranium or cesium can become irreversibly fixed in iron oxyhydroxide coatings, carbonates and clays by recrystallization, coprecipitation and collapse of clay interlayers. Simulations illustrating the effect of such processes on the flushing of uranium contamination from a mill tailings site will be presented.

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## A 3-D MODEL FOR TRANSPORTING A RADIO-ELEMENT IN POROUS MEDIA: RADON MIGRATION

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Radon 222, a daughter of Uranium 238, is the only radioactive gas that can migrate fairly long distances through soil. Radon 222 can thus be defined as a good marker for uranium tailings, or radioactive residues linked to Uranium 238. For these reasons, it is important to improve migration prediction of radon in soil. Some numerical models allow for these forecasts, but most of them only work at a two-dimensional level and they are unable to efficiently take into account parameters such as soil permeability. In this paper, we present a tri-dimensional model of radon transport in porous media. Due to its chemical and physical properties, radon is considered to be completely soluble in water. Radon transport is governed by two principal equations. The first equation expresses the fluid mass balance and relies on the Darcy equation. The second equation expresses solute mass balance and takes into account the principal phenomena of radon transfer, such as convection, molecular diffusion, hydrodynamic dispersion and physical properties such as radioactive decay. The computations are made using the SUPG (Streamline Upwind Petrov-Galerkin) method based on finite elements method, which takes into consideration irregular flows or dominant convection phenomena. The matrix systems are resolved by the preconditioned conjugate gradient method. We present various versions of modeling with each one containing different characteristics (e.g. heterogeneity, variable flows...). The results obtained from each version of modeling allow us to validate the simulations obtained with our computer code. For some of these validations, we tested different physical parameters, such as permeability, porosity and molecular diffusion rate according to different numerical scales. These tests showed limits within which the model is valid. Among the findings, we observe that the transport of radon in porous media is influenced less by permeability than by porosity.

## NATURAL SAFETY INDICATORS: USING NATURE TO ASSIST IN REPOSITORY PERFORMANCE ASSESSMENT

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Most performance assessments use dose and risk as the ultimate criteria by which the safety of a repository is assessed. However, dose and risk are imperfect assessment criteria because they rely on assumptions for future human behaviour which cannot be predicted with certainty. Furthermore, with a growing requirement to make safety demonstrations to the public, dose and risk have the disadvantage that they are not easily understood by non-technical audiences.

Nature offers an alternative method for assessing repository safety by providing a means to compare repository releases with naturally-occurring elemental concentrations and radioactive fluxes. If it can be shown that the repository releases are small compared to their natural equivalents, then it implies that the repository risk is also small compared to the risk posed by the natural materials. This assessment method is easily comprehended by the public.

An internationally-funded project is working to quantify the abundances of naturally-occurring elements in a range of rocks, waters and sediments. The elements examined include the natural-series nuclides, REEs (as chemical analogues to non-natural species in the waste) and chemotoxic elements (to provide further context for the natural hazards). A compartment code (AMBER) is used to calculate time dependent variations in the elemental concentrations and their fluxes, as well as the radioactive fluxes from the natural-series nuclides, that arise due to climate change impacts on processes such as erosion, groundwater flow and subsurface rock-water interactions.

The results from this modelling work are compared directly with performance assessment calculations. These comparisons indicate that nature can be used to provide an independent set of assessment criteria that can complement standard dose and risk. These comparisons also provide an ideal method to present assessment results in a format that can be readily understood by a wide range of audiences. This paper will present (i) the database of elemental abundances, (ii) the results of the radioactive flux modelling, and (iii) comparisons between repository releases and natural equivalents.

# MIGRATION '99

Program # PC5-03

## **A SYSTEM TO CARRY OUT SORPTION EXPERIMENTS DIRECTLY ON ROCK FRACTURE SURFACES AND A SIMPLIFIED COUPLED MODELLING APPROACH BASED ON NCR-SCS CONCEPTS TO STUDY THE MIGRATION OF RADIONUCLIDES IN A FRACTURED GRANITIC ENVIRONMENT (PALMOTTU SITE)**

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Complementary experimental and modelling approaches have been developed for a better understanding of the U migration in a fractured granitic environment at Palmottu site. On one side, an experimental system was built to study the chemical interactions between the fracture surface of rock samples and their corresponding groundwater. The system is based on the mechanical insulating of the fracture surface from the rest of the core. Several samples were studied. The chemical exchanges between the fracture coating and the solution have been followed by analysing the uranium (ICP/MS), the anions  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  (Ion chromatography) and  $\text{HCO}_3^-$  (IR detection of acid digestion  $\text{CO}_2$ ) and cations  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  (Capillary ion analysis) in the liquid phase.

On the other side, a model was constructed, using the coupled "Network of Chemical Reactor - Specific Chemical Simulator" (NCR-SCS) concept. The modelled area is divided into unit volumes, or chemical reactors, taking in to account the chemical and mineralogical heterogeneity of the system. For each reactor, a Specific Chemical Simulator (SCS) is built, which contains the main mechanisms involved in the considered elements partitioning between the solid and liquid phase: speciation, sorption, dissolution/precipitation. Each chemical reactor includes the SCS, a hydrological module based on a relation between head and flow rate, and several modules that contain a flow molar balance equation for each of the chemical elements considered. This strategy of modelling relies on the use of the user-friendly and modulable ALLAN-NEPTUNIX modelling tools package.

For all the experimentally studied rock samples, each contact of U-free synthetic groundwater with the fracture surface results in a rapid release of uranium, followed by a steady state or a slower increase of the U content. The slower increase of the U content is often associated to the release of K and Cl in the solution. By single reactor tests of the model, the experimentally observed rapid U-release is reproduced, which appears linked to surface complexation reactions rather than exchanges with sites of the clay fraction.

The coupling of several reactors in series, each corresponding to a specific observation point along the assumed hydrodynamic, mass-transfer pathway, conducts to more or less comparable trends as seen at the site.

## **MICROBIAL DIVERSITY IN THE TERRESTRIAL SUBSURFACE—IMPLICATIONS REGARDING THE FATE OF RADIONUCLIDES AND OTHER CONTAMINANTS**

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Research carried out mostly during the last 15 years has shown that microorganisms commonly occur in terrestrial subsurface environments that were once thought to be almost devoid of living forms. Microorganisms, primarily bacteria, have been detected in saturated and unsaturated sub-surface environments, at depths ranging from near-surface to 2.7 km below land surface, and at temperatures ranging from 8 to 65°C. They have also been detected in a wide range of different sediments and lithologies, including: coastal plain sands, lacustrine sediments, paleosols, fluvial sands and gravels, deep mine gallery clays, volcanic tuffs, deep granites and associated groundwater, basalts and associated clay-silt interbeds, Cretaceous shales and sandstones, and Triassic basin siltstones. Studies on bacteria cultured from these environments indicate the many subsurface microbial communities are very diverse. As many as 45 genera, representing most of the known major groups of bacteria, have been cultured from some samples. Direct molecular biological methods have detected still higher levels of diversity. Subsurface microbial communities often include heterotrophs that can transform a wide range of organic compounds, various types of metal-reducing bacteria, and virtually all known types of chemolithotrophic bacteria (which oxidize inorganic compounds). The widespread occurrence and high diversity of bacteria in the sub-surface imply that these organisms have considerable potential to influence the transport and fate of metals/radionuclides in the geosphere. For example, metal/radionuclide solubility could be influenced by microbial oxidation and reduction reactions. Subsurface microbes that reduce U (VI), Tc (VII), Np (V), Cr (VI), Co (III), and other elements have been described, and others are likely to be found as culture collections are examined in more detail. Subsurface microbes that bioaccumulate metals/radionuclides could also influence the migration of these elements in the biosphere and, possibly, provide a means for removal of such elements from waste streams and contaminated groundwater. In this regard, bacteria are known to biosorb a wide range of elements, including Ca, Co, Ni, Sr, U, Th, Tc, La, Gd, Yb, and several others.

## COMPLEX FORMATION OF U(VI) WITH *BACILLUS*-ISOLATES FROM A URANIUM MINING WASTE PILE

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The genus *Bacillus* consists of more than 70 species of Gram-positive, aerobic or facultatively anaerobic spore-forming rod-shaped bacteria. Because of the high resistance of their spores, *Bacilli* were found in a large variety of natural habitats. For our accumulation studies with U(VI), we used vegetative cells and spores of three *Bacillus* isolates (JG-A 30, JG-A 12, JG-A 22, classified as *Bacillus cereus*, *Bacillus sphaericus*, *Bacillus megaterium*) from a uranium mining waste pile (Johanngeorgenstadt, Saxony) and their corresponding reference strains. Sorption studies at pH 5.0 have shown that in the concentration range examined (11–214 mg/L) *Bacilli* accumulate high amounts of uranium. Information on the binding strength and the reversibility were obtained from extraction studies with different extractants. With 0.01 M EDTA solution the uranium bound to the biomass was released almost quantitatively. The characterization of the bacterial-UO<sub>2</sub><sup>2+</sup>-complexes by time-resolved laser fluorescence spectroscopy (TRLFS) has proved the formation of inner-sphere complexes with the biomass. At pH 5 a ternary complex of uranyl with the biomass and hydroxide in solution was detected. After cell fractionation, we examined the spectroscopic properties of the U(VI)-complexes with the isolated cell walls and the isolated surface-layer protein fraction of the bacteria. Spectroscopic studies of these complexes have shown that with intact cells (vegetative cells or spores) the complexation of U(VI) is stronger than with isolated cell wall components. Therefore, the good complexation properties, the easy release of the bound uranium by EDTA-extraction, and the high resistance against harsh environmental conditions makes these bacteria applicable for bioremediation purposes.

## ACTINIDE INTERACTIONS WITH MICROBIAL EXOPOLYMERS AND SIDEROPHORES AND THEIR EFFECTS ON ENVIRONMENTAL MOBILITY

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Microorganisms are likely to effect the mobility and overall environmental behavior of radionuclides through solubility and speciation changes, biosorption, bioaccumulation or other biotransformations. Our goal is to understand how key interactions with aerobic soil microbes, extracellular sorption and siderophore mediated translocation, affect the migration of actinides. Specifically, we are studying:

- 1) the exopolymer binding of U and Pu using the glutamic acid polymer of *Bacillus licheniformis* and
- 2) siderophore mediated binding and translocation of U and Pu using *Streptomyces pilosus* which produces desferrioxamine (DFO) and *Rhodococcus rhodochrous* strain OFS which produces a catecholate siderophore.

The production of the glutamic acid capsule from *Bacillus licheniformis* has been optimized and conditions under which it remains stable have been determined. The surface charge distribution of capsules exhibits the expected behavior; that is, capsules are positively charged at low pH and negatively charged at high pH. The capsule has zero points of charge from 4.5 to 5.5, depending background electrolyte. Preliminary results indicate a high binding capacity of U(VI), approximately 8.02 mmol U(VI) per gram of capsule. Capsule-U(VI) complexes were examined by UV-Vis and ATR-FTIR spectroscopies. For ratios ranging from 1:1 to 1:5 (U:glutamate subunit) the U(VI)/capsule flocculated and formed white precipitates. When the ratio was increased to 1:10, no precipitate was observed and the spectra indicate a soluble, inner-sphere uranyl-capsule complex.

Plutonium and uranium species were combined with DFO and examined using UV-Vis, FT-IR and NMR spectroscopies. DFO forms an inner-sphere complex with U(VI) and does not reduce U(VI) to U(IV). From pH 2 to 6, Pu(VI) cleaves the DFO molecule and is rapidly and irreversibly reduced, but surprisingly to Pu(V), not directly to Pu(IV). Neither DFO nor the cleavage product appear to coordinate Pu(V) in the pH range examined. In the presence of DFO, Pu(V) is reduced to Pu(IV) at a pH-dependent rate. At pH <5, Pu(V) is stable in the presence of DFO for about a month. In contrast to literature reports of the solubilization of PuO<sub>2</sub> by DFO, the siderophore does not readily degrade colloidal Pu(IV) hydroxide.

Growth of *S. pilosus* for cellular translocation experiments has been optimized and experiments to determine DFO-mediated uranium and plutonium uptake by *S. pilosus* are underway. OFS siderophore production has been optimized and the product is being characterization.

## REDUCTION AND PRECIPITATION OF NEPTUNIUM(V) BY SULFATE-REDUCING BACTERIA

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Migration of neptunium, especially Np(V), has been identified as a potentially important pathway for actinide release at nuclear waste repositories and existing subsurface contaminations. Reduction of Np(V) to Np(IV) can reduce its solubility and mobility and may be an important process in minimizing actinide migration. Since sulfate-reducing bacteria (SRB) are active in many anaerobic aquifers and are known to facilitate the reduction of metals and radionuclides, we investigated their ability to utilize Np(V) as an electron acceptor. In these studies, pure and mixed cultures of SRB were able to precipitate Np during utilization of pyruvate, lactate, and hydrogen as electron donors in the presence and absence of sulfate. The Np in the precipitate was identified as Np(IV) using XANES analysis. When sulfide was present, biological reduction of Np(V) was more rapid than abiotic reduction by sulfide in sterile growth medium. However, no Np reduction was noted over the same time frame in pure sodium sulfide solutions, suggesting that trace metals in the growth medium participated in abiotic reduction of Np(V). In mixed culture studies, the addition of hydrogen to consortia growing by pyruvate fermentation stimulated Np reduction and precipitation. Experiments with pure cultures of *Desulfovibrio vulgaris*, growing by lactate fermentation in the absence of sulfate, confirm that the organism is active in Np reduction and precipitation. The results of this work suggest that the activity of SRB in the subsurface may have a significant, and potentially beneficial, impact on actinide mobility.

## AN ELECTROSTATIC APPROACH FOR THE PREDICTION OF ACTINIDE COMPLEXATION CONSTANTS

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A new semi-empirical method is presented for the prediction of actinide complexation with inorganic ligands, such as mononuclear carbonate, sulphate, fluoride and hydroxo complexes of An(III), An(IV), An(V) and An(VI). The approach is based on an energy term describing inter-ligand electrostatic repulsion. This term is derived from the known charge and inter-distance of ligands involved in a given complex and their angular distribution. Semi-empirical parameters are required to describe an effective dielectric field between complexing ligand ions with hydration water molecules between them. With the electrostatic repulsion term thus evaluated, the formation constant of a complex  $AnL_n$  is given by the relation:

$$\log \beta_n^\circ = n \log \beta_1^\circ - {}^{\text{rep}}E(AnL_n) / RT \ln 10$$

Where  $\beta_1^\circ$  is the first and  $\beta_n^\circ$  the  $n^{\text{th}}$  thermodynamic complexation constant for a given actinide ion  $An^{X+}$ , and  $n$  is the number of ligand ions.

Applying known complexation constants  $\log \beta_1^\circ$  and  $\log \beta_n^\circ$ , the semi-empirical parameters required for the calculation of the electrostatic repulsion term  ${}^{\text{rep}}E$  are evaluated. The method is then used to calculate complexation constants for actinides of different oxidation states and various inorganic ligands. The results are compared with experimental data available from the literature. Unknown constants and limiting complexes are predicted. The present approach describes more accurately complexes of large ligand numbers (up to  $n \leq 6$ ) than empirical correlations and semi-empirical models hitherto available in the literature.

The method is further applicable to ternary complexes. A notable example is demonstrated for the systems U(VI)-F-CO<sub>3</sub> and Cm(III)-OH-CO<sub>3</sub>.

## MODELING THE FORMATION OF COLLOIDS DURING NUCLEAR WASTE FORM CORROSION

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The electric double layer theory allows us to make some predictions on the stability of the colloids released during the alteration of nuclear waste forms under hydrothermal conditions. Smectite clay is a major colloidal alteration phase arising from the dissolution of nuclear waste glasses. During waste form reaction plutonium appears to form discrete particles along with Th, rare earths elements (REE), and phosphorus. These particles are presumed to be positively charged as they are often found associated with the smectite clay particles. Hence, the behavior of the smectite clay colloids is key to modeling the potential for migration of colloidal plutonium. The stability of smectite colloids will be virtually independent of pH under most groundwater conditions. The ionic strength, however, is an important factor in determining the stability of particles that form during waste glass weathering. If the ionic strength of the water in contact with a corroding waste form reaction increases, the electric double layer of released primary colloids compresses, and the particles will tend to flocculate. The electrical surface potential of smectite clay colloids with changing ionic strength can be calculated by applying the Gouy theory, as long as an estimation of the charge density for the particles is available. However, a model for colloid formation during waste form alteration is necessary to quantify the potential impact of colloids on performance assessment calculations which need to utilize experimental data. What models can be used to formulate a term for the production of colloids during waste form alteration and corrosion? In this paper, two different approaches are made for obtaining a term for Pu-colloid formation during glass dissolution, based on the known ways that clay colloids are produced. Clay colloids can be produced by precipitation of released glass elements, and therefore, this rate term is bounded by the glass dissolution rate, (i.e. the Grambow rate equation). If pre-hydration and glass reaction, including segregation of Pu, Th, Am, REE into discrete particles, occurs before contact with liquid water, the release of colloids may involve the repulsion of clay particles caused by a localized reduction in ionic strength as a drop of liquid water comes in contact with the reacted surface. This could cause an expansion in the clay particles' electric double layer, resulting in colloid formation. This mode of colloid release may be the most important process for the release of plutonium-bearing colloids from the waste form.

## WASTE FORM CORROSION MODELING: COMPARISON WITH EXPERIMENTAL RESULTS

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Results of geochemical modelling such as the geochemical milieu and the radionuclide concentrations are compared with experimental findings of corrosion tests with HLW glass and with cemented waste forms in highly concentrated brines. The full-scale cemented waste forms are corroded for periods up to 20 years, glass corrosion experiments using highly active R7T7 glass samples cover periods of 1 - 3 years.

Model calculations are performed using the EQ3/6 code and the INE PITZER database. To simulate the corrosion processes of the waste forms, a linear dissolution model is chosen with "special reactants" having compositions of the R7T7 glass or of the cemented waste form, respectively. All simulations were performed for the temperature of 25°C.

Comparison between computed and measured corrosion processes require a correlation between the experimental time scale and the computed reaction progress. This relation is defined in the case of cemented waste forms by the experimental and computed [Ca], [Mg] and pH and by [B] for HLW glass. Computed uranium concentration in the attacking solutions correspond well with the experimental findings for both waste forms. For R7T7 glass schoepite controls solubility of U, in the cement brine systems observed U concentrations indicate  $\text{Na}_2\text{U}_2\text{O}_7$  as limiting solid phase.

Np concentrations measured in the cement - brine systems are found to be close to the detection limit. For R7T7 glass in NaCl brine computed [Np] is about one order of magnitude above measured data. In the R7T7 - Q-brine system the pH decreases depending on the corrosion progress. As a result the computed [Np] concentration in Q-brine is determined by the progress of glass dissolution and not by the formation solids. Due to the high concentrations of Mg or Ca in the brines, the  $\text{CO}_3^{2-}$  concentration is limited and therefore actinide carbonato species will not play a significant role under the conditions considered.

## A LINEAR FREE ENERGY RELATIONSHIP FOR AQUEOUS IONS AND CRYSTALLINE SOLIDS OF $\text{MO}_2$ , $\text{M}(\text{OH})_4$ , GARNET, AND $\text{MZrTi}_2\text{O}_7$

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The standard Gibbs free energies of formation of one isostructural family of crystalline phases can be correlated to those of aqueous cations of a given charge (Sverjensky and Molling, 1992). For an isostructural family, the chemical formula of solids may be represented as  $\text{M}_v\text{X}$ , where M is a divalent cation  $\text{M}^{2+}$ , and X represents the remainder of the composition of solid (for instance, in zirconolite family, divalent M is Ca, Ba, or Sr, and X is  $\text{ZrTi}_2\text{O}_7$ ). The linear free energy correlation derived from Born solvation theory is:  $\Delta G_{f, \text{MvX}}^0 = a_{\text{MvX}} \Delta G_{n, \text{M}^{2+}}^0 + b_{\text{MvX}} + \beta_{\text{MvX}} r_{\text{M}^{2+}}$ . In this equation, the coefficients  $a_{\text{MvX}}$ ,  $b_{\text{MvX}}$ , and  $\beta_{\text{MvX}}$  characterize the particular crystal of  $\text{M}_v\text{X}$ , and  $r_{\text{M}^{2+}}$  is the ionic (Shannon-Prewitt) radius of  $\text{M}^{2+}$  cation. The parameter  $\Delta G_{f, \text{MvX}}^0$  is the standard Gibbs free energies of formation of the end-member solids, and the parameter  $\Delta G_{n, \text{M}^{2+}}^0$  is a radius-based correction to the standard Gibbs free energy of formation of the aqueous cation  $\text{M}^{2+}$ . The term  $\Delta G_{n, \text{M}^{2+}}^0$  is standard non-solvation energy and can be calculated using  $\Delta G_{n, \text{M}^{2+}}^0 = \Delta G_{f, \text{MvX}}^0 - \Delta G_{s, \text{M}^{2+}}^0$ , where  $\Delta G_{s, \text{M}^{2+}}^0$  represents the standard Gibbs free energy of solvation of aqueous cation that can be calculated from conventional Born solvation coefficients for the aqueous cations (Schock and Helgeson, 1988). The parameters for the zirconolite phases of  $\text{MZrTi}_2\text{O}_7$  are:  $a_{\text{MvX}} = 0.875$ ;  $\beta_{\text{MvX}} = 34$  (kcal/mole.Å),  $b_{\text{MvX}} = -864.4$  (kcal/mole).

Similarly, we can use the relationship for the tetravalent cations of  $\text{M}^{4+}\text{O}_2$  with fluorite structure and  $\text{M}^{4+}(\text{OH})_4$ :  $\Delta G_{f, \text{MvX}}^0 = a_{\text{MvX}} \Delta G_{n, \text{M}^{4+}}^0 + b_{\text{MvX}} + \beta_{\text{MvX}} r_{\text{M}^{4+}}$ .

The parameters for the  $\text{M}^{4+}\text{O}_2$  phases are:  $a_{\text{MvX}} = 0.67$ ;  $\beta_{\text{MvX}} = 32$  (kcal/mole.Å),  $b_{\text{MvX}} = -430.0$  (kcal/mole). The parameters for the  $\text{M}^{4+}(\text{OH})_4$  phases are:  $a_{\text{MvX}} = 0.78$ ;  $\beta_{\text{MvX}} = 148$  (kcal/mole.Å),  $b_{\text{MvX}} = -668.1$  (kcal/mole).

## SORPTION AND PRECIPITATION OF STRONTIUM AT KAOLINITE, GIBBSITE, SILICA GEL, AND GOETHITE

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Strontium-90 is a contaminant from testing and production of nuclear weapons that is found in soil, sediment, and/or groundwater at more than 50% of Department of Energy lands. We have studied strontium uptake to kaolinite, gibbsite, silica gel, and goethite surfaces using macroscopic sorption experiments, synchrotron X-ray absorption spectroscopy (XAS), and the Triple Layer surface complexation model to better understand its mobility in the geosphere. Strontium uptake is dominated by chemical sorption of hydrated surface complexes on all surfaces and, in some cases, as a strontium carbonate precipitate on goethite. These results are contrary to the accepted notion that hydrated surface complexes are dominated by non-specific, electrostatic sorption. Only a small fraction of the strontium in our experiments could be removed from solution as electrostatic (i.e., outer-sphere) complexes using surface complexation models. Strontium surface speciation is best modeled as  $>SiOSr^+nH_2O$  to amorphous silica, as  $>(Si,Al)OSr^+nH_2O$  to kaolinite, as  $>AlOSr^+nH_2O$  to gibbsite, and as  $>FeOSr^+nH_2O$  to goethite if carbonate sorption is limited, where  $>$  denotes a surface complex and  $n$  is the coordination of the strontium hydration sphere. From XAS analysis, strontium sorbed to kaolinite, silica gel, and goethite surfaces is coordinated by 8-9 ( $\pm 1$ ) first-neighbor oxygen atoms at 2.60 Å ( $\pm 0.02$ ). The distance between strontium and second neighbor Al, Si or Fe atoms in the substrate must be  $> 4$  Å because they are not detected in the XAS spectra.

In addition to a hydrated surface complex, strontium may form a surface  $SrCO_3$  precipitate on goethite, identified spectroscopically by characteristic Sr-O, Sr-C, and Sr-Sr bond distances. Our molecular and macroscopic strontium sorption results (modeled using carbonate sorption constants from Van Geen et al., 1994) suggest that surface nucleation of  $SrCO_3$  occurs between pH 7 and 8.5 where significant carbonate sorbs to the goethite surface. At pH above 8.5,  $SrCO_3$  does not precipitate on goethite because carbonate sorption is limited. Our results show that carbonate sorption plays an important role in the retardation of strontium, and perhaps other actinides, in groundwater.

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## **RADIOTRACER STUDY AND MODELLING OF SORPTION OF EUROPIUM ON GORLEBEN SAND FROM AQUEOUS SOLUTIONS CONTAINING HUMIC SUBSTANCES**

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The paper aims at the analysis of the distribution of europium, as a trivalent actinide homologue, in the system Gorleben sand – aqueous solution. The analysis should serve as a first step for the modelling of migration of europium and trivalent actinides in Gorleben ground water. At first, the sorption of europium is studied as a function of pH, ionic strength, composition of aqueous solution, solid-to-solution ratio, concentration of europium and contact time. Batch technique and radiotracer method are used. It is found that with the increasing pH the sorption passes through a maximum the position of which depends on the concentration of carbonates and humic substances in the solution. The effect of ionic strength (0.01 and 0.1M NaClO<sub>4</sub>) as well as of europium concentration ( $4.25 \times 10^{-8}$  and  $1.0 \times 10^{-6}$  M) is only small. The increasing concentrations of carbonates and humic substances suppress the sorption at higher pH values. A two step kinetics of the sorption is observed with rapid first step followed by a slow increase in the sorption after 1 day contact. An attempt is made to describe the distribution by a surface complexation model taking into account the formation of humate and carbonate complexes of europium, the surface complexation of europium species and sorption of carbonates and of humic acid on the sand. For this purpose, the sorption of carbonates and of humic acid on the sand is also experimentally determined.

## AQUEOUS Pu(IV) SORPTION ON BRUCITE

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Chemical and mechanistic information on Pu(IV) complexation and sorption on engineered or naturally occurring barrier materials can be used to help develop risk assessment models for transuranic (TRU) waste repositories by providing a technical basis for including sorption processes in actinide transport estimates.

Aqueous Pu(IV) sorption on brucite (Mg hydroxide) has been studied by a combination of surface spectroscopic and standard wet chemical techniques. Several different types of substrates were used: 1) colloidal brucite, with a mean particle diameter of 400 nm, used primarily for the solution phase experiments, 2) hydroxylated single crystal MgO (100) surfaces and 3) natural crystalline brucite. Planar surfaces of types 2 and 3 were used mainly in the surface spectroscopic work. The Pu(IV) used was freshly prepared and its purity verified by UV-VIS spectroscopy. X-ray and synchrotron source photoemission spectroscopy (XPS, PES) were used to gather direct evidence about surface composition and to characterize sorbed species before and after being exposed to solutions containing  $10^{-3}$  to  $10^{-8}$  M Pu(IV). Angle resolved XPS showed hydroxyl groups concentrated at the surface before Pu(IV) exposure. Alpha activity measurements coupled with angle-resolved XPS indicated that Pu became incorporated in the subsurface in the cases studied. Work is currently underway to reveal the nature of this incorporation using x-ray diffraction. The layered structure of brucite may lend itself to the intercalation of neutral Pu hydroxide species. Pu appears to have a tetravalent preference when sorbed on either crystalline brucite or hydroxylated MgO (100) surfaces. Batch techniques were used to develop an understanding of Pu(IV) solubility and sorption behavior as a function of solution pH, and citrate concentration. Sorption is near 100% complete throughout the pH range 8–12 and takes place within minutes. Even with most of the available surface sites occupied by citrate, and with an excess of a strongly complexing organic ligand available, Pu(IV) is removed from solution. The micro-environment near the dynamic brucite surfaces is expected to be highly alkaline. Under these conditions, Pu(IV) readily forms the colloid (an extended polynuclear hydroxo species) and may precipitate on the surface. In the absence of brucite, solubility data coupled with thermodynamic modeling suggest that Pu(IV) colloids are the dominant species in the solution phase experiments.

## MODELLING THE SORPTION BEHAVIOR OF U(VI) ON PHYLLITE

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Based on a detailed mineralogical characterisation of the rock phyllite, carried out with thin section microscopy, SEM/EDS, PIXE, and XRD, batch experiments with phyllite and its main mineralogical constituents, quartz, chlorite, muscovite, and albite, were conducted from pH 3.5 to 9.5. The experiments were performed at ambient pressure with  $1 \times 10^{-6}$  M uranium, a size fraction of 63–200  $\mu\text{m}$ , and a solid solution ratio of 0.5 g/40 mL. The ionic strength was held constant at 0.1 M ( $\text{NaClO}_4$  solution). It was found that the sorption of uranium onto phyllite was not exclusively attributed to uranium sorption onto the main mineralogical constituents, but that 30-40 % of the total amount of sorbed uranium was attributed to the newly formed Fe-mineral ferrihydrite. Transmission mössbauer spectroscopy measurements, showed that the ferric iron concentration increased during the batch experiments. This increase of Fe(III) was related to the formation of ferrihydrite. The source of leachable iron in the phyllite was identified as the mineral chlorite. Centrifugation experiments carried out at various centrifugal forces (1 – 46000 g) and the subsequent analyses of the filtrates with ICP-MS further confirmed the formation of Fe-hydroxide colloids.

To model the results potentiometric titrations and adsorption isotherms were performed with the individual mineralogical components of the phyllite and the phyllite itself to determine surface site densities and acidity constants. With the computer code FITEQL surface complexation constants of U(VI) with quartz, chlorite, muscovite, albite, and ferrihydrite were calculated. By using these surface complexation constants and the proportionate mass of the mineralogical constituents within phyllite we were able to model the sorption of U(VI) onto phyllite. Our results clearly showed that the sorption of U(VI) onto phyllite is determined by the proportional sorption to its mineralogical components and, in addition, to the formation of the secondary phase ferrihydrite. We therefore conclude that kinetic reactions of mineral dissolution and, especially, the formation of secondary phases have to be considered and included into the modelling of sorption reactions onto rocks.

## DETERMINATION OF ACTINIDE SPECIATION AT HIGH pH IN THE PRESENCE OF HUMIC SUBSTANCES : APPLICATION TO EUROPIUM

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As natural waters constitute the main transport medium for radionuclides in the geosphere, in the case of an accidental release of radioactivity from a radwaste disposal in geological formations, it is important to know (and predict) the radioelement speciation under the groundwater conditions, i.e. pH, ionic strength, presence of complexing agents and competing cations. In particular, the pH range of natural waters may vary from pH 6 to pH 9, and they may contain strong complexing ligands such as humic substances, in addition of inorganic ligands (hydroxide and carbonate ions). A lot of studies have been devoted to the study of complexation reactions of radioelements by humic substances in a pH range where competing reactions with hydrolysis or carbonate complexation are not existing. The question which is emerging is the extrapolation of these data at higher pH where competing ligands are present and where ternary complexes (or mixed complexes) can be formed. Hence, the objective of this study is to determine the possible existence of such complexes in the system humic acids/hydroxide ions/carbonate ions in the case of europium as an analogue of trivalent actinides. The technique retained for such a study is Time-Resolved Laser-Induced Fluorescence (TRLIF), which allows i) to work at very low concentrations of Eu ( $10^{-8}$ - $10^{-6}$  M), and also ii) to identify spectrally and temporally the different Eu-hydroxo and carbonato complexes  $\{Eu(OH)_m^{3-m}$  and  $Eu(CO_3)_m^{3-2m}\}$ , i.e. to perform directly Eu speciation. A spectrum data base concerning these different complexes will be presented with all spectroscopic characteristics (life time, fluorescence wavelengths). From these data, titrations of a Eu solution at fixed pH and ionic strength by humic acids (HA) are carried out under inert atmosphere (in glove-box) and at various  $pCO_2$ . By using this fluorescence titration method, complexing capacities and interaction constants are obtained. The possible existence of ternary or mixed complexes (Eu-HA-OH or  $CO_3$ ) is discussed as well as the implication on Eu speciation under natural water conditions (pH 6-9).

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## COMPLEX FORMATION OF URANIUM(IV) WITH PHOSPHATE STUDIED BY LASER-INDUCED PHOTOACOUSTIC SPECTROSCOPY

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Uranium can occur in reducing phosphate-containing environments as uranium(IV)-hydrogenphosphate,  $U(HPO_4)_2 \cdot 4H_2O$ . No thermodynamic complex formation constants are available for the uranium(IV)-phosphate complexes because of their low water solubility. For example, the solubility product  $K_{sp}$  of  $U(HPO_4)_2 \cdot 4H_2O$  limits the uranium(IV) concentration in 1 M perchloric acid to less than  $1.2 \times 10^{-4}$  M

We studied the formation of this complex at uranium concentrations between  $2 \times 10^{-6}$  M and  $1 \times 10^{-4}$  M by Laser-Induced Photoacoustic Spectroscopy in acid media. To determine the complex formation constant we measured and analyzed the spectra from 610 nm to 690 nm. The spectra were corrected for the absorption of the solvent water. The solvated uranium(IV) shows a very intensive absorption band with a maximum at 649.8 nm and a smaller maximum at 671.9 nm. We found a shoulder at 630.0 nm by deconvoluting the absorption spectrum. The spectrum changes with increasing phosphate concentration. At a total phosphate concentration of  $1.5 \times 10^{-3}$  M, we found maxima at 656.6 nm and 667.0 nm. Additionally a shoulder at 645.0 nm is found. Two isosbestic points were determined at 661.4 nm and 669.4 nm.

Results will be presented for the determination of the formation equilibrium and the complex formation constant(s).

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## POTENTIOMETRIC AND MULTINUCLEAR NMR STUDY OF THE BINARY U(VI)-GLYCOLATE AND THE TERNARY U(VI)-GLYCOLATE-FLUORIDE SYSTEMS

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Recently, we have studied the structure and the ligand substitution reactions in various ternary dioxouranium(VI) complexes which provided insight on isomer formation and inter,- and intra-molecular ligand exchange mechanism<sup>1,2</sup>.

As a continuation of the previous work, we have investigated the complex formation in the binary uranium(VI)-glycolate and the ternary uranium(VI)-glycolate-fluoride systems in 1.0 M NaClO<sub>4</sub> medium in the pH range of 2-8 by means of potentiometry, <sup>1</sup>H, <sup>17</sup>O and <sup>19</sup>F NMR spectroscopy. Besides the known species in the binary system (formed only by the coordination of the carboxylate group), both type of experiments confirmed the formation of chelated complexes (I-III) by deprotonation and coordination of the alcoholic OH-group in neutral or slightly alkaline medium. Potentiometric measurements using fluoride selective electrode as well, proved the existence of similar type of complexes in the ternary fluoride system.

The structure, the stability constants of the complexes and the dynamics of their ligand exchange processes will be presented. We expect these results to serve as models for the complexes with other hydroxy-carboxylic acids used in separation techniques and which can mediate transport of radionuclides in nature.

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## COMPLEXATION OF URANIUM WITH HUMIC ACID: MIXED SPECIES FORMATION

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The complexation of the hexavalent uranyl ion with aquatic humic acid from Gorleben groundwater (Gohy-573) is studied at pH 5 in 0.1 M NaClO<sub>4</sub> under inert atmosphere. The humic acid is quantified by its proton exchange capacity. The concentrations of uranium and humic acid are varied by more than an order of magnitude in the micromolar range. No reduction of the uranium by the humic acid is observed. Ultrafiltration, anion exchange, and time resolved laser fluorescence spectroscopy are used to determine the concentration of the uranium species. Since the experiments are performed above pH 4, hydrolysis of uranium is expected. Both simple and mixed uranium humate species are observed by time resolved laser fluorescence spectroscopy. The metal ion charge neutralization model is used to evaluate humic acid concentration, loading capacity, and the mixed species stability constant. The stability constant value is consistent with published numbers. Speciation calculations are performed and compared with literature results.

## PRESENT STATE AND FUTURE DIRECTIONS OF MODELING OF GEOCHEMISTRY IN HYDROGEOLOGICAL SYSTEMS

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The mobility of actinides and fission products in geological media strongly depends on major species in solution, mobile and immobile mineral phases, organic and inorganic components and gases. They form a complex ensemble of simultaneously interacting components, called the aquatic geochemical system. A primordial step towards understanding and controlling fate and dissemination of radioactive waste is to create a concise and comprehensive theoretical framework for the rather non-linear processes involved –hence the need for geochemical models. Two classes of geochemical models are commonly used, i.e., static and hydrodynamic models. In contrast with static models, hydrodynamic models combine geochemical reactions with hydrological processes such as ground-water flow, diffusion and dispersion. In this review, we establish the present state of geochemical models in terms of included processes, thermodynamic databases, missing phenomena, numerical behavior and performance. It is shown that over the past decade, significant progress has been made with respect to modeling of geochemistry in hydrodynamic systems: this is illustrated with help of several applications. Finally, we focus on the perspectives of geochemical modeling in assessment of the safety of nuclear waste disposal.

## MODELING COLLOID TRANSPORT FOR PERFORMANCE ASSESSMENT

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The U.S. Nuclear Regulatory Commission (NRC) and the Center for Nuclear Waste Regulatory Analyses (CNWRA) have developed a performance assessment (PA) computer model to simulate the long-term behavior of the Yucca Mountain (YM) geologic high-level waste repository. In the multiple barrier approach, the natural system is expected to provide some degree of isolation of the radioactive waste from the biosphere. Colloidal transport of radionuclides has been proposed as a potentially critical factor in enhancing radionuclide migration through the subsurface because of the possibility of reduced interaction of radionuclides with the geologic media. The latest version for the NRC total-system performance assessment (TPA) code, version 3.2, was completed in September 1998. Currently there is no colloidal transport model in the code. Sensitivity trials were conducted using TPA version 3.2 to simulate colloidal transport of a given radionuclide as a non-sorbing, non-diffusing solute. The purpose of these trials is to provide a conservative bounding case for plutonium and americium colloidal transport, and to investigate the need to modify the TPA code. Thus far, the trials for colloidal transport have shown no increase in the peak mean total effective dose equivalent (TEDE) within the compliance period of 10,000 years. However, at later times the TEDE from the colloidal models increased by over a factor of 60 from the base scenario case. Colloid transport is only of interest to PA to the extent that radionuclides are associated with a colloid phase. In addition to the conservative case investigated by sensitivity analyses, an approach is developed for using aspects of mechanistic sorption models to constrain the effects of colloids in PA calculations. Site-specific information on chemistry and natural colloid concentration of groundwaters in the vicinity of YM is combined with a surface complexation sorption model to evaluate the impact of natural colloids on estimated retardation factors ( $R_D$ ) for several radioelements of concern in PA, including plutonium, americium, thorium, neptunium, and uranium. In the abstraction of the detailed model results, calculated retardation in the absence of colloids can change significantly due to the effects of variability in chemistry, primarily pH and carbonate concentration. Introduction of colloids into the conceptual model can reduce the calculated effective retardation significantly. Strongly sorbed radionuclides such as americium and thorium are most affected by pseudocolloid formation and transport, with a potential reduction in  $R_D$  of several orders of magnitude. Radioelements that are less strongly sorbed under YM conditions, such as uranium and neptunium, are not affected significantly by colloid transport, and transport of plutonium in the +5 valence state is only moderately enhanced. By determining what parameters and transport processes affect the TEDE the NRC/CNWRA will be able to represent colloidal transport in the TPA code more accurately.

This abstract does not necessarily reflect the position or views of the Nuclear Regulatory Commission.

## **DETERMINATION AND UNCERTAINTIES OF RADIONUCLIDE SOLUBILITY LIMITS TO BE USED BY SKB IN THE SR 97' PERFORMANCE ASSESSMENT**

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The Swedish Fuel and Waste Management Co, SKB, is at present preparing a Performance Assessment exercise of its HLNW repository concept. The determination of solubility limits of the main radionuclides contained in the spent nuclear fuel, is necessary to constrain their potential migration in both the near and far fields.

We have calculated the solubility limits for 24 critical radionuclides in three granitic groundwater compositions (Äspö, Gidea and Finnsjön), as well as in MX-80 bentonite pore water. A sensitivity analysis of the calculated solubilities as a function of the contacting groundwaters in the temperature range 15° to 60° C is presented. Besides selecting the most likely individual solubility limiting phases, we have also determined their solubility limits by assuming coprecipitation processes for minor radionuclides as Ra, Am and Cm.

The calculated solubilities are compared to experimental data from relevant spent nuclear fuel dissolution tests and field observations from natural systems, particularly Natural Analogue study sites. The main uncertainties associated to the calculated solubilities are discussed in this work. Particularly, the ones related to: conceptual modelling approach, thermodynamic data bases, variability of groundwater composition, redox conditions and temperature of the system.

The results of the sensitivity analysis indicate that although some radionuclides are not affected by the parameter uncertainty (i.e. Ag, Pa, Pd, Ra, Th and Zr), in most of the cases they are strongly dependent, particularly for: Am, Cm, Ho, Nb, Ni, Np, Pu, Se, Sm, Sn, Sr, Tc and U.

In this work we will present the most relevant results of this uncertainty analysis in order to identify critical gaps or uncertainties where a dedicated experimental and modelling effort is required.

## A MODEL FOR THE OXIDATIVE DISSOLUTION OF SPENT FUEL AND THE RELEASE OF RADIONUCLIDES FROM AN INITIALLY DEFECTIVE CANISTER

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Our previous models have been developed further to include the release of actinides. Simulations are made to give insight into the critical steps for the oxidative dissolution of spent fuel caused by radiolysis and for the release of radionuclides from an initially defective canister in the repository. The most important mechanisms considered in the model are the radiolysis of groundwater, the oxidation and the congruent dissolution of the fuel matrix, the precipitation of porous secondary phases on the fuel surface, and the escape of oxidants and radionuclides through a damage in the canister to a receding reaction front in the backfill. The secondary phases are likely to be formed rapidly once dissolution commences. This has the ability to diminish the interfacial dissolution of the fuel matrix, to modify the productions of radiolysis and act as a mass-transport barrier for species diffusing to and from the fuel surface. The reaction front is formed due to the fact that the oxidising species, mainly oxygen, hydrogen peroxide and  $\text{UO}_2^{2+}$  complexes, diffuse away from the fuel surface into the backfill and react rapidly with the reducing species, mainly ferrous iron, in the groundwater once they meet. The reaction front will therefore slowly move outward from the canister as more and more oxidants are formed, and also act as a barrier for redox sensitive radionuclides moving away from the near field of a repository. The model integrates basic and experimental evidences about the characteristics of the spent fuel, the radiolysis of water and the oxidative dissolution of the fuel matrix. It makes up a conceptual and quantitative framework to study which mechanisms are the most important for the near field transport in a repository. Various simulations are presented. The sensitivities of the rate of release of uranium, neptunium and plutonium from the fuel surface and from the reaction front to various assumptions and parameters are systematically investigated. The results help guide future experimental work.

## LONG TERM BEHAVIOR OF A THORIUM-BASED FUEL

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For assessing the long term safety of a thorium-based fuel stored in a deep geological repository, we have considered the possible release of the radionuclides generated in the fuel and their transport from the disposal to some outlets of the geosphere over periods of time as long as  $10^6$  years. The simulation code MELODIE, tested in the case of an uranium-based fuel (EVEREST program), has been used to model this transport, with the same scenario and assumptions. The radioactive inventories and the matrix dissolution rate are the parameters of importance to be introduced into the calculation of the total radiological impact.

From leaching experiments, the  $\text{ThO}_2$  solubility is shown to be much less than for  $\text{UO}_2$ . An upper limit value of  $10^{-8}$  M has been finally chosen in order to take into account the effect of time, temperature and water composition.

Thermal output calculations have been performed in order to check the validity of the repository concept.

Finally, the contribution of the actinides, activation products and fission products to the total effective dose has been analysed separately. The behavior of each long lived radionuclide under consideration will be explained on the basis of its bonds with the  $\text{ThO}_2$  matrix, on its solubility and on the capacity of the geosphere to retain it. In the case of the transuranium elements, a comparison with the results previously obtained on  $\text{UO}_2$  will be presented. The influence of the burn up on the initial inventory and, consequently, on the radiological impact will be also discussed.

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## REDOX REACTIONS OF URANIUM, NEPTUNIUM AND PLUTONIUM IONS; THE PRESENT STATE OF KNOWLEDGE AND FUTURE NEEDS

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Oxidation states of U, Np and Pu (M) ions in a solution are liable to vary between (III) and (VI), and precise knowledge of thermodynamic and kinetic for the redox reactions is indispensable for elucidating or predicting the speciation of these elements. It has been understood that the redox processes of M(VI)/M(V) and M(IV)/M(III) in an acidic aqueous solution are generally reversible, while the process of M(V)/M(IV) is irreversible. There have been accumulated many data on the reversible processes of U, Np and Pu ions which were estimated from thermodynamic data and determined directly by conventional electrolytic methods such as voltammetry and polarography. The formal potential determined experimentally can be corrected to the standard potential through a proper treatment on the basis of a modern theory correcting for the activity coefficient. Experimental data are in good agreement with each other giving a reliable  $E^0$  for the reversible processes M(VI)/M(V) and M(IV)/M(III). On the contrary, there still remain problems unsolved for the irreversible redox process whose overall reaction has been expressed as ;  $MO_2^+ + 4H^+ + e^- = M^{4+} + 2H_2O$ . In fact, it is not easy to record the clear current-potential curve for this irreversible process by means of voltammetry or polarography. The equilibrium potential and even the chemical species participating in the reaction, therefore, have not yet been fully examined and understood. One of the most important subjects on the redox of U, Np and Pu ions is the elucidation of the electrode process of irreversible nature. The irreversible processes of these ions can be studied by the flow-coulometry using multi-step column electrodes. The other important subject is the elucidation of the redox of these ions in neutral or weakly basic solutions which is inevitable in the field of the nuclear waste disposal. In the present paper, the state of the art and the future needs of the redox electrochemistry of U, Np and Pu ions will be discussed.

## THE REDOX BEHAVIOUR OF NEPTUNIUM UNDER NATURAL AQUIFER CONDITIONS

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The redox behaviour of neptunium is studied under natural anaerobic aquifer conditions by static and dynamic experiments. Starting with the  $\text{NpO}_2^+$  ion in different groundwaters, its redox behaviour is observed by spectroscopy, solvent extraction and ultrafiltration. The initial  $\text{NpO}_2^+$  concentration is varied from  $1 \times 10^{-10}$  M to  $1 \times 10^{-4}$  mol/L in the pH range from 5 to 9, either in presence or absence of humic substances, also with the addition of ferrous or ferric ions. In the batchwise static experiment, the reduction of Np(V) to Np(IV) is found to be pH dependent and enhanced by the presence of humic substances as humic colloids or of the ferrous ion. Upon reduction from the initial chemical states  $\text{NpO}_2^+$  or  $\text{NpO}_2\text{CO}_3$  depending on the pH, the neptunium becomes sorbed onto humic colloids as Np(IV), which can be then separated simply by ultrafiltration. The reduction kinetics can be followed by spectroscopy speciation, supported with quantification by solvent extraction. In the dynamic experiment with a sandy sediment filled column, the reduction of Np(V) to Np(IV) takes place upon contact with the sediment surface. The thus formed Np(IV) migrates through the column as a colloid-borne species without retardation. Based on the present experimental results, the migration behaviour of neptunium in natural aquifer systems is postulated and the important geochemical effects are discussed in detail.

## REDUCTION OF Pu(V) BY HUMIC ACID

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The reduction of Pu(V) by humic acid in the presence of divalent cations (calcium and magnesium) was investigated. Tracer concentrations of  $^{238}\text{Pu}$  were used. Experiments were run in 5 m NaCl, in the dark, at pH values of 6 and 8, with humic acid concentrations between 0 and 10 ppm. The redox speciation of plutonium was determined by solvent extraction methods. The reduction of Pu(V) by humic acid without divalent cations was also investigated with samples exposed to light prior to or after the introduction of plutonium. Data from these experiments are of interest in the performance assessment of the Waste Isolation Pilot Plant (WIPP) project.

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## TRANSPORT BEHAVIOR OF IONIC AND COLLOIDAL FORMS OF Am, Np, Ce, AND Zr WITH SELECTED SOLID MATRICES

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We have investigated the transport behavior of both ionic and colloidal, aqueous forms of Am, Np, Ce, Eu and Zr in selected matrices of environmental interest. The goal was to provide a basis for evaluating/predicting migration behavior in circumstances encountered in the environment, and afforded a better understanding of nuclide transport. Both real- and pseudo-colloids were both considered in the work.

The ionic materials and colloids were studied using both batch-type and flow-through experimental techniques. The solid matrices chosen for these studies were sand, alumina, charcoal, "bioglass", kaolin and bentonite; some of these materials are of interest as geologic barriers for migration of nuclear materials in the environment. The colloids were characterized by different techniques with regard to their morphology, size and physical properties in order to establish transport and/or removal processes on the basis of aqueous conditions and/or their physiochemical properties, as opposed to chemical interactions. In regard to the former, the apparent pH, and colloidal diameter were factors that were considered.

The kaolin and bentonite matrices were found to be effective in removal of both ionic and colloidal species from the aqueous media employed. Colloid instability due mainly to a change in the nature and/or pH of the aqueous media and ion exchange of the colloid's stabilizing counter-ion at the solid's surface were observed frequently. Sorption at mineral surfaces appeared to be a major mechanism in controlling removal. With some ionic forms of these elements, alteration of oxidation states and/or the speciation were important factors.

The presentation will address important facets of the above studies with the ionic and colloidal forms of the elements discussed. Simple models will be offered to explain the transport or removal processes observed. The chemical and physical behavior of the colloids with the different matrices will also be discussed.

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## INFLUENCE OF HUMIC COLLOIDS ON THE ACTINIDE MIGRATION

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The influence of aquatic humic colloids on the migration of actinides was investigated in column experiments close to natural conditions (anaerobic conditions with Ar + 1 % CO<sub>2</sub> atmosphere). A pleistocene aeolian quartz sand from the Gorleben site was packed in columns (25 to 50 cm length and 5 cm in diameter) and equilibrated with different groundwaters. The groundwaters contain a wide range of humic colloid concentrations (1 to 80 mg DOC/L). Hydraulic properties of the columns were characterized with tritiated water as ideal tracer. Migration experiments were performed with Am(III) and Np(IV/V).

The migration behavior of Am(III) was investigated in two long-term experiments of more than one year. The Am breakthrough curves showed that a part of Am was transported by humic colloids with a flow velocity slightly higher than that of tritiated water. Another Am fraction was sorbed onto the sand. From the Am distribution in a column a retardation factor of about 10,000 was determined. The influence of Np(V) reduction on the humic colloid-borne migration is examined by also column experiments varying the Np(V) concentration ( $10^{-10}$  to  $10^{-4}$  mol/L) with different initial fractions of Np(IV). The recovery of the non-retarded humic colloid-borne Np depends drastically on the Np(V) reduction kinetics. The Np recovery increases with increasing the initial Np(IV) fraction. This is attributed to the stronger interaction of Np(IV) with humic colloids, than that of Np(V).

The column experiments give an insight into the processes controlling the humic colloid-borne migration of actinides. The results provide the basis for describing and predicting the subsurface migration of colloidal actinide species in natural aquifers.

## NAGRA'S GAM PROJECT – PRELIMINARY RESULTS FROM COLLOID AND SOLUTE MIGRATION TESTING IN A GRANITE SHEAR ZONE .

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International scientific research cooperation continues to evaluate solute, colloid and gas transport through fractures/shear zones. Data will help better portray aquifer structure in concert with numerical transport/sorption models. Solutes undergo matrix diffusion, colloids do not. Used together, they become 'intelligent tracers' differentiating pore and migration process characteristics. Gas tracers move with an injected air backbone and can be used to estimate water content. This research is needed to define pathway/release scenarios for radionuclides migrating from nuclear waste repositories in granite environments. Prior solute tracer work has been done in other shear zones at Grimsel (GTS), central Swiss Alps. NAGRA's current GAM project further documents hydraulic, geologic, and transport characteristics in a new shear zone which appears to have lower permeability than others investigated to date at GTS. Core and in-situ tracer tests examine the nature of near-field transport mechanisms and processes. An initial compatibility test was done through a 'planar' shear feature in a core (40-cm long, 14 cm Ø) with a ~1 percent (gross) porosity. Three colloids (1-micron fluorescent microspheres, 0.15- by 0.05-micron biocolloids (bacteriophage H40), 19 nm nanoparticles) and a solute (uranine) were used as tracers. Injection, first of tracer (1.5 days), and second of formation water (8.5 days), was done at 18 ml/hr. Pressure varied from 2.5 to 3.5 bar. Uranine concentrations and microspheres were measured online in real time. No nanoparticles were detected above background. Results showed both colloids and both tracer types eluting two hours after injection. Uranine reached an expected 'plateau/saturation' after 20 hours and increased marginally thereafter. Colloids behaved differently 'peaking' 14 hours before tracer injection ended. Recovery and  $C/C_0$  were 90 and 82 percent for uranine and 15 to 20 and 25 to 45 percent for particles, respectively. Tailing behavior also differed. Insitu tracer work began with a pilot test set up with a 1.2m injection-extraction 'dipole' (1 ml/min) between two boreholes' shear zones. A solution of 16 ppm naphionate also containing dissolved helium as a tracer was circulated opposite the interval for 3.5 hours. Both tracers responded similarly arriving 12 hours and with double peaks at from 20 to 30 hours, after injection. Naphionate concentration peak was 60 times lower at extraction than injection. Total solute recovery reached 30 and 40 percent after 5 and 19 days, respectively. Results from future GAM multi-tracer tests will be compared to the core and pilot results and a gas tracer test protocol finalized for the Fall-1999 program.

## EVALUATION OF <sup>239,240</sup>Pu AND <sup>241</sup>Am SOLUBILITY IN SOIL/WATER SYSTEMS USING AN ELECTROCHEMICAL CELL TO REGULATE SYSTEM E<sub>H</sub>

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An environmental isolation system was developed to study the effects of reducing environments on the release of metals and radionuclides from a soil matrix to solution at specified E<sub>H</sub> values. The system as utilized: 1) provides a controlled redox environment; 2) allows for the containment a soil/water slurry with constant mixing; 3) allows for periodic spectrophotometric measurements without exposure of samples to oxidizing conditions; 4) provides a variable electrical potential and electron current across the slurry; 4) allows for the relatively rapid determination of system redox potential (E<sub>H</sub>); 5) provides the means for rapid separation of the liquid and solid phases, thereby effectively halting further reaction; 6) provides the means to easily monitor and adjust the pH at periodic intervals and 7) allows the removal of samples and the introduce new material and equipment into the isolation chamber without compromising the redox status of the experimental environment. Gross system E<sub>H</sub> was regulated using an IBM Instruments, Inc., EC/225 Voltammetric Analyzer. Actual E<sub>H</sub> was monitored using redox sensitive dyes (e.g., indigo-5,5',7,7'-tetrasulfonate; pe<sup>o</sup> = 6.22). The application of the method will be described in the context of the desorption of <sup>239,240</sup>Pu and <sup>241</sup>Am from Rocky Flats soil isolates. The redox values investigated range from -90 mV to +800 mV.

## FUTURE RADIONUCLIDE RELEASES AND DOSE RATES FROM NUCLEAR TESTING AT MURUROA AND FANGATAUFA ATOLLS

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Between 1966 and 1996, 178 nuclear tests (41 atmospheric and 137 underground) and 15 safety trials (5 atmospheric and 10 underground) were carried out on Mururoa and Fangataufa atolls in French Polynesia. An international study, organized by the IAEA, of the radiological situation at the two atolls was carried out between 1996 and 1998. The major part of the study was devoted to estimation of the long-term release of radionuclides from the underground tests.

All the underground nuclear tests were carried out in water-saturated basalt rock at depths between 500 and 1100 m. Seven safety trials were carried out in the more permeable carbonate formation. The release rates from the basalt into the carbonate zone were calculated from estimates of the temperature-induced flow of groundwater, the sorption coefficients taken from the literature, and leach rates from the solidified lava, which effectively traps the less volatile radionuclides. The release from the carbonate zone to the lagoon or directly to the ocean at depth was difficult to model because of tidal effects in the karstic zones. In the absence of physical data, a simple mixing model was used. Release of plutonium from the debris of safety trials was assumed to be solubility limited.

Samples of water were taken from two test cavities and from various locations in the carbonate formations and in the lagoons. These samples were analyzed for <sup>3</sup>H, <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>239+240</sup>Pu, <sup>36</sup>Cl, <sup>129</sup>I and <sup>14</sup>C. From these analyses, it was possible to make minor adjustments to the model parameters to better fit the measured data. The models were then used to estimate the concentrations of radionuclides in the carbonate formation, the lagoons and the ocean over the next 100,000 years.

The models predict that, for the next few decades, most of the released radionuclides will come from the small number of nuclear tests where there is inadequate confinement within the basaltic rock. In terms of activity, tritium will dominate but at concentrations which are of no radiological significance. Most other radionuclides, including <sup>137</sup>Cs and <sup>90</sup>Sr, will be effectively retained and will decay before they can reach the environment. Plutonium will continue to be released over long periods of time but at very low rates.

The overall conclusion from the study was that there will be no radiation health effects that could be medically diagnosed or epidemiologically discerned, either now or at any time in the future, from the residual radioactive material. Consequently, there is no need for remedial action.

# MIGRATION '99

Program # SS-02

## STUDIES OF RADIONUCLIDE MIGRATION AT THE NEVADA TEST SITE IN THE ERA OF THE COMPREHENSIVE NUCLEAR TEST BAN

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For more than four decades the Nevada Test Site (NTS) has served as the United States' on-continent nuclear weapons proving ground. More than 900 nuclear tests (atmospheric and underground) have been conducted from 1951 until 1992 when a United States moratorium on nuclear testing went into effect. Since the test moratorium, the NTS has diversified into other programs including underground subcritical explosive experiments using plutonium, low-level radioactive waste management, and environmental remediation. Underground testing of nuclear weapons has left a residual radionuclide source term below the water table in excess of  $\sim 3.7 \times 10^6$  TBq. The potential for contamination from nuclear weapons testing was recognized early, and field studies of radionuclide migration were initiated in the mid-1970's. These studies suggest that serious contamination of groundwater is unlikely. As part of an environmental management program, the U.S. Department of Energy, Nevada Operations Office began a project in 1989 to characterize groundwater throughout the NTS. Results from more than 20 wells drilled or rehabilitated near sites of saturated underground nuclear weapons tests suggest that  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{85}\text{Kr}$ ,  $^{99}\text{Tc}$ , and  $^{129}\text{I}$  are dissolved in and migrate conservatively with groundwater. Cationic radionuclides including  $^{22}\text{Na}$ ,  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{125}\text{Sb}$ ,  $^{95}\text{Zr}$ ,  $^{137}\text{Cs}$ ,  $^{155}\text{Eu}$ , and  $^{239}\text{Pu}$  are distributed heterogeneously during an underground nuclear explosion and variably released from rubble and melt-glass fractions. Sorption on clays and zeolites in rhyolite lava and tuff aquifers largely attenuates down-gradient transport. Notably insoluble radionuclides including Eu and Pu have been observed in groundwater samples produced from near-field wells completed in these fractured rock aquifers. These data suggest Pu and other radionuclides may be transported in low concentrations sorbed to  $< 450$  nm zeolite, clay, and feldspar colloids at near ambient groundwater velocities.

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## R&D ACTIVITIES ON RADIOACTIVE WASTE MANAGEMENT SUPPORTED BY THE EUROPEAN COMMISSION

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The European Commission has, by implementing the Euratom Treaty, carried out and supported since more than 20 years research on radioactive waste management and disposal.

This research has been carried out either by its own Research Centres or by research institutions in the Member States, the latter on basis of shared-cost contracts with the Commission. Although the main aim of this research has always been to develop acceptable solutions for the management and disposal of radioactive waste which ensure isolation from man and its environment, emphasis has been shifted somewhat with time. In the early years research e.g. on geological disposal was dealing mainly with basic research, that is understanding of processes in potential host rocks for generic geologic sites, which are of relevance for repository performance assessments.

In the mid eighties the European Commission launched e.g. the well-known project MIRAGE (Migration of Radionuclides through the Geosphere). Under this umbrella project e.g. activities on influence of colloids and complexation (CoCo group) on radionuclide migration were co-ordinated. Furthermore, database and computer codes on geochemical processes were developed (CHEMVAL project) and long-term processes were studied through Natural Analogues. Here the European Commission launched the international recognised Natural Analogue Working Group,

With time, research became more site-specific in so far as potential repository sites were available. The basic research was in various geological formations (crystalline rocks, clay and salt) accompanied with projects aiming at demonstrating the technical feasibility of constructing and operating repositories and at investigating the long-term behaviour of mainly engineered barriers under disposal conditions. Such projects have been carried out in Underground Research Laboratories available in the European Union.

In the beginning of 1999, the European Council of Ministers adopted a new 5-year R&D programme on "Nuclear Energy" covering also issues on Radioactive Waste Management and Disposal. Although the main objectives of the programme haven't changed very much, the motive of the research should shift somewhat from "research driven" to "problem solving". Moreover, in addition to the scientific and technical research areas, studies on public attitudes and involvement in decision-making processes would be carried out. Also for the selection of research projects, non-technical criteria such as European dimension of the research and contributions to socio-economical objectives have gained in importance.

Investigations of relevant processes for the assessment of the long-term behaviour of the barriers – engineered and natural – including research on migration and retardation of radionuclides within repository concepts and its application to performance assessment of repository systems, will certainly remain a significant part of the programme.

# MIGRATION '99

Program # SS-04

## THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

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Yucca Mountain, located in Nye County Nevada, is under investigation by the U.S. Department of Energy as a potential site for geologic disposal of high-level nuclear waste, principally that from commercial nuclear power sources. Years of scientific research in the areas of the natural geologic environment, candidate waste package materials and waste form degradation have been conducted as part of the site evaluation program. This work has recently been summarized in a viability assessment which also included repository design and safety considerations. Current efforts are focussed on the preparation of a site recommendation document which will be presented to the President, who will forward it to Congress. Pending positive evaluation of the site recommendation the Department of Energy will prepare a license application to the Nuclear Regulatory Commission. Advancement of the program requires attention to scientific advances, regulatory concerns, public policy and perception.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

## PRESENT STATUS AND FUTURE PLANS FOR THE WASTE ISOLATION PILOT PLANT

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On March 26, 1999 the Waste Isolation Pilot Plant in Carlsbad, New Mexico received it's first shipment of waste for disposal. The reception of this waste marked the opening of the worlds first operating deep geologic repository for transuranic (TRU) waste. To showcase the success and experience of the WIPP project, Sandia National Laboratories/WIPP is actively pursuing international research collaborations in deep geologic repository with countries in Europe, Canada, and the Pacific Rim. On-going technical activities to support WIPP re-certification (required by EPA once every five years) and design/operation modifications are being performed by Sandia National Laboratories, the WIPP science advisor to DOE. The activities have led to technical advances in the areas of repository chemistry, effect of repository backfill, and performance modeling. New data have been collected on the use of MgO, as a backfill material for the repository, and chemical conditions in the disposal room that will control actinide chemistry and mobility. The new data indicate that releases due to possible human intrusion (exploratory drilling) after repository closure may be less than first anticipated and reported in the Compliance Certification Application (CCA) submitted to the Environmental Protection Agency for WIPP Certification.

## THE OECD/NEA THERMOCHEMICAL DATA BASE PROJECT

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The objectives of the OECD/NEA Thermochemical Data Base (TDB) Project are to make available a comprehensive, internally consistent, internationally recognised and quality-assured thermochemical data base of selected chemical elements. This database is intended to meet the specialised modelling requirements for safety assessments of radioactive waste disposal systems. The quality-assured database is made available in publications and on-line to the OECD/NEA member countries. The project also aims to promote an exchange of information on activities of relevance to the TDB Project in member countries.

High priority is assigned to the critical review of relevant data for compounds and complexes containing the actinide elements uranium, neptunium, plutonium and americium, as well as the fission product technetium. Data on nickel, selenium and zirconium are also being compiled. The data are selected by review teams, consisting of suitably qualified and experienced scientists from all over the world. The final reports are reviewed by an independent group of experts before being published.

There are currently review teams working on reviews of the thermochemistry of the following compounds:

- Inorganic compounds of Tc
- Inorganic compounds of Np and Pu
- Inorganic compounds of Se
- Inorganic compounds of Ni
- Inorganic compounds of Zr
- Simple organic compounds of U, Am, Tc, Np, Pu, Se, Ni and Zr

Two reviews on the inorganic compounds of U and Am have already been published, and are currently being updated by a separate review team. The reports on inorganic compounds of Tc and Np/Pu are expected to be published in 1999. The other reviews started in 1998/1999 and are expected to be published in 2001.

The funding for the TDB Project is provided by the following organisations:

ANSTO, Australia; NIRAS/ONDRAF, Belgium; RAWRA, Czech Republic; POSIVA, Finland, ANDRA, France; IPSN, France; FZK, Germany; JNC, Japan; ENRESA, Spain; SKB, Sweden; SKI, Sweden; HSK, Switzerland; NAGRA, Switzerland; PSI, Switzerland; BNFL, UK; Nirex, UK; and DoE, USA.

## SORPTION MODELLING ACTIVITIES COORDINATED BY THE NEA, PARIS

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This paper summarises the findings from Phase 1 of the NEA's Sorption Modelling Forum. The forum was established by the Performance Assessment Advisory Group (PAAG) to investigate the potential of mechanistic models for improving the confidence in the representation of sorption in performance assessment. The group organised an international workshop on sorption modelling to establish the current state of knowledge in the field and produced a detailed status report. From these activities it was concluded that there are now many documented cases of the successful application of Chemical Thermodynamic Models to describe radionuclide sorption onto complex natural materials, and certain engineered materials such as cements and engineered clays, in both the laboratory and the field. The potential utility of these models has been clearly demonstrated. There are many instances where detailed mechanistic sorption models have been used to support the K<sub>d</sub> value selected for a particular element or to justify an uncertainty range.

However, it is acknowledged that there is still a major limitation to the use of these models to derive K<sub>d</sub> values for performance assessment in a similar manner to their use in the selection of solubility values. Although the models themselves are based on well-established theory, the chemical and physical complexity and heterogeneity of most geological materials make it very difficult to establish a unique set of values for critical input parameters (number of sorption sites, site concentrations, mass action laws, activity correction models) based on the information which can be measured on samples. Multiple model representations of the same data are therefore possible. This means that the methodology used in determining the model becomes of prime importance. It can be noted that a general consensus exists concerning the main features of such a methodology.

The consensus of the group is therefore that the experimental determination of radionuclide K<sub>d</sub> values will remain the main source to estimate their sorption properties throughout the repository system and that this will continue for a timescale of at least the next 5 – 10 years. As the models depend critically on a detailed understanding of both the chemical composition and physical distribution (e.g. as discrete phases or surface coatings) of mineral components in the solid, the need for a field programme and careful characterisation of any potential disposal site will continue to be a key input to the performance assessment.

As a next step in advancing international consensus in this field there is a need to carry out a critical and systematic evaluation of the conceptual and parameter value uncertainties associated with the application of the various sorption models to heterogeneous, large-scale natural systems.

## THE FRENCH R&D PROGRAM ON RADIONUCLIDE RELEASE AND MIGRATION FOR A DEEP GEOLOGICAL FORMATION RADWASTE DISPOSAL PROJECT

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R&D activities regarding radionuclide (RN) release from specific waste-forms (vitrified, spent fuel, bitumen,...), and RN migration and retention in engineered barrier systems (concrete, bentonite) and in the geosphere (host formation, aquifers), are key components of the French program for evaluating the feasibility of deep geological disposal of high activity, long lived radioactive wastes. This program must produce an evaluation report by the year 2006 of the feasibility of disposal facility concepts in two specific geological contexts, a silt-rock formation (Callovo-Oxfordien near Bure in the Meuse-Haut Marne Depts) and an out-cropping granite (site selection in progress). Underground research laboratories (URL) are to be constructed at each of these sites in order to provide information which can only be obtained *in situ*.

This paper presents a brief overview of (i) the critical questions being addressed, (ii) the present state of progress and (iii) key aspects of work programmed over the next 5 years, in the above mentioned technical areas. Particular emphasis is placed on those aspects of the R&D program concerned with characterizing the chemical composition and radioelement sorption properties of the silt-rock host formation, and solute mass transfer in the silt-rock and over- and underlying water-bearing formations. Examples are given of the types of experiments planned to be carried out in the Bure site URL.

Examples of key research questions which will be presented include:

### Waste packages

- Effect of radiolysis and hydrogen on UOX/MOX spent fuel dissolution? Radionuclide release rates during UOX/MOX dissolution?
- Role of the gel phase in vitrified waste dissolution? The long-term evolution in the specific surface area?

### Engineered barrier systems

- Coupling between chemical evolution rates of cement materials and changes in their mass transport properties? Radionuclide retention (precipitation, coprecipitation, sorption) in cement materials for different chemical states?
- Effect of concrete pore-water on the physical-chemical properties of clay-based materials? Retention properties of composite materials (clay + zeolites) for radionuclides?

### Migration and retention in the Bure site host formation

- Dominant RN mass transport mechanism? (effect of anion exclusion, potential contribution of thermodiffusion (geothermal gradient) and other phenomena, likely long-term evolution in the hydraulic head difference across the host formation, etc.)
- In situ chemical composition and speciation of silt-rock pore-waters? (measurement, chemical modeling)
- Realistic values for solid-solution partitioning of RN in the host formation?
- Capacity of the host formation to resist changes in its physical-chemical characteristics due to reactions with concrete water or oxygen?