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Geochemistry of long lived transuranic actinides and fission products

Final report of a Co-ordinated Research Programme
1987–1991

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GEOCHEMISTRY OF LONG LIVED TRANSURANIC ACTINIDES
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FOREWORD

The fundamental concept for disposal of high level radioactive waste is to dispose of the waste product in deep geological formations. Not only will the isolation of the waste product rely on the geology as a barrier, but on a series of barriers (the multibarrier concept), each intended to prevent, delay or restrict the release of radionuclides to the biosphere. These barriers may include engineered barriers (the waste form, waste packaging or canister, packing or buffer materials) and natural barriers (the host rock formations). An important aspect of the natural barriers of a site which must be evaluated is the retardation of key radionuclides due to geochemical interactions with the host rock.

The contents of this document reflect the results reported on by a number of Member States who participated in this Co-ordinated Research Programme which investigated the geochemical processes and mechanisms which affect rock-water interactions and migration of the chemical elements in geological media as scientific background in support of safety assessments of repositories for high level radioactive wastes. Studies conducted considered the migration of the long lived radionuclides of Tc, I, Np and Pu in both the near and far field. The programme investigated natural occurrences and geochemical processes and mechanisms which may affect migration of the chemical elements under consideration in geological media which may be used for disposal of radioactive wastes.

A draft of this report was prepared by two consultants, Mr. C.J. Hardy of Australia and Mr. J.I. Kim of Germany with the assistance of Mr. D.J. Squires of the IAEA Division of Nuclear Fuel Cycle and Waste Management, who served as Scientific Secretary to the Consultants Meeting. This group met in Vienna from 29 October to 2 November 1990. After the draft of the report had been reviewed by the principal investigators from Canada, China, Japan, Poland, UK, USA and the two consultants, comments were incorporated and final revisions were made by Messrs. Z. Dlouhy and D.J. Squires of the IAEA Division of Nuclear Fuel Cycle and Waste Management.

The IAEA would like to express its thanks to all those who took part in this programme, especially Mr. I.F. Vovk who initiated this Co-ordinated Research Programme in 1987, for the final preparations of this report.

EDITORIAL NOTE

LIST OF SUBJECTS STUDIED BY ORGANIZATIONS PARTICIPATING IN THE CRP

Subject	Organization
Solubilities, Speciation and Complexing	
Solubilities	TUM, JAERI
Speciation in solution	BGS, TUM, AECL
Complexing with organics	BGS, TUM
Colloids in groundwater	AECL, TUM, ANSTO
Basic retention mechanisms	
Sorption	TUM, AECL, JAERI, BRIUG, LSO
Diffusion	BGS, LANL, ANSTO
Mineralogical controls	JAERI, LANL
Redox processes	BGS, AECL, LANL
Natural and chemical analogues	
Natural production of NRPs	IPNT, LANL, ANSTO
Natural analogues	AECL, BGS, ANSTO
Chemical analogues	BRIUG, LANL
Analytical methods for natural NRPs	LANL, ANSTO
Thermodynamic databases	AECL, BGS, TUM
Transport modelling	BGS, ANSTO

LIST OF ORGANIZATIONS PARTICIPATING IN THE CRP

Country	Organization		Papers
Australia	Australian Nuclear Science and Technology Organisation, Sydney	(ANSTO)	I/II
Canada	Atomic Energy of Canada Ltd., Whiteshell	(AECL)	I/II
China	Beijing Research Inst. of Uranium Geology	(BRIUG)	0/II
Germany	Institut für Radiochemie, TU München	(TUM)	I/II
Japan	Japan Atomic Energy Research Institute, Tokaimura	(JAERI)	I/II
Netherlands	Laboratory for Radiation Research Bilthoven	(LSO)	I/0
Poland	Inst. Phys. Nucl. Tech. Krakow	(IPNT)	I/II
UK	British Geological Survey Keyworth	(BGS)	I/II
USA	Los Alamos National Laboratory Los Alamos	(LANL)	I/II

Papers refer to I, First RCM, Keyworth, 1988
II, Second RCM, Munich, 1990

CONTENTS

APPENDIX. SUMMARIES OF WORK REPORTED AT RESEARCH CO-ORDINATION MEETINGS

1. INTRODUCTION

The Co-ordinated Research Programme (CRP) on the "Geochemistry of Long Lived Transuranic Actinides and Fission Products" was initiated in 1987, with research co-ordination meetings (RCMs) being held in 1988 and 1990 to review results of the research conducted by participants of the CRP. At the 1988 RCM, research efforts were reported on by participants from Australia, Canada, Denmark, Germany, Japan, the Netherlands, Sweden, UK and USA, and in 1990 by Australia, Canada, China, Germany, Japan, Poland, UK and USA.

This CRP applies particularly to the migration of the long lived radionuclides of Tc, I, Np and Pu in both the near and the far field. The programme investigated natural occurrences and geochemical processes and mechanisms which may affect migration of the chemical elements under consideration in geological media which may be used for disposal of radioactive waste. Besides the study of migration characteristics of solute species, investigation of colloid transport in groundwater of both actinides and fission products was also conducted. Other important questions which included the effect of radiolysis on the redox state and hence the mobility of the long lived multivalent nuclides, their matrix diffusion, the effect of different kinds of accessible minerals and organic matter on retardation were investigated.

Investigations in a number of geological media have been ongoing in a number of Member States for disposal of high level radioactive wastes. High level radioactive wastes (HLW) include highly radioactive residues from reprocessing spent nuclear fuel and other wastes with similar characteristics. They contain high concentrations of certain radionuclides that will remain radioactive for periods of time much longer than human lifetimes. Spent nuclear fuel (if disposed of as a waste) can also be classified as HLW.

The fundamental concept is that the disposal in deep geological formations has been chosen to rely not on one single barrier, but on a series of barriers (the multibarrier concept), each intended to prevent, delay or restrict the release of radionuclides to the biosphere. These barriers may include engineered barriers (the waste form, waste packaging or canister, packing or buffer materials) and natural barriers (the host rock formations).

An important aspect of the natural barriers of a site which must be evaluated is the retardation of key radionuclides due to geochemical interactions with the host rock.

2. OBJECTIVE AND OUTLINE OF CRP

The objective of the programme was to promote the exchange of information on the studies undertaken to understand geochemical processes and mechanisms which affect rock-water interaction and migration of the chemical elements in geological media as scientific background for safety assessments of repositories for high level radioactive wastes. It is considered to be a part of the large research and development programme for high level radioactive waste disposal which is now under way in Member States including laboratory and field experiments and all kinds of geoscientific physico-mathematical modelling.

This CRP is timely with respect to the assessment of various concepts for disposal of radioactive wastes in different countries. The CRP can make an important contribution to the understanding of the behaviour of radionuclides in a disposal scenario. It is therefore necessary to keep in mind the kind of information needed by the assessment modellers and safety assessors. The inclusion or exclusion of certain processes from a model should only be taken from the vantage point of adequate knowledge.

3. RESULTS AND DISCUSSION OF CRP

3.1 Solubility, Complexation, Speciation

The chemistry of long lived transuranic elements and fission products in natural aquatic solutions is, in certain aspects, different from their known chemistry in laboratory and industrial processes. The general distinctions are the following:

- In natural aquatic media of near neutral solution (pH = 5-9), metal ions of higher oxidation state ($Z \geq 3^+$) are very unstable to hydrolysis reactions. As a consequence, low solubility results for all oxidation states, except for the pentavalent state (e.g., Np(V)), with concentrations far below 10^{-6} mol/L.

- Natural aquatic solutions contain dissolved heavy metal elements in amounts near the solubility concentrations of transuranic elements and some fission products. This gives rise to multicomponent competition for chemical reactions of transuranic or other radionuclides.

- Complexing anions present in natural water, e.g. carbonate ions, humate/fulvate ions etc., stabilize some transuranic ions as monomeric ions, while some others are associated with natural water colloids and thus are present as pseudocolloids. In the latter case, the chemical properties of transuranic elements and some fission products are submerged in the behaviour of natural water colloids.

- The above reactions depend primarily on the oxidation state of each element. The stability of individual oxidation states in natural water is different from element to element and is influenced by oxidation state changes depending on the chemical properties of a given aquifer. Consequently, the kinetics of redox and disproportionation reactions vary accordingly.

- For understanding the microscopic chemical behaviour of transuranic elements and fission products in a wide variety of natural aquatic systems, basic knowledge of potential chemical reactions is indispensable. They are solubility, hydrolysis reactions, complexation, redox reactions and colloid generation. The first three subjects are mainly dealt with in this section (although for redox processes, see Section 3.3), whereas the last subject is, due to its particular importance in natural waters, treated separately in Section 3.2.

3.1.1 Solubility

The word "solubility" for a metal compound in natural aquatic solutions needs to be defined somewhat differently from that for well-defined laboratory solutions, because in natural waters the dissolution process involves complex multicomponent chemical reactions. The primary reactions accompanying the dissolution of a metal compound in natural water involve, first of all, hydrolysis reactions which produce monomeric, polynuclear and colloidal species. Depending on the nature and concentration of complexing anions present as water constituents, complexation reactions compete with the hydrolysis reactions and thus stabilize the transuranic ions in water. The anions of importance are known to be carbonate and humate/fulvate ions.

Apart from the normal chemical reactions associated with the dissolution of transuranic elements and some particular fission products, their colloid generation is of great importance in natural systems. Through hydrolysis reactions the metal ions of higher oxidation state may produce their own colloid (called real-colloid) or they can interact with and be sorbed on natural water colloids already present in a given water and thereby produce pseudocolloids. The natural water colloids are different in size and chemical composition in every water and they can change appreciably according to the surrounding geochemical conditions. Whenever colloid generation is involved in the dissolution of transuranic elements in natural waters, this being mostly the case, the assessment of "solubility" is not easy to realize. To ascertain the solubility defined in thermodynamic terms, the separation of transuranic colloids from solution is necessary. However, inseparable colloids of ultrasmall size (< 1 nm) are always present in the solution so that it is still difficult to determine universally applicable solubility data in natural waters.

3.1.1.1 Solubility of Am(III) hydroxide in natural groundwater

A typical example is shown in Fig. 1 with solubilities of ^{241}Am(OH)$_3$ in two different groundwaters from the Gorleben area in Germany. The Am hydroxide precipitate was introduced into saline (Gohy-2122; 2.5 M NaCl) groundwaters, which were prefiltered at 450 nm pore size. After 6 months of equilibration time, the Am concentrations were determined after ultrafiltrations at different pore size, ranging from 450 nm down to near 1 nm. In a non-saline groundwater (Gohy-1061), the Am concentration in filtrates decreased with lowering the pore size of filters nearly four orders of magnitude from unfiltered water to a filtrate from 1 nm pore size. Because real-colloid formation under the same pH and ionic strength was observed to account for less than 60% of the dissolved Am it is quite certain that in the Gohy-1061 groundwater the generation of pseudocolloids enhanced the Am solubility considerably. The solubility of Am(OH)$_3$ at pH = 8.2 in 0.1M NaClO$_4$ was found to be about 5 x 10^{-10} mol/L which corresponds closely to the value found in the filtrate at 1 nm in Fig. 1. All other filtrates contain pseudocolloids of different sizes. In saline groundwater (Gohy-2122), the high ionic strength (2.5 M NaCl) suppresses the generation of

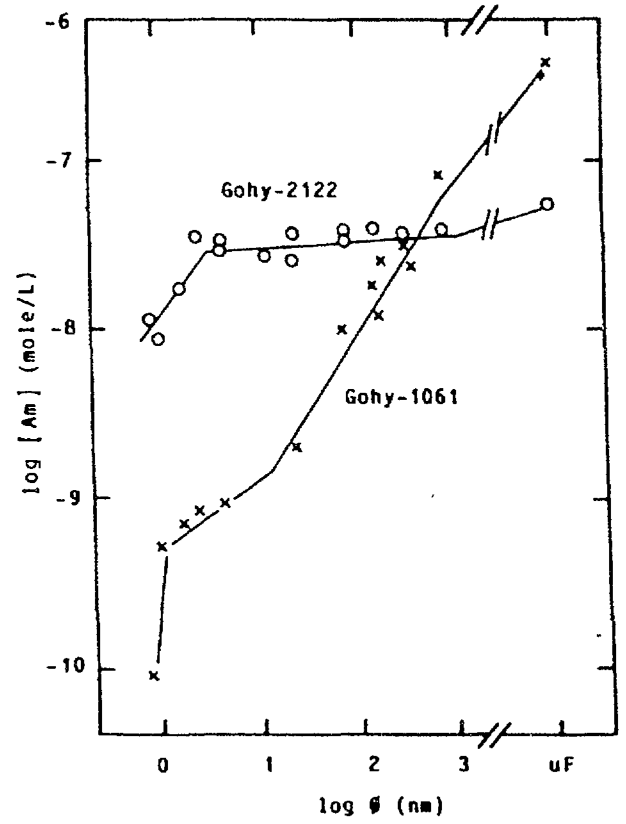

FIG. 1. Solubilities of ^{241}Am hydroxide in non-saline (Gohy-1061) and saline (Gohy-2122, 2.5 M NaCl) groundwaters from the Gorleben area in northern Germany. The concentration of Am in solution was determined as a function of the ultrafilter pore size applied for colloid separation.

groundwater-colloids, particularly relatively larger sizes (> 450 nm). As is evident in Fig. 1, colloids of smaller sizes are still present in this water, which amount to about 68% of the dissolved Am(III) in the solution. The relatively high solubility of Am in saline groundwater may be attributed partly to chloride complexation of Am(III).

3.1.1.2 Solubility of NpO_2 in aqueous solution

Under reducing conditions that might be expected to be present at some of the geological disposal sites for high level radioactive waste, neptunium will be present in the tetravalent state. By hydrolysis, neptunium (IV) hydrous oxide $NpO_2.xH_2O$, will be precipitated. The initially formed amorphous compound will gradually transform to a crystalline state. The solid formed in a near field around a waste repository could become a source of neptunium release into the surrounding geological media.

Dissolution experiments were performed under ambient atmospheric conditions. Measured amounts of NpO_2 powder (^{237}Np, ca. 99 wt%), 12 to 17 mg, were contacted with 40 mL of $NaClO_4$ solution (0.001 or 0.1M) in a Teflon vessel. The pH values of the suspensions were adjusted by the addition of $HClO_4$ or NaOH. The effect of pH on the dissolution was studied at pHs between 4 and 5 in 0.001M $NaClO_4$ and between 2 and 6 in 0.1M $NaClO_4$. The vessel was shaken in an oil bath kept at 30 ± 1°C. During the runs, the pH was monitored with a combination glass electrode and adjusted to keep within ± 0.1 or ± 0.2pH. The Eh value was measured with a platinum electrode at the beginning, 200th day and the end of the runs. The experiment to examine the effect of temperature was conducted for 30 to 90 ± 1°C at pH 4.0 ± 0.1. Aliquots of a supernatant (100 or 200 μ L) were drawn at preset time intervals and filtered with a Millipore ultrafilter (10,000 molecular weight cutoff). The following results are preliminary confirmed from the ultrafiltration experiments: (1) the amount of neptunium sorbed on the filter is negligibly small, and (2) no significant amount of precipitate is formed on/in the filter due to the depression of solution temperature during the filtration. The concentration of the neptunium dissolved in the solution was radiometrically determined. Fifty or a hundred μL of the filtrate was dried on a cleaned stainless steel planchet and the α-radioactivity was measured by a 2 π gas-flow proportional counter.

A general tendency observed in all runs is that a constant dissolution rate was obtained after the initial non-linear dissolution stage terminates within the first two to three weeks. The constant dissolution rate obtained is 82, 49 or 32 ppm/d at pH 4.1, 4.9 or 5.2, respectively, in 0.001M $NaClO_4$. In 0.1M $NaClO_4$, the rate is 115, 100, 88, 42 or 11 ppm/d at pH 2.0, 3.1, 4.1, 5.1 or 6.0, respectively. Dissolution rates measured in 0.001M and 0.1M $NaClO_4$ are very similar at the same pH, i.e., the effect of the ionic strength is insignificant. At pH > 4, the rate shows a rather strong dependence on pH. Extrapolation to a neutral solution gives the value of the order of 1 ppm/d.

Measurements ware carried out to examine the temperature dependence of the amounts of neptunium dissolved in 0.001M $NaClO_4$ at pH 4.0. In the runs to examine the effect of temperature on the dissolution rate, NpO_2 powders were repeatedly washed with 0.001M $NaClO_4$ solution prior to use, to eliminate the rapid dissolution observed at the initial stage in the runs for the pH dependence of the dissolution rate. The constant dissolution rate was 82, 86, 120, 132 or 118 ppm/d at 30, 40, 50, 70 or 90°C, respectively. The effect of temperature on the dissolution rate of $NpO_2(s)$ was found to be insignificant. This temperature dependence is considerably smaller than that observed with minerals. In all runs solubility equilibria were not established. The neptunium concentrations before and after the ultrafiltration are similar, indicating that no colloidal materials are formed.

3.1.1.3 Comments on the solubility in natural aquatic solutions

Laboratory experiences on the solubility of long-lived transuranic elements and some fission products of higher oxidation state ($Z \geq 3^+$) in natural aquatic solutions lead us to the following comments on the subject.

- Solubility equilibria of transuranic compounds in natural aquatic solutions cannot easily be described thermodynamically, since there is no possibility to quantify the colloid generation involved.

- α-radiation assists the generation of microcolloids (< 10 A^o) of transuranic elements which are hardly separable by the ultrafiltration with the smallest pore size available.

Although the solubility constraint results in concentrations of transuranic ions usually less than 10^{-6} mol/L in natural aquatic solutions, except for the pentavalent state, e.g. Np (V), which can reach 10^{-4} mol/L under the normal geochemical condition, they do not remain stable in the solutions but tend toward sorption on the surface of geological surroundings.

They can be stabilized by coordinated complexation with water soluble anions, e.g. CO_3^{2-} or humic/fulvic acids. The CO_3^{2-} ion is ubiquitous in different concentrations. In some natural aquatic solutions such organics are abundant but in others they are not. Theoretical estimations of solubilities of transuranic elements in natural aquatic solutions are not simply achieved, since there are not enough thermodynamic data to describe multicomponent chemical reactions. However, the solubility is an important primary chemical parameter which may give insight into the chemical nature of the aquatic system under investigation as well as the underlying chemical reactions of transuranic ions in the system.

3.1.2. Complexation

Complexing inorganic anions present in substantial amounts in natural waters, particularly in groundwaters, are HCO_3^-/CO_3^{2-}, Cl^-, SO_4^{2-}, PO_4^{3-}, etc. The complexation properties of anions are in the following order:

$$CO_3^{2-} > SO_4^{2-} > PO_4^{3-} > Cl^- > \ldots$$

for transuranic ions. Because of the omnipresence in nature and strong complexation properties of CO_3^{2-}, the carbonate complexation of transuranic ions appears as one of the most important chemical reactions.

Important organics in natural waters are typically humic/fulvic acid and low chain organic acids, e.g. citric acid. There is a large number of small chain organics present in soil solution but the abundance of species is generally small and their complexation properties with transuranic ions are not yet fully understood.

Fig. 2 illustrates the stability constants of the first complexation reaction with various ligands for actinides of different oxidation states. The chelate anion, e.g. EDTA, appears as the strongest complexing agent for all oxidation states, followed by carbonate, humate and citrate ions. The hydrolysis reaction undergoes a strong competition with the complexation with the latter anions.

The F^- ion is also an interesting anion which stabilizes transuranic ions but its concentration in natural waters is often insignificantly small.

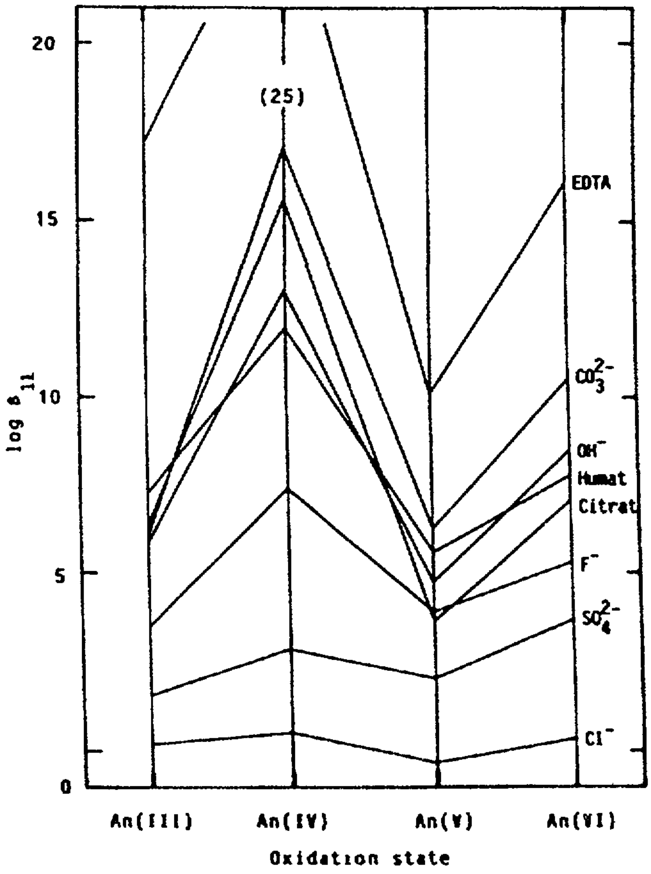

FIG. 2. Comparison of complexation properties of different actinide oxidation states for various ligands.

SO_4^{2-} is ubiquitous but its relatively small concentration makes this ion play a less important role. The role of the Cl^- ion becomes significant only in saline waters of considerable NaCl concentration. However, due to the very low complexation property of Cl^-, even in saline waters the hydolysis reaction prevails in neutral or higher pH. Natural saline waters contain in general a very high concentration of SO_4^{2-}, some tens of millimol, that may influence the chemical behaviour of some transuranic ions. However, in natural saline water the total concentration of metal ions is also substantially higher than normal natural water so that the multi-cation competition, as to the complexation, is much greater.

Within the CRP programme, no particular work has been carried out directly for the complexation of transuranic ions or fission products of higher oxidation state with naturally occurring ligands of importance, e.g., carbonate ion, humic acid or fulvic acid. However, the influence of natural organics, like humic/fulvic acids, on the migration behaviour of long lived radionuclides in different geological media has been indirectly investigated.

Since the complexation involves many important geochemical reactions which influence directly the solubility as well as the migration behaviour of transuranic elements and fission products, the two most important reactions, carbonate and humate complexation, are treated here for brief discussion.

3.1.2.1 Carbonate complexation

In natural waters, the concentration of carbonate ions (as given by the bicarbonate ion in the literature) ranges from 0.1 mmol/L to 13 mmol/L: an average of 1 mmol/L for river water, 2.5 mmol/L in sea water, and 1-13 mmol/L in groundwater. In groundwaters the concentration of carbonate ions varies with pH and the partial pressure of CO_2 gas with which they are in contact. The relation between the concentration of the bicarbonate ion, pH and the partial pressure of CO_2 gas in various groundwaters illustrates that a large number of groundwaters contains the bicarbonate ion in concentrations between 1 mmol/L and 10 mmol/L. These amounts of carbonate ions can certainly influence the chemistry of transuranic ions, once they are exposed to groundwaters.

Under natural conditions (pH = 5-9), the solubility equilibria of An(III) and An(IV) are competitively related to their hydroxide or hydroxocarbonate precipitates.

Although carbonate complexation is generally understood as an important chemical reaction in natural water, only a small number of studies on this subject is presently available for transuranic ions in the literature. The primary reason is attributable to experimental difficulties. The carbonate concentration in a given solution is directly related with pH at a constant partial pressure of CO_2 and thus the experiment should take into account the two variables at the same time. As a consequence, the interpretation of experimental results should be carried out under a three-dimensional co-ordination which gives rise to a certain ambiguity for the speciation of reaction products and also for the evaluation of relevant stability constants.

The constants (given in a relative scale in Fig. 2) show relatively high stabilities of transuranic carbonate complexes; particularly An(IV) carbonates are so stable that in a carbonate rich solution the Pu(IV) carbonate ions undergo neither disproportionation nor redox reactions but remain stable. Under similar conditions Am(III) and Np(V) appear to be the most stable species. Since in groundwaters the total carbonate concentration is relatively high the transuranic ions can be stabilized to a certain extent as carbonate complexes.

In the study of the fall-out plutonium activity in different lakes in North America, it is observed that in Mono Lake with its relatively higher total carbonate concentration, 260 mmol/L, the plutonium concentration is found to be about 20 fCi/L, which is 30 to 100 times higher than the concentrations measured in other lakes. Considering other important complexing anions in this lake, 86.5 mmol/L SO_4^{2-} and 2.5 mmol/L F^- and the complexation behaviour of plutonium ions, it is quite plausible that the predominant effect on the plutonium stabilization may be the carbonate complexation.

3.1.2.2 Humate/fulvate complexation

The importance of the complexation behaviour of humic substances with trace metal ions in natural waters is well recognized in areas such as agriculture, water quality and geochemistry. Humic substances are amorphous, brown or black, polydisperse substances of molecular weights ranging from several hundred to tens of thousands. They are divided into three main fractions: humic acid, which is soluble in dilute alkaline solution but is precipitated by acidification of the alkaline extract; fulvic acid, the fraction which remains in the acidified solution; and humin, which is the soil fraction being not extracted by base and acid. Structurally the three fractions are similar, but they differ in molecular weight and functional group content. The fulvic acid fraction has a lower molecular weight than humic acid and humin fractions. The insolubility of humin arises from the strength of the bonds of its combination with inorganic soil constituents. The two common functional groups which are most likely to be involved in the complexation of metal ions are aromatic carboxylates and phenolics. At least two types of metal ions-humate complexations have been identified: electrostatic binding due to polyelectrolyte effects, and inner sphere complexation including chelation. Transuranic humates belong presumably to the latter category.

Complexation studies of humic/fulvic acids (HA/FA) with transuranic ions and fission products are scarce in the literature, although their complexations with transition elements of divalent oxidation state have been investigated more frequently. Formation constants of some actinide humates and fulvates which are available in the open literature are summarized [1], including the values for Eu(III) which are taken for the purpose of comparison with Am(III). The distinction between humate and fulvate formations is astonishingly small and not systematical as can be seen from the data in this table. The formation constants of Th(IV) and U(IV) are considerably different from one another whereas the values of Am(III) and Eu(III) are in reasonably good agreement. Contrary to the situation with other complexation studies, the evaluation of humate complexation constants differs between authors. The resulting values may, therefore, deviate from one another. Another cause for the discrepancy may be the different experimental procedures applied by different authors.

In comparison with hydrolysis constants and stability constants of carbonate complexation, the humate/fulvate formation constants for tri- and hexavalent ions are not much larger, except for the An(IV) carbonate complexation which shows distinctively higher values. Accepting the known constants, it is expected that in natural waters the three reactions are competing against one another, unless one of the three ligands is predominating. The tetravalent actinide ion will tend toward stronger hydrolysis reactions or carbonate complexation than humate/fulvate formation. This fact also suggests that the study of humate complexation of transuranic ions in near neutral solutions confronts a difficulty for the differentiation of the reactions under study from the other competing reactions e.g. hydrolysis reaction or carbonate complexation. Furthermore the generation of actinide colloids takes place in the wide pH range and can then be aggregated with humic acid to produce soluble pseudocolloids.

In natural waters, the soluble humic substance also contains colloidal species, which can be characterized as an intermediate species between humic acid and humin as defined above. Such a species, complexed already with metal ions of water constituent elements, e.g. Fe^{3+}/Fe^{2+}, Ca^{2+}, REE ions etc., may act as an ion exchanger or may create pseudocolloids of transuranic ions. This kind of pseudocolloids is separable from the solution either by ultrafiltration or by ultracentrifugation. The distinction between humic acid and water soluble humic colloids is somewhat ambiguous. However, the humic colloid is not precipitated upon acidification but can be separated from the solution by ultrafiltration or ultracentrifugation and thus distinguishes itself from humic acid as well as fulvic acid. This species is probably an aggregate of metal colloids and humic acid. Metal contents in different humic acids are considerable; they can take part in an exchange process of other metal ions, like transuranic ions, with a greater complexation affinity.

The complexation of transuranic humates may eventually accompany redox reactions of these ions of different oxidation states. In the interaction between humic acid and actinide ions of U, Np and Pu, only the hexavalent uranyl ion remains stable, while Np(VI) is reduced to Np(V) and Pu(VI) to Pu(IV). A similar reduction is observed in the interaction of fulvic acid at pH $<$ 3.1 with Pu(IV), which is then partially reduced to Pu(III). As in the case of carbonate complexation, which stabilizes Pu(IV) in solution, the Pu(IV) humate appears to be the most stable species in the humic acid solution. Although some investigations have been made to date, the humate complexation of transuranic ions is not yet well understood and requires further study, not only on their complexation reactions but also on their effects on the migration of transuranic ions in natural aquatic systems.

In the framework of CRP, the British Geological Survey has undertaken the investigation on the influence of natural organics (humic substances, acetate) and man-made organics (EDTA) on the radionuclide migration under laboratory as well as in-situ conditions.

3.1.3 Speciation

The word "speciation" infers here the characterization of physical and chemical states of soluble transuranic species in aquatic solution. Since solubilities of transuranic compounds in near neutral solutions are generally very small ($< 10^{-6}$ mol/L) except for An(V), their direct speciation under natural conditions appears very difficult to realize. The colloid generation of transuranic ions of tri-, tetra- and hexavalent states in natural waters adds an extra difficulty for the speciation.

Conventional absorption spectroscopy is a straightforward method but its sensitivity does not even reach solubility concentrations of transuranic elements in natural waters. The method of sensitive differential pulse polarography is, for obvious reasons, not directly applicable to multicomponent natural systems, whereas an electromigration technique provides only qualitative information for the charge state of species. Characterization of colloidal species can be done by a combination of radiometry and ultrafiltration or ultracentrifugation. Because of the relatively low colloid concentrations in natural waters, their detection by conventional light scattering techniques appears not always possible. In view of the absence of direct speciation methods which can provide the desired sensitivity and capability, the speciation of transuranic elements in natural waters has resorted to chemical methods, mostly coprecipitation and solvent extraction.

3.1.3.1 Chemical speciation methods

Chemical methods are sensitive and capable of speciating concentrations down to radiometric sensitivities for nuclides concerned. The most commonly used methods are coprecipitation with MF_3 and MF_4 for tri- and tetravalent transuranic ions, and oxidation state selective chelate extractions, e.g. TTA extraction (thenoyltrifluoroacetate) for tetravalent transuranic ions. The former is, by its nature, less selective than the latter, but a combination of both procedures gives rise to useful results.

The age-old TTA extraction procedure, used since the Manhattan Project days, is beneficial for the speciation of transuranic ions of tetra and hexavalent oxidation states at $pH < 4$ but not applicable for solutions at $pH > 4$ for the reason of TTA decomposition. However, such an extraction procedure requires the acidification of the sample solution, in which redox reactions of transuranic ions may take place and thus lead to ambiguous results. Furthermore, the photolysis reaction in TTA-organic solvent systems may reduce the higher oxidation states, like An(V) and An(VI). In order to improve some limitations of the TTA extraction, the use of dibenzolymethane, 1.3-diphenyl-1.3-propanedione (HDBM), was suggested [2], with which different oxidation states (III, IV, V and VI) could be separated starting with a solution of $pH = 8$ and 0.7 M NaCl. The applicability of this procedure for a real natural water is still to be tested.

3.1.3.2 New speciation methods

Recently much effort has been concentrated on developing direct speciation methods, which are based on non-perturbing optical spectroscopy with the sensitivity of detection considerably higher than conventional spectrophotometry. These methods are laser-induced thermal lensing spectroscopy [3] and laser-induced photoacoustic spectroscopy (PAS) [4,5]. Both use a laser as the light source but the detection techniques differ. They are briefly discussed here.

3.1.3.2.1 Laser-induced thermal lensing spectroscopy (LTLS)

The principle of laser-induced thermal lensing spectroscopy is as follows. A laser beam from a wave scanning system focused into the absorbing medium creates a local temperature gradient and so a refractive index gradient. The spacial redistribution of the refractive index makes the absorbing medium behave as a thin optical lens, which can then be observed by a change of the divergence of the probe laser beam or by its defocusing. The method, first described in Ref. [6], has been developed intensively in recent years. Recent experiments have resulted in a method which is capable of measuring the dissolved uranyl ion in nitric acid with a sensitivity of 4×10^{-6} mol/L.

The major difficulty arises from adjusting the two beams exactly collinear before and after crossing the sample cell and thus insuring that the probe beam is submitted to the thermal lens created by the excitation beam. This difficulty can, however, be suppressed by set-up adjustment devices and so spectral investigation is possible in routine experiments. Further development is in progress to set up differential dual beam thermal lensing spectroscopy, using either pulsed or continuous excitation. Such a development facilitates its practical application with improved sensitivity. This new spectroscopic method provides a speciation sensitivity about 2-3 orders of magnitude better than is possible by conventional spectrophotometry.

3.1.3.2.2 Laser-induced photoacoustic spectroscopy (LPAS)

The difference between laser-induced photoacoustic spectroscopy and the thermal lensing method is particularly in the detection technique. On absorption of photons, the electronic states of actinide ions, or their complexes, are raised to excited energy levels, which decay by radiation emission or non-radiative relaxation. The latter process causes a temperature rise of the light-absorbing solute. In an adiabatic and isobaric expansion, the temperature change creates pressure waves which are detected with a piezoelectric crystal. The photoacoustic signal thus produced is directly proportional to the concentration of a particular actinide species in the solution. The spectroscopic method developed by using such a photoacoustic detection technique is capable of providing spectral information for a wide range of absorption bands (300 nm - 900 nm) of actinide ions in liquid samples with a sensitivity of an average 3 orders of magnitude higher than attainable by conventional spectrophotometry.

The speciation sensitivities attained experimentally for different metal ions are given in Table 1. The sensitivity obtained with this method for U(VI) is found to be somewhat better than the value obtained by thermal

Table 1 Speciation sensitivities of laser induced photoacoustic spectroscopy [7]

Ion	Solution	Sensitivity (mol/L)	Molar extinction coefficient
Ho(III)	1.0 M $HClO_4$	2×10^{-6}	3
Pu(IV)	1.0 M $HClO_4$	7×10^{-8}	76
Pu(VI)	1.0 M $HClO_4$	3×10^{-8}	500
Am(III)	0.1 M $HClO_4$	8×10^{-9}	400
U(VI)	0.1 M $HClO_4$	8×10^{-7}	7
U(VI)	0.1 M H_2SO_4	5×10^{-7}	10

lensing spectroscopy. With the aid of ultrafiltration or ultracentrifugation, this spectrometry can also be used to ascertain the generation of actinide colloids, either real-colloids or pseudocolloids.

The spectral work capability of the LPAS is the same as conventional spectrophotometry but with a much higher speciation sensitivity. The method is not yet fully exploited and further development of the instrumentation is still on the way to improve the sensitivity down to 10^{-9} mol/L.

3.1.3.2.3 Time resolved laser fluorescence spectroscopy (TRLFS)

The radiative relaxation, i.e. fluorescence emission, can be measured directly by optical spectroscopy and thus be detected more easily than the non-radiative relaxation. Two spectroscopic parameters are involved in the fluorescence emission: relaxation time and fluorescence wavelength. Application of a combination of both properties provides time resolved laser fluorescence spectroscopy (TRLFS). Fluorescence of aqueous actinide ions is known for UO_2^{2+}, Am^{3+} and Cm^{3+}. TRLFS is expected to yield more specific information than absorption spectroscopy and hence to increase the speciation capability in solution. Experiments have been carried out to measure the excitation, emission and life time spectra of Cm(III) in $HClO_4$, EDTA, $NaHCO_3$, Na_2CO_3 and Gorleben groundwater.

The excitation spectrum of the noncomplexed aqueous Cm^{3+} ion in 1 M $HClO_4$ in the spectral range of 370-400 nm is measured by fluorescence detection at 575-615 nm. The excitation spectrum shows the same spectroscopic features at the absorption spectrum. Three well distinguished excitation bands are observed, which correspond to the bands, F, G and H absorbing at 396.3, 381.1 and 375.4 nm, respectively. The excitation bands are narrower by a factor of 0.6 than normal absorption bands because of the better spectral resolution of TRLFs, 0.1 nm steps with 0.08 nm FWHM of the laser beam compared to 0.5 nm spectral band width used for the absorption spectrum. The background absorption due to the presence of radiolytically generated H_2O_2 contributes only a negligible effect to the excitation spectrum.

The speciation experiment with TRLFS demonstrates its potential applicability for the geochemical speciation of fluorescing actinide ions. The experiment with the UO_2^{2+} ion is also in progress at Technical University Munich, Germany, which shows the detection sensitivity for this ion down to 2×10^{-12} mol L^{-1}. A combination of LPAS and TRLFS provides a powerful spectroscopic speciation method that can give a new dimension of high reliability to the study of actinide migration.

3.2 Colloids in groundwater

There are always colloids involved in natural water containing transuranic elements. They are defined as being of three kinds: real-colloids, natural water-colloids and pseudocolloids. Real-colloids are produced by the aggregation of hydrolyzed transuranic ions, natural water-colloids are ubiquitous in all aquifer systems and pseudocolloids are generated by sorption of transuranic elements on natural water-colloids, The size of colloids under discussion is defined as being less than 0.45 µm; these remain suspended in natural water stably. Those metal ions which tend to hydrolyze will generate either real-colloids or pseudocolloids. All transuranic ions belong to this category: the tendency is strongest with trivalent and tetravalent ions, followed by hexavalent ions, and least with ions of pentavalent state. In near neutral solutions of low ionic strength, the generation of real colloids of tri-, tetra- and hexavalent transuranic ions is prevalent, each to a different extent. Since the solubility of these ions in such solutions is generally very low, and accordingly the concentration of real-colloids is low, its quantification can often be pursued only by ultrafiltration combined with radiometric measurements. Our discussion of transuranic colloids in natural aquatic systems deals with the following three subjects: characterization, generation and geochemical interactions.

3.2.1 Characterization

Natural water-colloids are the first important substance to understand as for their chemical composition, size distribution and stability in a given water. The generation of pseudocolloids of transuranic elements is, for obvious reasons, directly related with the chemical nature of natural water-colloids.

The size distribution extends to a broad range, from the lower limit of 1 nm, or in some cases even smaller, to the upper limit of 2000 nm (2 µm), which soil scientists generally regard as colloids. In natural waters, particles over 450 nm (0.45 µm) are, in general, shown to be unstable and tend to sediment, once water is separated from a geomatrix in equilibrium. The fractionation size of 450 nm is arbitrary, because such a straight cut-off does not exist in natural systems. Experience shows that a filtrate of natural water separated at 450 nm contains soluble constituents, ionic and non-ionic species including colloids which remain in the solution stably. In the present discussion, it is assumed arbitrarily that the natural water-colloids smaller than 450 nm are potentially migrational in natural aquifer systems, although in soil solutions mobile Pu species are observed to be smaller than 10 nm.

Natural water-colloids differ drastically in chemical composition, depending on the surrounding geomatrix. Metal hydroxide aggregates, polymers of silicate, hydrated minerals of micro-fractures, various natural organics (e.g. humic substance), etc. are commonly known constituents on the macroscopic scale. In deep groundwater, the age-old geological contact of water with surrounding matrices yields solubility equilibria of a wide variety of elements and also generates groundwater colloids which contain many heavy metal elements as trace constituents.

The size distribution of groundwater-colloids can be characterized by different physical and chemical methods, such as correlation spectroscopy, sedimentation process, reverse osmosis, dialysis, electrodialysis, ultracentrifugation, ultrafiltration, etc. Since stably dissolved groundwater-colloids are in very small concentration with small particle sizes (< 0.45 µm) of heterogeneous complex species, the size distribution can be established only by ultrafiltration and ultracentrifugation. For different reasons, all other methods appear to be inappropriate for the purpose.

3.2.2 Generation

The dissolution of any transuranic compound in near neutral solution produces hydrolyzed monomeric, polynuclear and colloidal species. In slightly acidic conditions ($pH < 7$), the solubility of transuranic elements is usually higher than in alkaline conditions ($pH > 7$), so that a higher transuranic concentration leads to a greater colloid generation. Freshly generated real-colloids of transuranic ions are readily separable by ultrafiltration. However, aging of real-colloids under α-recoil effects results in a particle size so small (<1 nm) that they are not easily separable by ultrafiltration. It is observed that the structure changes most likely as $M_x(OH)_y \longrightarrow (MO)_x(H_2O)_z$. The thus formed species, so called oxiaquate, is not readily soluble by acidification, showing slow dissolution kinetics in comparison with freshly generated colloids. The surface of real-colloid produced as a hydrolysis product can be either negatively or positively charged depending on the pH of the solution, as demonstrated by the following model:

$$\left[(M)\begin{matrix}OH_2^{1-\delta}\\ \\ OH_2^{1-\delta}\end{matrix}\right]^{2-2\delta} \overset{H^+}{\longleftarrow} \left[(M)\begin{matrix}OH_2^{1-\delta}\\ \\ OH^{-\delta}\end{matrix}\right]^{1-2\delta} \overset{OH^-}{\longrightarrow} \left[(M)\begin{matrix}OH^{-\delta}\\ \\ OH^{-\delta}\end{matrix}\right]^{-2\delta}$$

where (M) represents the surface metal ion bound to a colloid and δ is the negative charge gained by the oxygen atom from M-OH bond polarization and may have values between 0 and 1. This illustration reflects the surface charge being made positive at $pH < 7$ and negative at $pH > 7$. Real colloids of transuranic elements together with monomeric and polynuclear hydrolyzed species are easily sorbed on natural water-colloids, thus generating pseudocolloids.

3.2.3 Geochemical interaction

Geochemical interactions of transuranic colloids are complicated phenomena which are not yet intensively investigated. An important feature can be characterized by determining their influence on the solubility and sorption behaviour of transuranic elements in natural aquifer systems. Fig. 3 illustrates the reciprocal change in solubility and sorption coefficient of An(III) influenced by their colloid generation. The lefthand side of the figure demonstrates solubilities of $Am(OH)_3$ in non-saline (Gohy-1061)

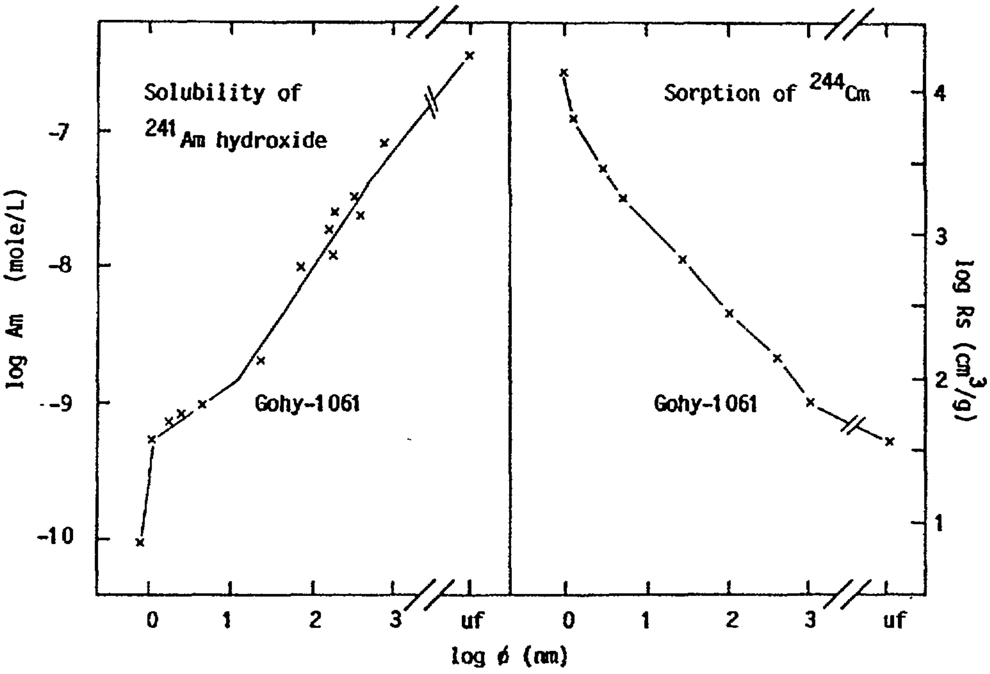

FIG. 3. Solubilities of ^{241}Am hydroxide and sorption coefficients of ^{244}Cm in the Gorleben aquifer system (Gohy-1061) as a function of the ultrafilter pore size applied for the colloid separation (uf: unfiltered).

groundwater (see Fig. 1). Solubilities are determined after ultrafiltrations at different pore sizes. As the filter pore size decreases, the Am concentration in solution decreases continuously. At the righthand side of Fig. 3, the reciprocal effect is observed for the determination of sorption coefficients, R_s (cm^3/g), of ^{244}Cm on sediment sands in contact with the groundwater. R_s increases with decreasing size of the filter pore applied for the phase separation. Here R_s is equivalent to the commonly known distribution coefficient K_d in the literature. The experimental results manifest clearly the colloid effects on the solubility and sorption of actinides in a given aquifer system, which are greater in non-saline groundwater than in saline groundwater.

For the transport calculation of radionuclide (RN) in natural aquifer system, it is a common practice to use its retardation coefficient, defined as the ratio of water flow rate to RN transport rate. The distribution coefficient of a radionuclide between water and geomatrix involved is a major physico-chemical parameter to calculate the retardation coefficient. This is generally known as the K_d value (cm^3/g). The applicability of such a physico-chemical parameter for RN transport modeling has been the subject of long debates in many meetings dealing with RN migration. One of the important physico-chemical problems in the definition of K_d is the generation of colloids in aquifer systems under consideration. This is a fundamental subject to deal with for the understanding of the migrational behaviour of transuranic elements in natural aquifer systems. For the evaluation of retardation coefficients of transuranic elements in a given aquifer system, it is indispensable to take consideration of transuranic colloids, namely their pseudocolloids present as soluble species. The study in this direction has just begun but demands concerted efforts.

3.3 Basic retention mechanisms

Retention mechanisms in the near and far field of an underground radioactive waste repository provide major barriers to the migration of radionuclides to the biosphere. A number of processes can contribute to this retention, including sorption on and diffusion into solid surfaces and chemical reactions and redox processes which may produce insoluble or less soluble species. The need to identify, understand and model these processes has led to extensive studies in the organizations participating in this CRP. The results of the work on the basic mechanisms are summarized below.

3.3.1 Sorption

Some of the most extensive studies of sorption were reported by British Geological Survey (BGS), from natural analogue systems, in-situ migration studies and laboratory experiments, and these studies highlighted the importance of organic components in retarding migration of uranium. At the Needle's Eye uranium analogue site, U/Th series data on rock, soil and sediments indicated that uranium had migrated slowly from the source in the cliffs to the sediments, which retarded the uranium significantly [8,9]. Uranium accumulated at two distinct levels in the sediment profile, at around 50 cm depth and between 100-150 cm. Fission track registration indicated that at the 50 cm level uranium was located within the fine organic matter of the peaty matrix and was strongly enhanced around open root-channels where concentrations reach several hundred ppm. This suggested fixation due to reduction. In the deeper accumulation, U was located almost exclusively within plant roots, and was particularly concentrated (often >1000 ppm) within specific cellular structures related to water transport. In addition, U-As-Cu and Bi bearing minerals found on root surfaces indicated that metal-fixing fungi may be important in arresting mobile uranium.

At the South Terras analogue site, the BGS work examined the movement of uranium from pitchblende in old mine spoil heaps into a small stream through a region of alluvial deposits. They found that these alluvial deposits acted as an efficient retardation barrier for uranium [10,11]. The modelling studies implied that uranium is being actively leached, that direct precipitation of uranium phases was unlikely, and some form of sorption must be responsible for retardation of the uranium. The migration of uranium through the sediments was modelled with the CHEMTARD code [11,12] based on surface complexation reactions. It was stated that this model simulated the observed results well without use of the simplistic reversible K_d concept.

At the Broubster analogue site, BGS examined the sorption of U and Th on colloidal material. Five slightly acidic, oxidizing groundwaters from the peat sink area were passed through a 0.45 micron filter then through a portable chromatographic separation kit [13], before subsequent elution and analysis for U and Th. In all samples, the majority (57-99%) of the soluble U was bound to high molecular weight organic acids; only relatively minor amounts were associated with Fe/Mn oxyhydroxides or in the cationic uranyl form. The analytical recovery for Th was poor (indicating some colloidal participation) but the results did indicate that the bulk of the Th present was with Fe/Mn oxyhydroxides.

The BGS concluded that organic matter played a vital role in retarding uranium. They set up a major programme of in-situ migration studies particularly to examine the effects of organics on the mobility of radionuclides under controlled conditions in-situ in a confined glacial sand aquifer [14]. Groundwater was re-circulated between two boreholes 3.4 m apart and tracers were injected in a third borehole 0.94 m from the recharge borehole. Tracer migration was monitored with gamma probes and by removing water samples at various levels. Organic matter was in the range 0.1-2.5%. Total organic carbon in the sand horizon was 6-12 mg/L and in the silt/clay horizons 20-70 mg/L. Most of the dissolved carbon was shown to be fulvic acid. Extensive analysis of micro-organisms was undertaken and these were shown to be present in all core and water samples. The concentration of natural colloids was assessed in groundwater samples [15]. SEM analysis of filters yielded values of 10^8 - 10^{10} particles/L. Uranium series disequilibrium measurements were used to determine the partition of natural actinides between particulate, colloid and solution phases. The colloid phase was found to hold 0.1-0.5% of total uranium and 1-5% of thorium.

Batch laboratory experiments were used to assess the effects of natural organics, EDTA and acetate on the sorption of Cs, Sr, Co, Eu, Np, U and I [16,17]. Cobalt was chosen for most experiments because it is relatively insensitive to redox changes, is known to form complexes with organics and could thus be used in technique development. Radionuclide complexation with natural organic material in groundwater was assessed by separating the 'free' from 'complexed' radionuclide species using gel chromatography [18]. A series of diffusion experiments using the through diffusion and infinite couple geometries was conducted with ^{36}Cl, ^{125}I, ^{58}Co and ^{58}Co/(^{14}C) EDTA. Under sterile conditions, iodine moved at the same rate as Cl. Under non-sterile conditions, iodine was immobile and the influence of microbial activity was suspected [19]. Column experiments were used to simulate the migration of various organic/radionuclide complexes in the field tracer test and to identify the dominant sorption mechanisms. Tracer tests and associated modelling are still in progress.

In contrast to these sorption-dominated studies, BGS reported work on the migration of halides (Cl, Br, I) in sediments at an analogue site at Loch Lomond. They interpreted the measured concentration profiles in terms of diffusion without retardation in the presence of significant organic material [20,21].

Atomic Energy of Canada Ltd. (AECL) reported work on the sorption behaviour of iodine as iodide and iodate in contact with common granitic fracture-filling minerals [22]. Iodate was found to sorb on several of the minerals used, notably chlorite and hematite. No significant sorption of iodide occurred with any of the geological minerals studied.

The sorption of several fission products (Se, Sr, Tc, Cs, Ce) and the actinide Am on primary and secondary minerals in a gabbroic pluton have been documented [23]. With the exception of technetium, sorption of the radionuclides used in this study was significantly greater on secondary than on primary rock-forming minerals. Technetium did not sorb under aerobic conditions but was found to sorb on magnetite under low-oxygen conditions.

The determination of the sorption characteristics of the actinides U, Np and Pu on common granitic fracture-filling minerals as a function of total dissolved solids (TDS) content of the contacting solution under normal and reduced oxygen conditions was completed by AECL. A preliminary examination of the experimental results indicated that individual mineral type plays a key role in the removal of these actinides from solution. Hematite showed the greatest affinity for each of the actinides studied under all experimental conditions. Goethite and kaolinite also showed a high affinity for U, while illite and kaolinite removed substantial amounts of Pu from solution. Quartz consistently showed the least affinity for each of the radionuclides used under the spectrum of experimental conditions studied. Epidote and gypsum showed low sorption of U and Np. Muscovite and kaolinite also showed little affinity for Np under these experimental conditions. The effect on measured sorption of the total dissolved solids content of the synthetic groundwater also varied with the sorbing mineral type. For example, there is no apparent effect of TDS on U sorption by geothite, hematite or kaolinite under high oxygen conditions while U sorption on chlorite and muscovite decreases markedly with increasing TDS under the same conditions. In general, reduced oxygen levels resulted in marginal increases in the amount of actinide removed from solution. A detailed examination of the results of this study is being prepared for publication.

Japan Atomic Energy Research Institute (JAERI) reported work on the sorption of neptunium on naturally-occurring hematite, magnetite, goethite and biotite in 0.1M $NaNO_3$ solution at 30°C for pHs between 4 and 11. The mass to volume ratio was 1 g/L. The sorption-desorption reaction was reversible for all the minerals in the pH ranges studied. The dependence of neptunium sorption on pH differed between goethite and the other three minerals; goethite showed a strong sorption at pHs above 6 while the sorption on hematite, magnetite and biotite occurred at pHs above 9. Other oxyhydroxides, lepidocrocite and boehmite, have similar pH dependence of sorption to goethite. The sorption on hematite was similar to that on alumina.

JAERI reported earlier work on the batch sorption behaviour of ^{237}Np and ^{241}Am on sands and solid at the first RCM in 1988. Three types of soil and sand from shallow sites were studied in 0.01M perchloric acid solution at 30°C for pHs between 3 and 11. The Np concentration was 10^{-5}M. The Kd's increased from pH 3 to 7 and were then constant at pHs from 8 to 11 in the range 6-20 cm^3/g for the sands and 800 cm^3/g for the solid (loam). The sorption of ^{241}Am showed a different behaviour with the Kds reaching a maximum at pH 6 to 7 for three types of sands, the maximum Kd values being 1000 cm^3/g for a coastal sand, 100 cm^3/g for another sand, and 10 cm^3/g for a silica sand.

The Laboratory for Radiation Research (LSO), Netherlands, also reported some sorption data for batch and column experiments on glauconite sands for ^{239}Pu, ^{240}Pu, ^{241}Am, ^{237}Np and ^{99}Tc at the first RCM in 1988. Pu and Tc were sorbed in the top few cm of the sand column at pH 5 whereas Am and Np migrated a few cm over periods of 2-4 months. The redox state of the isotopes does not appear to have been closely controlled in the early experiments, but was made reducing in later experiments. A number of batch Kd values were also measured. Typical values for Am at pH 5-6 were 1000-4000 cm^3/g; for Pu 2000-14000 cm^3/g and Np 10-30 cm^3/g (at pH 6). The experiments led to the following reference Kd values being recommended for the Dutch safety study: Am, 1000 cm^3/g; Pu, 4000 cm^3/g; Np, 60 cm^3/g; Tc, 30 cm^3/g.

Sorption of ^{90}Sr, ^{137}Cs, ^{241}Am and ^{237}Np on montmorillonite buffer materials was reported by Beijing Research Institute of Uranium Geology (BRIUG). The sorption of ^{90}Sr and ^{137}Cs was measured by batch and column techniques and both isotopes were shown to give similar results. The saturation sorption capacities of ^{90}Sr was 21-38 mg/g on Ca-bentonite and 18-29 mg/g on Na-bentonite at a pH of 7 and a ^{90}Sr concentration of 50-200 ppm. Batch experiments with ^{241}Am showed that equilibrium was established in 7-12 hr for Ca-bentonite and 17-20 hr with Na-bentonite. $K_{d(Am)}$ values were 1740 cm^3/g for Ca-bentonite and 780 cm^3/g for Na-bentonite. Equilibrium was established in 10-14 hr for ^{237}Np sorption on these bentonites. $K_{d(Np)}$ values were 8000 cm^3/g for Ca-bentonite and 5900 cm^3/g for Na-bentonite. The pH value strongly affected the sorption behaviour for ^{241}Am and ^{237}Np.

It is noted that additional results on sorption of various radioisotopes are being produced in a parallel CRP on "Nuclear Techniques in Study of Pollutant Transport in the Environment: Interaction of Solutes with Geological Media (Methodological Aspects)". A review of the programme was provided by the IAEA at the second RCM describing the scope of this CRP. Sorption processes were studied by several laboratories by batch and column techniques. One conclusion of the above CRP was that although the use of Kds could be criticized, the concept could not be abandoned at this stage. Alternative approaches, e.g. surface complexation theory, required further experimental study and modelling before they could replace the use of simple Kd values. The parallel CRP indicated that multitracer techniques (using a conservative tracer and a pollutant tracer) gave a good basis for comparing water and pollutant migration.

The conclusion to be drawn from the work in both of these CRPs is that a large amount of data on the sorption of transuranic actinides and fission products, both in field studies and in carefully controlled laboratory studies, is being accumulated. These data will enable comparisons to be made with the models available of whether Kds or other concepts are better able to describe the migration behaviour of radionuclides in the geosphere. Several factors have, however, been identified as important in controlling the migration. These include complexing or sorption with organic materials, redox chemistry (see also Section 3.3.4), sorption on specific minerals (see also Section 3.3.3), and the possible influence of colloids (see also Section 3.2).

3.3.2 Diffusion

The importance of slow diffusion in a geological medium on retention of a radionuclide was illustrated in work by BGS on iodine (and other halides) in sediments at the Loch Lomond analogue site [20,21]. The profiles of concentration of iodine, chloride and bromide with depth in the sediments were interpreted and modelled in terms of diffusion and release from enriched bands [24], see Fig. 4. The half-life for iodine in the organic matter was about 2 Ma, ie., less than 1% was lost by release and diffusion since the return of freshwater conditions to this original marine environment over 5000 years ago.

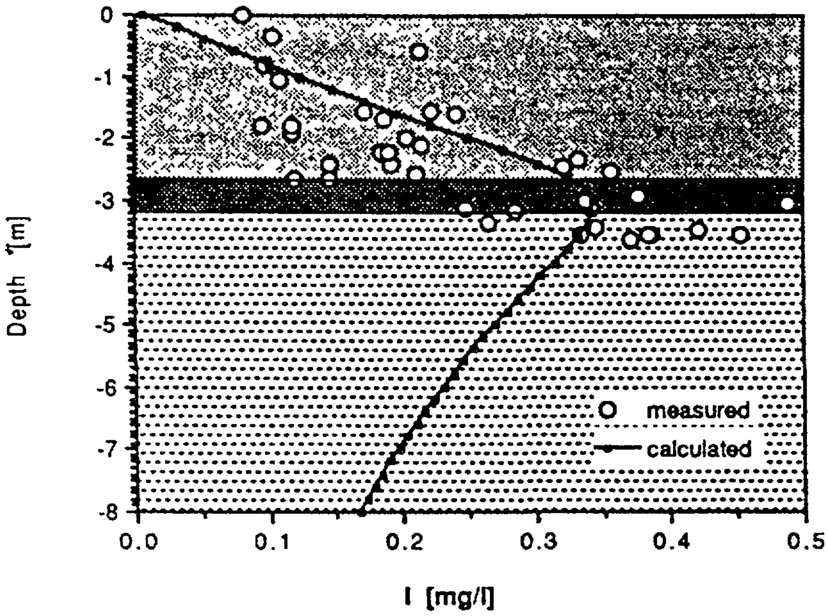

FIG. 4. Comparison between measured iodide interstitial water concentration data and the calculated profile for sediment core LLMA in Loch Lomond, Scotland. Redistribution of the initial seawater iodine concentration of 0.067 mg/L is accompanied by slow release (0.08 mgm^{-3}y^{-1}) of iodine from the organic matter of the marine horizon and occurs by diffusion.

JAERI described at the first RCM in 1988 results for the diffusion of Tc as the pertechnetate anion ($^{95m}TcO_4^-$) in samples of Na-bentonite and deep sea sediments at room temperature [25]. Measured apparent diffusion coefficients in sediments (6-8 x 10^{-10} m^2/s) and Na-bentonite (1-3 x 10^{-10} m^2/s) were linearly correlated with log scales for water contents and porosities of the materials. Retardation of Tc in the sediments was attributed to interaction with small regions rich in pyrite which could have reduced the Tc.

3.3.3 Mineralogical controls

Los Alamos National Laboratory (LANL) has examined the importance of mineralogical controls on the geochemistry and migration of transuranic actinides and fission products in their work. JAERI has also contributed data on the way in which key minerals, such as chlorite, are altered over long time periods.

LANL concluded from their work on plutonium production in uraniferous rocks that the composition of the minerals surrounding a uranium ore sample over a distance of the order of 0.5m influenced the neutron flux and therefore the amount of ^{239}Pu or ^{99}Tc or ^{129}I produced by neutron-induced reactions. The presence of reducing materials in the host rocks also has a considerable influence on the migration of key radionuclides, and LANL addressed this in their study of the geochemistry of Pu in a redox front in a sample of uranium ore from the Osuma Utsumi mine in Brazil. It was concluded that Pu and U behaved similarly geochemically in the system at that site and that the two elements had remained unfractionated in the highly uraniferous rock for the last 10^5 years.

The JAERI work described the alteration of the mineral chlorite, and how cations redistribute over long time periods. The samples of chlorite were obtained from the Koongarra uranium deposit as part of the Alligator Rivers Analogue Project (ARAP) analogue study. Clay minerals were identified and the techniques of scanning electron microscopy (SEM), optical microscopy (OM) and electron microprobe analysis (EMPA) were used to study the alteration reactions. Chlorite was altered progressively to form vermiculite, kaolinite, and an iron mineral (probably ferrihydrite) was also formed. Other iron minerals (goethite and hematite) were also found in the weathered zone at the Koongarra site. Complementary studies within the ARAP project have shown the importance of these iron minerals in strongly sorbing heavy metals, e.g., uranium. Part of the JAERI work was concerned with the identification of the distribution of uranium among the constituent minerals using the alpha-track technique. The conclusions were that the strongly altered zone had a high uranium concentration and that chlorite itself is also a good absorbent of uranium. The uranium migration at Koongarra might therefore be related to the alteration of chlorite to other minerals, and the influence of iron minerals in retarding the migration.

3.3.4 Redox processes

Redox processes are considered to be important in the migration or retardation of radionuclides because the redox state of an element strongly influences its solubility in aqueous media, e.g., U(VI) is generally more soluble than U(IV), and similar characteristics are known for transuranic actinides and some fission products (e.g., Tc).

A considerable part of the BGS work described in Section 3.3.1 was concerned with redox conditions controlled by inorganic or organic materials. Retardation of uranium in soils and silts at the Needle's Eye analogue site was considered to be due to reduction by organic materials or by iron oxyhydroxides in the deeper silts. However, work at the Broubster analogue site indicated that the best modelling results for uranium migration were obtained with U in the VI state and no U(IV) species were predicted. Uranium (VI) carbonates predominated in the aqueous phase at that site. Modelling at the South Terras analogue site indicated also that U(VI) was important in solution, but primarily as a phosphate complex.

The AECL work on the Cigar Lake uranium deposit indicated the variability of the oxidation state of the uranium in different drillcore samples, although it was pointed out that some changes could have occurred after sampling. U(VI)/U(IV) ratios in drillcore samples varied between 0.16 and 0.29 for one set of new samples and were 0.7 for a second set compared with 0.24-0.57 for an earlier set of samples. These different ratios would considerably affect the interaction of the uranium minerals with the groundwater. In AECL radionuclide sorption studies in the laboratory, it was found that Tc did not sorb on minerals under aerobic conditions but sorbed on magnetite under low-oxygen conditions, confirming the importance of the redox conditions for multi-oxidation state elements.

The importance of redox conditions was referred to previously in Section 3.3.3 in the context of the LANL work on plutonium geochemistry in a redox front. The redox conditions were controlled over geological time by a combination of reduced iron minerals and oxidizing groundwater flow which led to concentration of uranium in nodules. The study concluded that Pu and U had resided, unfractionated, in the uraniferous rock for the last 10^5 years.

3.4 Natural and chemical analogues

BGS summarized the situation as: "It is now well recognized that the study of natural geochemical systems can help us to gain a better understanding of the different processes of radionuclide mobilization, transport and retardation in the far field, and to provide a means of testing the thermodynamic databases and transport codes which underpin performance assessments of radioactive waste repositories".

Results of work at several analogue sites (mainly uranium deposits) were presented within the CRP, e.g.

- BGS - Loch Lomond sediments (halides)
  - Broubster sediments (uranium)
  - Needle's Eye sediments (uranium)
  - South Terras disused uranium mine

- ANSTO - Koongarra uranium deposit

- LANL - Koongarra uranium deposit
  - Osuma Utsumi uranium mine
  - Cigar Lake and Key Lake uranium deposits
  - Oklo uranium deposit
  - Katanga uranium mine

- BRIUG - Lianshanguan uranium deposit

- AECL - Cigar Lake uranium deposit

- JAERI - Koongarra uranium deposit

The results which are directly relevant to transuranium actinides and fission products relate to the production of these in-situ and this is discussed in Section 3.4.1. The measurements of these radionuclides in-situ is discussed in Section 3.4.2 mainly with respect to ^{239}Pu, ^{99}Tc, ^{129}I

and ^{36}Cl, but also with respect to complementary results on U/Th disequilibria. Some results on chemical analogues (e.g. rare earth elements for transuranic actinides) are discussed in Section 3.4.3. Finally, analytical techniques for the measurement of long lived radionuclides in natural systems are reviewed in Section 3.4.4.

3.4.1 Natural production of NRPs

Within the CRP only LANL and IPNT reported original work on the natural production of nuclear reaction products (NRPs). The long-lived radionuclides of importance in radioactive waste management are also constantly produced in rocks by various nuclear processes with neutrons or with alpha particles, or from spontaneous fission of uranium isotopes, primarily ^{238}U [26]. These radionuclides are: ^{14}C, ^{36}Cl, ^{81}Kr., ^{99}Tc, ^{129}I, ^{237}Np, ^{239}Pu. (See Figures 5 and 6). Calculation of the extent of natural production of these requires information on the neutron or alpha particle fluxes and the detailed composition of the minerals and rocks and other information, e.g. porosity, water content, etc.

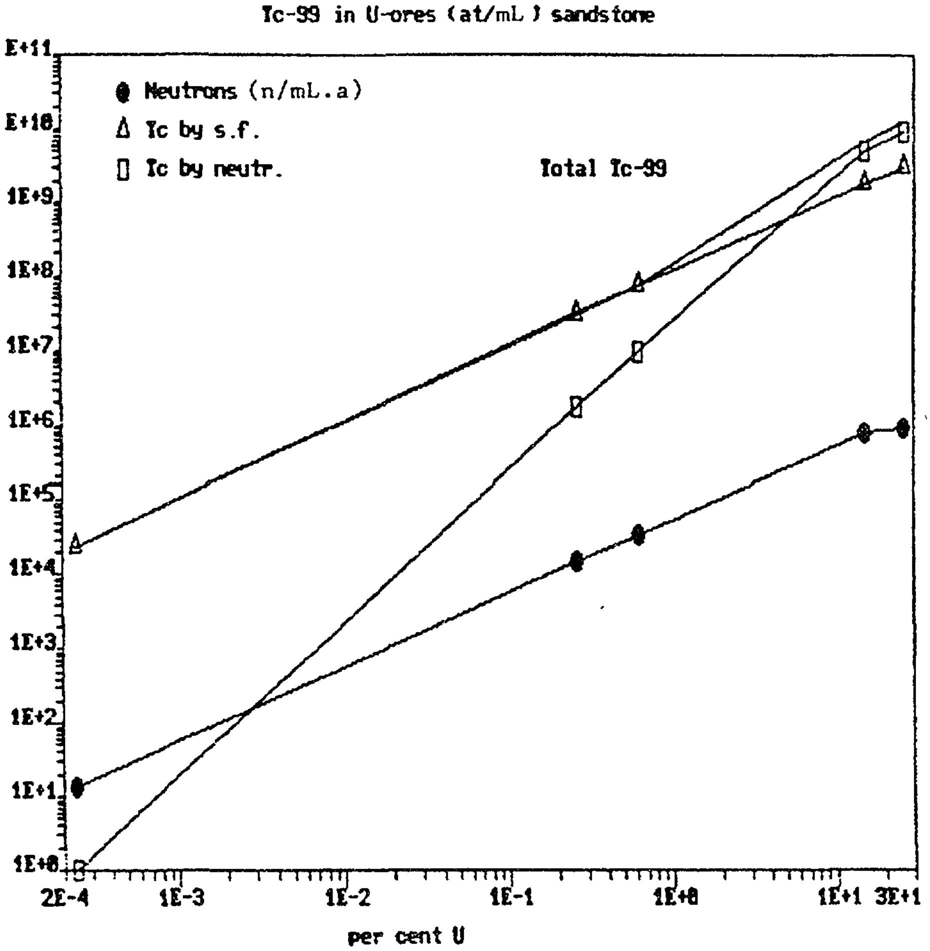

FIG. 5. Production of ^{99}Tc atoms in sandstone versus uranium content.

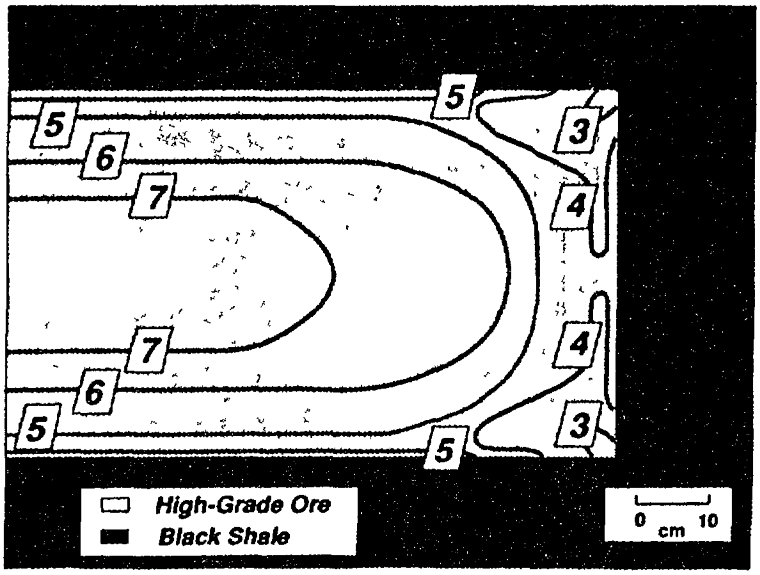

FIG. 6. Calculated Pu/U ratio contours (× 10^{12}) in model OKLO fossil reactor zone [27].

The work of IPNT showed that the production of ^{99}Tc and ^{129}I in rocks is only from spontaneous fission, whereas neutron-induced fission is more important in U ores. The ratio of ^{239}Pu/^{238}U in rocks is of the order of 10^{-12} and increases with U content. However, work by LANL clearly indicated that there is no simple correlation of Pu/U ratio with sample composition, because samples are usually small and the neutron flux at that sample position was influenced over time by the rock composition over distances of 0.5m. Figure 7 shows the calculated ratios ^{239}Pu, ^{129}I and ^{99}Tc to ^{238}U for increasing U content.

3.4.2 Natural analogues

The LANL work provided reliable direct measurements of the natural abundance of ^{239}Pu and ^{99}Tc in uranium ore samples from several sources. The ^{239}Pu/U ratio varied from 0.8 - 5.3 x 10^{-12} representing ^{239}Pu production rates of 60-390 atoms Pu/mgU/a. LANL is also processing samples for ^{129}I measurements at the University of Rochester. See Fig. 8.

ANSTO reported work on the measurement of ^{129}I and ^{36}Cl in association with LANL, University of Arizona, University of Rochester and the Australian National University, all within the Alligator Rivers Analogue Project (ARAP). ^{129}I/U ratios were obtained in the range 1-3 x 10^{-12} for uranium contents of 6-25% in ore samples. ^{129}I/I ratios measured in water

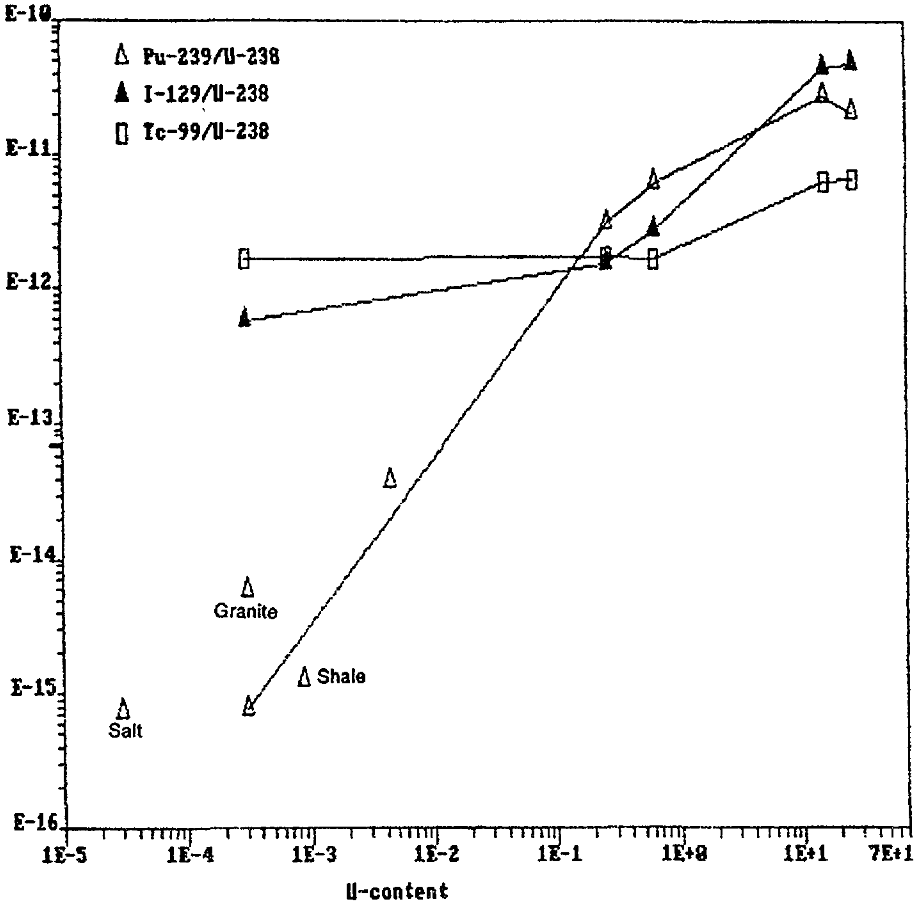

FIG. 7. Ratios of ^{239}Pu, ^{129}I and ^{99}Tc to ^{238}U for increasing uranium content.

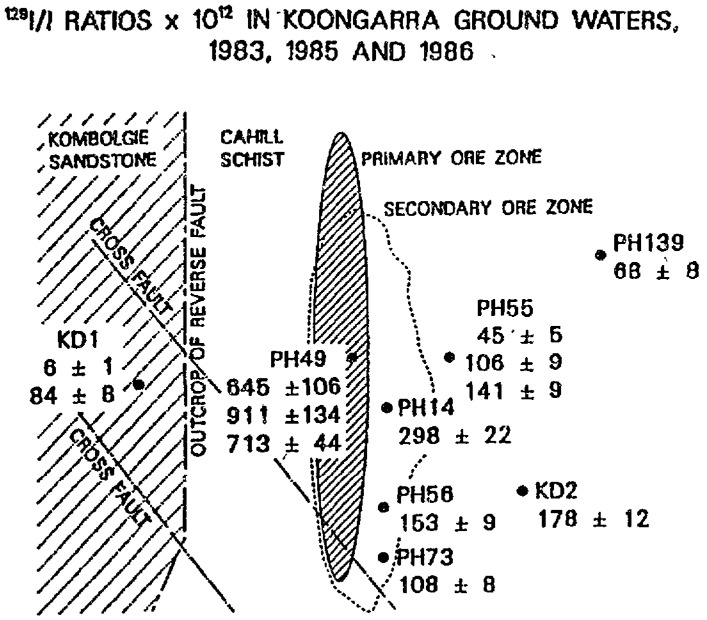

FIG. 8. Distribution of ^{129}I in Koongarra groundwaters.

samples from the primary ore zone were 3 orders of magnitude higher than background levels up-gradient. The ratios down the water gradient were factors of 2-7 lower than in the primary zone and well above background.

AECL reported preliminary ^{129}I data for Cigar Lake sample (in association with LANL) of 2-3 x 10^{-12} for ^{129}I/U ratios, which were greater than the predicted ratio of 1 x 10^{-12} for spontaneous fission of ^{238}U alone (assuming a 0.05% mass 129 yield). Two samples measured at the University of Toronto ranged from 2.6 - 3.9 x 10^{-12} for the ratio, in good agreement with the LANL results.

The major results of the natural analogue studies at the UK sites reported by BGS have already been reviewed in Sections 3.3.1 and 3.3.2 in the context of the retardation of uranium and diffusion of halides in natural systems. The data were incorporated in models to describe radionuclide migration in natural systems.

3.4.3 Chemical analogues

Much of the early work carried out by LANL and others at the Oklo uranium deposit, at which natural uranium reactors operated over geological time, provided information on elements which can be used as chemical analogues for important actinides or fission products [28]. Rare earth elements (REEs) have been used as chemical analogues for transuranic actinides, particularly in three- and four- valence states, because of the difficulty in measuring these transuranic actinides directly in natural geological systems. However, comparison of the behaviour of (generally) trivalent REEs with trivalent transuranic actinides should be made with caution. The BRIUG presented detailed analyses of REEs in bentonites on which sorption properties were measured, but gave no interpretation of the significance of the REE composition in the materials, which varied considerably between different samples, even from the same site.

3.4.4 Analytical methods for natural NRPs

The measurement of naturally occurring NRPs especially ^{239}Pu, ^{129}I and ^{99}Tc, has only been possible by the application of two techniques which have the required sensitivity. These are isotope dilution mass spectrometry (IDMS), which has been used extensively at LANL on samples from natural analogue systems (see above), and tandem accelerator mass spectrometry (TAMS), which has been used particularly for ^{129}I and ^{36}Cl in recent years within the Alligator Rivers Analogue Project (ARAP) using accelerators at the University of Rochester in association with research at the University of Arizona and LANL, and at the Australian National University. Recently, AECL has collaborated with the University of Toronto Isotrace Laboratory for ^{129}I measurements, as well as with LANL.

In addition to having suitable mass spectrometers or accelerator/mass spectrometers, it is essential to have specialized laboratories and procedures for the preparation of samples to minimize contamination. The upgrading of both procedures and clean-room facilities at LANL has recently been demonstrated to reduce the background levels of radionuclides and improve reproducibility considerably [29]. Prior to 1987, the average ^{239}Pu blank was approx. 3 x 10^8 atoms and the detection limit (3 sigma) was 13 x 10^8 atoms, whereas after 1987 new procedures were used and the average was reduced to 0.8 x 10^8 atoms with a detection limit of 3 x 10^8 atoms.

New techniques for the measurement of speciation of aqueous actinide ions have been developed and applied by J.I. Kim and associates at TUM. The methods are laser-induced photoacoustic spectroscopy (LPAS), time resolved laser-induced fluorescence spectroscopy (TRLFS), and photoacoustic detection of light scattering (PALS). These are applicable to analysis of selected actinides in the concentration range from 10^{-6} to 10^{-12}M. LPAS can be used with Am^{3+} and its complexes in solution down to about 6 x 10^{-9}M. TRLPs can be used for actinide ions and complexes which fluoresce down to very low concentrations, e.g. 10^{-11}M for Cm^{3+} and 10^{-12}M for UO_2^{2+}. PALS is particularly applicable to detect and quantify colloids in groundwaters. These three techniques still do not have the sensitivity to measure natural NRPs which commonly occur at concentrations orders of magnitude lower than the above-quoted sensitivities.

3.5 Thermodynamic databases

A thermodynamic database for long lived transuranic elements and fission products of higher oxidation state is of great importance for appropriate modelling of the geochemical behaviour of these elements in surrounding aquifer systems of a given repository site. There is a considerable number of thermodynamic data available in the literature particularly for the aqueous species of the elements under discussion, whereas for the solid state complexes of these elements the useful thermodynamic data are scarce for the moment. Geochemical modelling, however, requires both sets of thermodynamic data for a reliable prediction of the migrational behaviour of the elements in a given aquifer system.

Much effort has been devoted to produce thermodynamic databases, especially for long lived transuranic elements and fission products of higher oxidation state by different working groups all over the world, for example, OECD/NEA, CHEMVAL (UK/CEC) EQ 3/6 (USA), MINEQL (USA) etc., databases. All these databases have resorted to the same literature sources but the interpretation of given data differs somewhat from one database to another. However, the original thermodynamic data selected from the literature are not treated with thorough verification. Many data included already in the various databases are of poor quality and others require well qualified verification. As for the thermodynamic data for transuranic elements and fission products of higher oxidation state, there are for the moment more compilations done than experimental production of new data. This phenomenon arises from some significant reasons: expensive and time consuming efforts being necessary for laboratory thermodynamic experiments, a small number of laboratories being capable of handling transuranic elements for the study and the basic transuranic chemistry being less encouraged by the funding authorities. An internationally consolidated effort is essential in the field of experimental work on thermodynamic data, particularly for transuranic elements.

3.6 Transport modelling

Transport modelling for water and radionuclides forms an essential part of performance assessments and safety assessments for radioactive waste repositories. A number of simple and increasingly complex codes have been developed for this purpose. Input data of high quality are equally important and the data needed include transport characteristics of the actinides and fission products which are the source term of the radioactive waste. The understanding and quantification of the processes which occur are essential to ensure that the models and codes adequately represent natural and practical systems.

BGS and ANSTO reported extensive interaction between experimental data gathering and application in both research and generalized models, usually for U/Th systems or halide (I, Cl, Br) systems. LANL reported comparisons between experimental measurements of NRPs and predictive models for NRP production. Examples of these results are summarized below.

The modelling of halides in sediments at the Loch Lomond analogue was reported by BGS (see Section 3.3.2), and it was concluded that the observed profiles could be explained in terms of very slow diffusion without retardation [24]. Less than 1% of the iodine was lost over at least a 5000 year period.

Modelling of uranium migration at the Needle's Eye, Broubster and South Terras analogue sites was also described by BGS. A series of codes were used in these studies, e.g. METIS [30], STELE [31], PHREEQUE [32], CHEMVAL [33], CHEMTARD [11,12], in association with thermodynamic databases, e.g. the OECD/NEA database (see Figure 9). Equilibrium speciation modelling with Broubster data was based on the concept that U was released from the mineralized source rocks; was advected downslope and fixed by organic material in peat. The study highlighted deficiencies in modelling uranium-organic interactions as simple ion-association reactions, and the problems of colloids and co-precipitation in the modelling of Th migration. The observation was made that the modelling of uranium migration from South Terras data using surface complexation reactions was satisfactory without recourse to the simplistic reversible Kd concept.

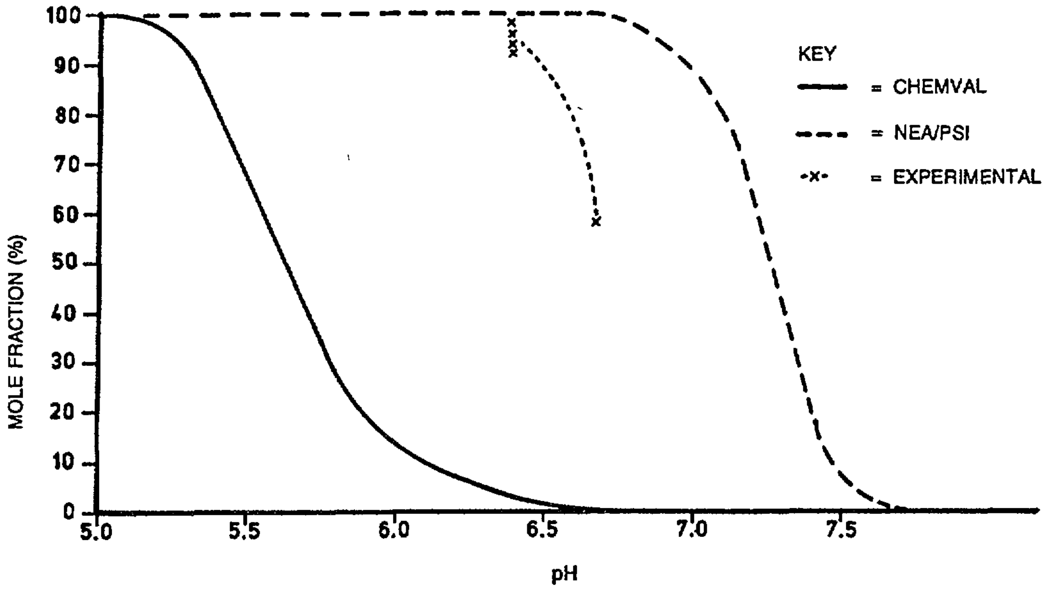

FIG. 9. Uranium humates in Broubster soil waters showing variations with pH, and comparison with calculated variations using two databases.

Conclusions included in the BGS report were that organic matter plays a pivotal role in the retardation of uranium and that the capability of the relevant codes to deal with these interactions is poor [34]. Nevertheless, the relevant codes can be applied to the natural analogue data within limitations. The use of the surface complexation concept rather than the Kd concept was recommended provided that appropriate laboratory data are available or will be measured. A modification of the PHREEQUE code to include complexation and surface complexation concepts has been developed [34].

ANSTO has also carried out extensive modelling studies within the ARAP project and reported some of the results at the first RCM in 1988. The majority of the work was the development and application of research models to the migration of uranium in the secondary dispersion zone near the surface of the Koongarra uranium deposit. The result was an estimate of the migration of uranium over a distance of about 80 m over a period of about 1-3 Ma [35]. The more recent data are now being modelled by several laboratories as part of the INTRAVAL international validation exercise sponsored by the Swedish Nuclear Power Inspectorate [36].

Additional information on transport modelling and the interaction of experimental data and models is being generated within the complementary CRP on "Nuclear Techniques in Study of Pollutant Transport in the Environment: Interaction of Solutes with Geological Media (Methodological Aspects)", which was briefly reviewed at the second RCM of the present CRP in June 1990 (see also comments on sorption data in Section 3.3.1).

4. CONCLUSIONS AND PROSPECTS

It must be noted at the outset that the organizations which participated in this CRP largely reported results from ongoing long term projects rather than completed studies with well developed results and conclusions. Based upon these results, the following conclusions can be drawn:

- Considerable effort was devoted to studying natural analogue systems, speciation of radionuclides in solution including organic complexation, colloids and sorption, with a consequently large amount of data being generated.

- The data from sorption studies used batch and column experiments in the laboratory and also field studies. A trend is emerging to find new ways of quantifying the sorption process, e.g., surface complexation instead of the hitherto used Kd concept in transport modelling.

- Sensitive analytical methods have been developed and are being refined and used increasingly for (i) the measurement of naturally produced levels of nuclear reaction products (NRPs), e.g. ^{239}Pu, ^{129}I, ^{99}Tc and ^{36}Cl (which are important in long-term safety assessments), and (ii) for the analyses of extremely low levels of aqueous species of important transuranic actinides. Isotope dilution mass spectrometry (IDMS) and tandem accelerator mass spectrometry (TAMS) are currently the only methods available to measure naturally produced levels of NRPs.

- Considerable interaction is evident between experimentalists and modellers with consequent efficiency in the use of limited expert resources. Improvements are needed in some areas of modelling, e.g., uranium-organic interactions, sorption databases, neutron flux distributions in natural rocks/mineral systems.

International and regional collaboration has been increasing steadily in the radioactive waste management field in recent years, e.g. the major EEC programmes, international analogue programmes, etc. IAEA may consider continuation as the lead for co-ordination and dissemination of technical information in this field, especially to developing countries which may not be members of the major radioactive waste research and development programmes. The IAEA can make a cost-effective contribution by selecting and co-ordinating subjects of common basic and long term interest to all countries, e.g. thermodynamic databases, geochemistry, analytical methods, model validation, etc., especially those activities associated with geological disposal of radioactive waste.

It is noted that several of the major natural analogue studies involving uranium deposits will be completed within a 2-3 year timeframe and should publish well-evaluated results which would lead to improvements in transport modelling. The available transport models at that time are likely to be adequate for performance assessments and safety assessments for proposed repositories within acceptable levels of uncertainties which are inherent in dealing with complex natural systems. Benefits should also continue to be generated from the ongoing complementary CRP on "Nuclear Techniques in Study of Pollutant Transport in the Environment: Interaction of Solutes with Geological Media (Methodological Aspects)", which incorporates work on sorption, transport models and analytical methods.

Specific suggestions which the IAEA may wish to consider for future work includes:

(1) The wider development and application of the advanced analytical and modelling capabilities utilized by organizations in the CRP.

(2) The development and distribution of quality assured thermodynamic databases appropriate to performance and safety assessment modelling in close collaboration with the OECD/NEA, which has a significant involvement in this area.

(3) Maximum interaction between experimental and modelling projects in organizations in developed and developing countries so that maximum use of scarce expert resources can be achieved.

(4) Interest in geochemistry in natural analogue systems which would be of considerable interest to Member States, and more particularly it might participate in some way in the re-emerging interest in more detailed examination of the OKLO fossil reactor system in Gabon.

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Appendix

SUMMARIES OF WORK REPORTED AT RESEARCH CO-ORDINATION MEETINGS

SPECIATION OF AQUATIC ACTINIDE IONS BY PULSED LASER SPECTROSCOPY

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A speciation of the chemical state of actinides in groundwater is an essential prerequisite for a better understanding of their migration phenomena in a given aquifer system. This exercise, however, demands a direct speciation method of high sensitivity which corresponds at least to the solubility range of actinides in groundwater. For this purpose, a number of highly sensitive spectroscopic methods have been developed in our laboratory, using laser as a powerful light source, and applied to the speciation of aqueous actinides in the submicromolar range: from 10^{-6} mol/L to 10^{-12} mol/L. Three different spectroscopic methods are presented in this paper, which are briefly described as follows.

The first method is spectroscopy based on the detection of non-radiative relaxation processes by a photo-acoustic method, which facilitates in fact detecting the microscopic molecular calorimetric process occurring in solution. This method, called laser-induced photoacoustic spectroscopy (LPAS), provides a speciation sensitivity down to 6×10^{-9} mol/L for Am^{3+} or its complexes in solution.

The second method, called time-resolved laser fluorescence spectroscopy (TRLFS), measures the radiative relaxation, i.e. fluorescence emission, directly by optical detection. Two spectroscopic parameters can be characterized in the fluorescence emission: fluorescence energy and relaxation time. The measurement of both properties in parallel provides the high speciation sensitivity for fluorescing actinides, e.g. 10^{-11} mol/L for Cm^{3+} and 10^{-12} mol/L for UO_2^{2+}.

The third spectroscopic method, named photoacoustic detection of light scattering (PALS) is to detect and quantify groundwater colloids. The method is based on measuring the scattered light by photoacoustic processes occurring in an electrode placed on the piezoceramic disk. An acoustic wave generated in the electrode causes a piezoelectric signal directly from the detector.

This spectroscopic method, in combination with size fractionation by ultrafiltration with various pore sizes down to 1 nm, has been applied to quantify colloid populations in various Gorleben groundwaters in different size groups.

THE ALLIGATOR RIVERS ANALOGUE PROJECT — RADIONUCLIDE MIGRATION AROUND URANIUM ORE BODIES

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Uranium ore bodies in the Alligator Rivers Uranium Province in Australia have been studied since 1981 as analogues of radioactive waste repositories. The main objectives were to understand the processes governing the migration of radionuclides, particularly uranium- and thorium- series radionuclides, under groundwater flow, to develop and test models to describe this migration, and to demonstrate the applicability of the results to the safety analysis of radioactive waste repositories.

The International Alligator Rivers Analogue Project (ARAP) was established in 1987 with participation by six organizations in five member countries of the OECD Nuclear Energy Agency, which sponsored the project. The detailed technical results for the Koongarra uranium deposit were published in a series of quarterly working documents and papers at international conferences. The work was reviewed at the first and second RCMs of the IAEA RCP in 1988 and 1990, with emphasis on results for transuranic actinides and fission products.

The technical results were obtained in six major projects carried out in parallel: modelling of radionuclide migration, hydrogeology of the uranium deposit, uranium/thorium-series disequilibria, groundwater and colloid studies, fission product studies and transuranic nuclide studies. Samples of rocks and groundwater were obtained from a large number of drillholes at Koongarra and analyzed in the laboratories of the six participants and other contractors. The majority of the analytical work on the key long-lived isotopes plutonium-239, iodine-129, technetium-99 and chlorine-36 was carried out by the Los Alamos National Laboratory and the University of Arizona.

Plutonium-239 was measured by isotope dilution mass spectrometry (IDMS) on 0.5 - 5 g samples of primary uranium ore from two drillholes with the following results: G2698, 19.1%, 2.6×10^{-12} Pu/U atom ratio; G4674, 12.2%U, 1.3×10^{-12} Pu/U atom ratio. Technetium-99 was also analyzed by IDMS in the same primary ore sample G2698 and gave a $\leq 1.8 \times 10^{-12}$ Tc-99/U atom ratio. An analysis of a water sample (PH49) gave 11 atoms Tc-99/mL.

Iodine-129 and chlorine-36 were measured in rocks and water samples by tandem accelerator mass spectrometry (TAMS). Two methods of sample preparation for iodine-129 were used, alkaline fusion which gave poor reproducibility, and microwave heating which gave low blanks. Iodine-129/U atom ratios were obtained in the range 1-3 x 10^{-12} for uranium contents of 6-25%. Iodine-129/I ratios measured in water samples from the primary ore zone were 3 orders of magnitude higher than background levels up-gradient. The ratios down the water gradient were factors of 2-7 lower than at the primary zone and well above background [37].

Initial chlorine-36 measurements in groundwaters collected within or up-gradient of the uranium deposit before 1989 gave low ratios of Cl-36/Cl of 1-2 x 10^{-13} which confirmed the absence of bomb pulse fallout. Higher ratios of Cl-36/Cl of 2-113 x 10^{-13} in water samples down-gradient of the deposit could indicate mixing with waters containing bomb-pulse material. Measurements on samples collected in 1989 gave Cl-36/Cl ratios orders of magnitude higher and hypotheses to explain these are still being developed [38].

In parallel with the measurements of these long-lived isotopes, predictions of their contents in closed systems have been made at LANL, coupled with measurements of neutron fluxes in ore samples. A Monte-Carlo Neutron/Photon Transport Code was used. The initial conclusions were that there is no correlation between the concentration of uranium and the concentrations of Pu-239 or I-129, due to the effect of heterogeneity around the drillholes, and that spontaneous fission in uranium-238 accounts for more than 80% of the production of Tc-99 [27].

JAERI RESEARCH ACTIVITIES ON THE GEOCHEMISTRY OF LONG LIVED TRANSURANIC ACTINIDES AND FISSION PRODUCTS

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This paper summarizes the recent activities in the research programme "Geochemistry of Long-Lived Transuranic Actinides and Fission Products". The following three important geochemical processes have been studied under laboratory conditions:

- dissolution of neptunium dioxide in aqueous solution,
- sorption of neptunium on naturally-occurring iron-containing minerals,
- alteration of chlorite and its relevance to the uranium redistribution in the vicinity of the ore deposit.

Dissolution of neptunium dioxide in aqueous solution has been studied to elucidate the effect of pH and temperature on the dissolution kinetics. A constant dissolution rate was observed after the initial stage of rapid dissolution. The rate of dissolution increased with an increase of pH and with a decrease of temperature. The temperature dependence of the dissolution rate was considerably smaller than that expected with minerals.

Sorption of neptunium on naturally-occurring hematite, magnetite, goethite and biotite in 0.1M $NaNO_3$ solution has been studied at 30°C for pH between 4 and 11. The mass to volume ratio was 1 g/L. The sorption-desorption reaction was reversible for all the minerals in the pH range studied. The pH dependence of neptunium sorption for goethite was different from other three minerals; goethite showed a strong sorption at pH above 6, while the sorption on hematite, magnetite and biotite occurred at pH above 9. Other oxyhydroxides, lepidocrocite and boehmite, had a similar pH dependence of sorption to goethite. The sorption on hematite was similar to that on alumina.

The alteration of chlorite and the uranium distribution between chlorite and its alteration product have been examined systematically. Water penetrated into the chlorite structure preferentially through its domain boundaries to alter chlorite to vermiculite, and then to kaolinite and possibly smectite. During the alteration, iron minerals were formed. The uranium concentration increased in the minerals as the alteration proceeded. The abundance of chlorite, vermiculite and kaolinite was well correlated with the absorbed uranium concentration and this strongly suggested that the alteration of chlorite affects the uranium migration in the ore deposit.

NATURAL PRODUCTION OF LONG LIVED RADIONUCLIDES

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The calculation of the natural production of long-lived radionuclides has been studied. Long-lived radionuclides (^{129}I, ^{99}Tc, ^{81}Kr, ^{36}Cl, ^{239}Pu, ^{237}Np, ^{14}C) are constantly produced in underground rocks by various nuclear processes such as reactions with neutrons or with alpha particles and also spontaneous fission of ^{238}U [26]. Calculation of natural production of radionuclides requires information on the chemical composition of the rock and various physical parameters.

The underground flux of neutrons originates mainly from the (alpha, n) reaction of light elements in the rock matrix; in shallow depths also from reactions with cosmic muons. The neutron flux controls the production rate and equilibrium concentrations of radionuclides in question. The energy spectrum of neutrons depends on the type of the rock, its porosity and water saturation. A calculation method for the neutron energy distribution in 25 energy groups has been elaborated and used for the estimation of radionuclide production rate for energy dependent nuclear reactions [39].

The rock properties for neutron slowing down and nuclear reactions in question can be calculated only when the trace element concentrations in the rock are known. Production rates and equilibrium concentrations of long-lived radionuclides in various types of host rock and U-ore are calculated taking into account such nuclear processes as spontaneous and neutron induced fission in uranium and also the reactions with fast and thermal neutrons. The production of ^{81}Kr and ^{238}Np is shown to be negligible in comparison to the production of ^{239}Pu, ^{129}I, ^{99}Tc and ^{36}Cl. The production of ^{129}I and ^{99}Tc in rocks is only by spontaneous fission and in U-ore the contribution by neutron induced fission is predominant. The ratio of $^{239}Pu/^{238}U$ in rocks is in the order of 10^{-15} and in U-ores in the order of 10^{-12} and increases with U-content.

In present calculations, the homogeneous distribution of all atoms in the rock is assumed and, therefore, the concentration data obtained are probably overestimated. The comparison of calculated data with experimental data obtained from the rock and U-ore samples will provide information on the degree of approximation. On the other hand, the calculations can be improved by taking into account boundary conditions between the high U-content and the host rock with medium U-content.

NATURAL ANALOGUE STUDIES AND GEOCHEMISTRY OF LONG LIVED TRANSURANIC ACTINIDES AND FISSION PRODUCTS

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Natural analogue studies at Cigar Lake

The initial natural analogue studies at the Cigar Lake uranium deposit were reported at the first RCM in 1988 and additional work has been undertaken since 1989 in co-operation with the Swedish Nuclear Fuel and Waste Management Co. (SKB). Field and laboratory work was carried out on samples of ore, host rock and groundwater and cores from a new drillhole through the ore zone were examined in detail. Two new samples (CS-615 and CS-620) were analyzed by a number of methods including X-ray Photo-electron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), chemical and instrumental analysis [40]. Analysis of plutonium-239, iodine-129 and technetium-99 were carried out at Los Alamos National laboratory (LANL), as well as iodine-129 at the University of Toronto.

Values of U(VI)/U(IV) ratios in earlier uranium ore samples by XPS were in the range 0.24 - 0.57. The analyses of the two new core samples gave different results, with CS-615 having ratios between 0.16 - 0.29, indicating little oxidation, and CS-620 at about 0.7 indicating considerable oxidation (which may have occurred after sampling). Results for plutonium-239, iodine-129 and technetium-99 are only available for previous samples (CS-235L, 54.4 - 56.8 wt%U; W-83A, 37.2 - 40.8 wt%U; and W-83C, 46.8 wt%U). Elemental analyses indicated that CS-235L was clay-rich while the other two were sulphide-rich. Plutonium-239/U ratios for the three samples were $1.7 - 3.5 \times 10^{-12}$ with no correlation between the ratios and the uranium contents. The iodine-129/U ratios were $2\text{-}4 \times 10^{-12}$, which were greater than the ratio of 1×10^{-12} expected for spontaneous fission of uranium-238 alone, the rest arising from induced fission. An upper limit of technetium-99/U was reported of 1.8×10^{-12} for sample W-83A, which is slightly higher than the predicted ratio of 1.6×10^{-12} for spontaneous fission of uranium-238. The ore samples had uranium-234/238 and thorium-230/uranium-234 activity ratios of 1.00 which indicates that they have behaved as closed systems.

Colloid studies

Groundwater studies in the Whiteshell Research Area near Pinawa, Manitoba have shown that groundwaters in granite fractures may contain colloids (1 to 450 nm) consisting of aluminosilicates, carbonate and organic material. Suspended particles (> 450 nm) in these waters were derived from typical fracture lining minerals. Although concentrations of suspended particles were observed to be as high as 14 mg/L, colloid (10 to 450 nm) concentrations were usually less than 1 mg/L, with an average of 0.34 mg/L. The wide range (10^3 to 10^5 cm^3/g) of field derived K_d's, describing U distribution between particles and groundwater, suggested a lack of equilibrium between dissolved U and U associated with colloids. The field derived Th K_d's varied between 3 x 10^4 and 7 x 10^5 cm^3/g. While the activities of ^{234}U and ^{238}U are in equilibrium with each other in unaltered granite, $^{234}U/^{238}U$ ratios of dissolved and particulate U were significantly greater than 1.0. The similarity of dissolved and particulate $^{234}U/^{238}U$ ratios indicates that U associated with particles was acquired from groundwater.

Natural colloids in the Cigar Lake U deposit may be considered as a natural analogue to radiocolloid formation in a used fuel disposal vault. Colloids in Cigar Lake groundwaters consisted of aluminosilicates with variable amounts of organic material. Significant amounts of U were associated with suspended particles, as well as colloids in the 1 to 10 nm and 10 to 450 nm size ranges. The wide range of field derived K_d's for U, Th and Ra indicated that the particulate forms of these radionuclides were not in equilibrium with dissolved species in groundwater. During collection, selected 50 L groundwater samples were spiked with U, Zn, Co, Ni, Cs, Sr, and Li, and then filtered in order to evaluate the ability of colloids and suspended particles to sorb elements from groundwater.

Laboratory experiments similar to those described [41] are under way to evaluate the ability of latex spheres and natural colloids to sorb ^{241}Am and ^{60}Co. Radiolabelled natural and synthetic colloids will be used in migration experiments, provided that radionuclide sorption onto colloids is not reversible.

Static radionuclide sorption studies

A study to examine the sorption characteristics of iodine as iodide and iodate in contact with common granitic fracture-filling minerals has been documented [22]. Results indicate that no significant sorption of the iodide anion occurred with any of the geological materials used. Iodate was found to sorb on several of the minerals used, notably chlorite and hematite.

The sorption of several fission products (Se, Sr, Tc, Cs, Ce) and the actinide Am on primary and secondary minerals in a gabbroic pluton have also been documented [23].

The determination of the sorption characteristics of the actinides U, Np and Pu on common granitic fracture-filling minerals as a function of total dissolved solids (TDS) content of the contacting solution under normal and reduced oxygen conditions has been completed. The experimental results indicate that individual mineral type plays a key role in the removal of these actinides from solution.

Thermodynamic data for elevated temperatures

To estimate how the range of conditions for which TcO_2 undergoes oxidative dissolution is affected by temperature, values of the apparent molar heat capacity of pertechnetate salts in solution (as a function of concentration and temperature) are required. No heat capacity measurements for pertechnetate solutions have been reported previously in the literature. Heat capacity and density measurements for aqueous $NaTcO_4$ solutions have been made at 16, 20, 25, 50, 75 and 100°C for concentrations from 0.01 to 0.25 mol/kg. The apparent molar heat capacities are similar to, but perhaps slightly more positive than, those previously measured for solutions of $NaReO_4$.

Calculated equilibrium solubilities of uranium in model groundwaters

Previous work on the solubility of uranium in model groundwaters has been extended to waters conditioned by clay buffer materials. In general, the concentrations of complexing ions such as carbonate, fluoride and phosphate are expected to be greater in a groundwater conditioned by a clay buffer than in high ionic strength groundwaters [42]. Functions for the solubility of uranium as a function of groundwater composition have been developed for a wide range of conditions considered possible for a nuclear fuel waste disposal vault.

STUDIES OF RADIONUCLIDE BEHAVIOUR VIA NATURAL ANALOGUES AND IN SITU MIGRATION EXPERIMENTS

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Introduction

It is now well-recognized that the study of natural geochemical systems can help us to gain a better understanding of the different processes of radionuclide mobilization, transport and retardation in the far field, and provide a means of testing the thermodynamic databases and transport codes which underpin performance assessments of radioactive waste repositories. The British Geological Survey has been carrying out a programme of natural analogue studies of radionuclide migration at four sites: the sediments of Loch Lomond, Scotland [24], and the sediments at Broubster in Caithness, N Scotland [43,44], at Needle's Eye near Dalbeattie, SW Scotland [45], and at the disused South Terras mine, near St. Stephen, Cornwall [46]. In various ways these post-glacial sediments have played host to the transport and retardation of U/Th decay series isotopes, rare earth elements and iodine over long time-scales and over distances up to 100 m or more.

The chief merit of researching natural systems associated with mineralized concentrations of uranium, thorium and rare earth elements is the ease with which concentration gradients accumulated over long periods of time and large distances can be measured. Although the large time-scale and distance aspects make natural analogue studies uniquely valuable over laboratory experiments, there are difficulties and uncertainties in the quantification of initial boundary conditions, in the assumed past groundwater flow rates and in distinguishing the major processes contributing to the elemental distributions. In situ radiotracer tests in a shallow confined sand aquifer under controlled hydraulic conditions constitute a major research programme that overcomes many of the uncertainties in analogue studies.

Natural analogue studies

The objectives were as follows, with the first one relying heavily on the other two:

1. To test the applicabilities of thermodynamic databases in particular CHEMVAL [33], and research codes such as PHREEQE [32], CHEMTARD [11],

METIS [30] and STELE [31], for modelling natural systems and the far fields of radioactive waste repositories.

2. To understand the geochemistry and migration rates of uranium and thorium decay series elements, rare earth elements (REE) and iodine in different sediment environments.

3. To study the processes involved in their geochemical and hydrochemical distributions and to devise ways of measuring their speciation in the solid and water phases.

The approach has involved:

(i) the development and application of field and laboratory techniques for determining the chemical concentrations and forms of U, Th and I and Br in groundwaters; this has included the examination of colloids;

(ii) an attempt to discover the role of organic compounds in the geochemical distribution of the uranium and thorium decay series radioisotopes;

(iii) the interpretation of hydrogeochemistry data with equilibrium speciation codes such as PHREEQE and CHIMERE [24], and to test the thermodynamic databases, especially CHEMVAL, employed in the codes;

(iv) the determination of groundwater flows and U/Th distributions to make comparisons with the outcomes of modelling with coupled chemical transport codes such as CHEMTARD and STELE.

In situ migration studies

A programme to study the effects of organics on the mobility of radionuclides under controlled in situ conditions of groundwater flow in a field site in a confined glacial sand aquifer was carried out with the following aims:

1. to characterize the physical and chemical properties of core material and natural groundwater, and to undertake laboratory sorption

experiments to enable predictions to be made of the outcome of a field tracer test with selected radionuclide species; in particular to study the effects of natural organics (humic acids) and acetate and EDTA on radionuclide mobility;

2. to use available geochemical models to determine the speciation and mobility of radionuclides in the presence of relevant organic compounds;

3. to undertake tracer tests with selected organics in addition to those naturally present in order to determine their influence on radionuclide mobility.

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NATURAL ANALOGUE STUDIES IN CHINA

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Beijing Research Institute of Uranium Geology has carried out a research programme of deep underground disposal for high-level radioactive wastes sponsored by the China National Nuclear Corporation (CNNC) since 1985. Analogue studies have been focused on bentonite as a buffer material. Evaluation of a uranium ore body in granite as an analogue of a radioactive waste repository was commenced last year under the support of CNNC and IAEA.

Buffer material studies

Two deposits were selected for the study in Lin An and An Ji Counties, Zhejiang Province, Southeast of China. The Na-bentonite deposit that occurs in Lin An County belongs to the Jurassic continental volcano-sedimentary type. Its host rock is montmorillonitized sedimentary tuff. The Ca-bentonite deposit that occurs in An Ji County is located in a syncline formed in the Jurassic period. Its host rock is the Cretaceous vitroclastic tuff.

The microscopic and electron microscopic investigation, DTA, TGA, IRA and X-ray diffraction analyses indicated that the principal mineral in the Na-bentonite was Na-montmorillonite; in the Ca-bentonite it was Ca-montmorillonite. The other minerals in both deposits are quartz, zeolite, hydromica, calcite, chlorite etc. Detailed chemical compositions were obtained, typical ranges in wt% were: SiO_2, 53-68; Fe_2O_3, 0.7-1.8; Al_2O_3, 11-16; CaO, 0.6-2.2; MgO, 1.5-2.9; K_2O, 0.3-2.7; Na_2O, 0.04-2.2; P_2O_5, 0.05-0.66.

Detailed rare earth element (REE) analyses were also obtained. The Ca-montmorillonite samples were relatively rich in the light REE's, e.g., Y, La, Ce, Pr, Nd, whereas the Na-montmorillonite samples had significant levels of higher REE's, e.g., Dy, Ho, Tb, Yb and Lu, as well as substantial levels of light REE's. Free expansion rates, effective porosities, etc., were also measured.

The sorption properties of ^{90}Sr, ^{137}Cs, ^{241}Am and ^{237}Np were measured on samples of these bentonites. The sorption of ^{90}Sr and ^{137}Cs was measured by batch and column techniques and both isotopes were shown to give similar results. The saturation sorption capacities of ^{90}Sr was 21-38 mg/g on Ca-bentonite and 18-29 mg/g on Na-bentonite at a pH of 7 and a ^{90}Sr concentration of 50-200 ppm. Batch experiments with ^{241}Am showed that equilibrium was established in 7-12 h for Ca-bentonite and 17-20 h with Na-bentonite. $K_{d(Am)}$ values were 1740 cm^3/g for Ca-bentonite and 780 cm^3/g for Na-bentonite. Equilibrium was established in 10-14 h for ^{237}Np sorption on these bentonites. $K_{d(Np)}$ values were 8000 cm^3/g for Ca-bentonite and 5900 cm^3/g for Na-bentonite. The pH value strongly affected the sorption behaviour for ^{241}Am and ^{237}Np.

Natural analogue study at the Lianshanguan Uranium Deposit

There is interest in the PRC in disposing of radioactive waste deep underground in granite regions, hence a study was commenced of an analogue in northern China where there is a uranium deposit in granite. The Lianshanguan Uranium Deposit [49] situated about 100 km south of Shenyang, Liaoning Province, was chosen for study for the following reasons:

(a) The Deposit occurs in the white migmatitic granite whose isotope age is 2,340 Ma;

(b) Formation age of the pitchblende from the Lianshanguan Uranium Deposit is 1,900 Ma;

(c) The Deposit is under exploration and samples for measurement of elements suitable for study can be obtained easily;

(d) The uranium deposit is a high-grade uranium deposit and is rich in vein and massive pitchblende. Uranium content in some ore is up to 30-40%.

The migmatitic granite massif in which the Lianshanguan Uranium Deposit occurs consists of gneissose biotite granite, red migmatitic granite and white migmatitic granite. Uranium ore bodies only occur within the latter type of granite. Alkali feldspar, plagioclase and quartz are the principal rock-forming minerals of this rock.

The area studied is one of low mountains. The groundwater flows in a generally southerly direction and contains Ca, Mg, bicarbonate and sulphate with total dissolved solids of 0.05-0.07 g/L and pH of 6.2-6.8.

The ore body was sampled in tunnels and at several points over a distance of about 8 m in the host rocks and in fractures. Work is under way on groundwater analysis, distribution of U, Th and REE, ^{129}I, ^{36}Cl and ^{239}Pu in the samples and permeability measurements.

PLUTONIUM GEOCHEMISTRY
Plutonium production in uraniferous rock, plutonium geochemistry in a redox front

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Plutonium and Uraniferous Rock [27]

Natural plutonium is exclusively the product of uranium neutron capture. The rate of natural plutonium production is a function of the uranium concentration and the fluence and energy spectrum of neutrons in the rock. In natural systems that have been closed to the loss and/or gain of plutonium and uranium for several half-lives of the radioactive product ^{239}Pu - about 10^5 years - the two actinide elements attain a state of secular equilibrium. In such a state the Pu/U ratio is proportional to the plutonium production rate.

LANL has measured abundances of plutonium and uranium in ten samples of uranium-rich rock from five uranium deposits: Koongarra, Australia; Key Lake and Cigar Lake, Canada; Oklo, Gabon; and Katanga, Zaire. The method used was isotope dilution mass spectrometry. The mineralogy of the samples was also measured by X-ray diffraction. Rates of Pu production were calculated using a Monte Carlo neutron transport code. In these samples, the atomic ratio of plutonium-239 to uranium varied between $0.8 - 5.3 \times 10^{-12}$ representing Pu production rates of 60-390 atoms Pu/mgU/a. There was no simple correlation of Pu/U ratio or production rate with the sample composition.

The model calculations demonstrate that the plutonium production rate within a given sample is sensitive to the composition and the spatial distribution of elements within a radius of about a half a meter. The calculations indicate that the measured Pu/U ratios are consistent with production in extremely uraniferous rock such as those from which the samples were taken.

Plutonium in a Redox Front [29]

Plutonium, like uranium, is a multivalent element that is more soluble in higher valence states than in lower ones. To characterize the geochemistry of plutonium in an open geologic system, the concentration of natural plutonium in a centimeter-sized pitchblende nugget from a redox front exposed in the Osuma Utsumi uranium mine in the Brazilian state of Minas Gerais was measured. Redox fronts in the mine are visually defined by sharp transitions between minerals bearing ferric iron and those containing the ferrous form of the element. The rock, within centimeters of the ferric/ferrous transition, contains spatially distinct enrichments of elements. Enrichment processes have produced ore grade concentrations of uranium at some of the redox fronts. The valence state transitions and element enrichments are thought to be the result of meteoric water moving through uraniferous volcanic host rock. Elements were dissolved and precipitated in response to changes in the chemical system produced by interactions between the fluids and the rock.

Extreme radioactive disequilibrium between uranium and its radioactive daughter ^{230}Th unambiguously demonstrates that the ore body has been open to the gain and/or loss of uranium and thorium until very recent geologic times. A detailed examination of the state of disequilibrium of uranium and its radioactive daughter products in a pitchblende nodule showed that the spherical features were growing, or had grown, concentrically at rates about 2 mm/10^5 yr. Uranium and its radioactive progeny, ^{230}Th, are in disequilibrium in the nodule. The activity ratio ^{230}Th/^{234}U was 0.62 indicating that thorium has been preferentially lost from, or uranium preferentially added to the nodule at some time in the last 10^5 yr. If there has been no alteration in that time, the plutonium was produced in-situ. If alteration has occurred more recently, the processes did not significantly fractionate plutonium from uranium.

The Pu concentration in the nugget, corrected for the analytical blank, was $2.3 \pm 0.7 \times 10^8$ atoms per gram. The uranium concentration was 43 (±2)%, and the atom ratio of Pu/U was $2.1 \pm 0.7 \times 10^{-13}$. Model calculations indicate that Pu/U in the pitchblende nodule is consistent with a state of secular equilibrium in a matrix of reduced leucocratic phonolite, containing 3000 ppm U. Although we do not know the composition of the rock from which the nodule was taken, the composition used in the model calculations is descriptive of the most uranium-enriched rock that has been observed at the deposit. Simply, the Pu/U ratio in the nodule suggests that the two elements have resided, unfractionated, in the most highly uraniferous rock in the deposit for the last 10^5 years.

We hypothesize that uranium and plutonium are geochemically similar in the hydrogeochemical system that produced the uranium ore in the Osuma Utsumi mine. Plutonium must have migrated at a rate similar to uranium, and concentrations of uranium on the order of thousands of ppm have existed for at least 10^5 years. The hypothesis can be tested by measuring Pu/U in samples from well characterized regions of the redox front that are in extreme disequilibrium with respect to uranium and its radioactive thorium daughter.

THE MIGRATION STUDY OF TRANSURANIC ELEMENTS AND TECHNETIUM BY STATIC AND DYNAMIC EXPERIMENTS

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The migration behaviour of transuranic elements Np, Pu, Am and Tc has been studied by static and dynamic experiments under aerobic as well as anaerobic (N_2 + 3% H_2) conditions for the geological samples from Gorleben aquifers (Germany) and also for the glauconite mineral. The geochemical parameters varied are: pH from 5 to 7, Eh by addition of $SnCl_2$ or hydrazine and salinity with NaCl concentration from 0.01 to 3.0 M.

The sorption results from two different experiments using static (batch) and dynamic (column) methods under anaerobic conditions are found to be within the comparable ranges for Np, Pu and Am. The sorption coefficients expressed by Kd (cm^3/g) are in general over 1000 for Pu and Am at pH=6 for glauconite, being independent of pH and Eh, whereas the Kd values are lower than 1000 for the natural samples of Gorleben. The sorption of Np on glauconite is somewhat inferior to that on the samples of Gorleben, in general Kd < 50. Even a hydrazine reduction of the glauconite column does not increase the Kd value of Np.

The sorption behaviour of Tc on the glauconite mineral is much different from that on the Gorleben samples. Under anaerobic conditions, Tc shows a higher sorption on glauconite in the column experiment than in the batch experiment. The Gorleben samples show a stronger sorption of Tc (Kd = 40 ~ 2000) than the glauconite mineral (Kd = 3-5).

The experiment on the sorption behaviour is still in progress, so that no detailed explanation can be given for individual sorption characteristics of each element in the aquifer systems under investigation.

NUCLEAR TECHNIQUES IN POLLUTANT TRANSPORT STUDY IN GEOLOGICAL MEDIA

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The programme, of which the results were discussed in this document, has been implemented in close co-operation with another Co-ordinated Research Programme of the Agency, namely F2.30.06 - Nuclear techniques in the study of pollutant transport in the environment: interaction of solutes with geological media (methodological aspects). The main goal of this CRP is the elaboration of nuclear techniques for laboratory and field determinations of pollutant migration mechanisms and those characteristics of geological media and pollutants which control environmental mass transfer.

Isotope tracer methods, and to a lesser degree nuclear well logging, are being elaborated and evaluated within the framework of the programme.

Nuclear well logging is used to obtain in situ data which reflects geological section distributions of soil density, porosity, permeability, clay particle content and natural and artificial radioactivity. This information is used in calculating retardation factors (functions) for pollutants in geological bodies. Artificial tracers are applied in laboratory (batch, column, radiography) and field experiments to study sorption/desorption, solution, precipitation, complexation, diffusion/dispersion and hydraulic transport as well as transport with colloids, organics, weighted and bed-loaded materials.

Environmentally distributed isotopes, including natural (stable and radioactive, cosmogenic and radiogenic) and man-made (released into geological media due to bomb-tests and from nuclear industry in normal and accidental conditions) isotopes.

Artificial tracer techniques in laboratory conditions provide a very effective tool to study mechanisms of pollutant migration. The batch technique allows the evaluation of kinetic and static sorption characteristics of soils/rocks in respect to pollutants. By reaching an equilibrium state, a distribution sorption coefficient K_d can be estimated. In turn, this coefficient is used to evaluate a retardation factor. Although the K_d concept has been severely criticized, it could not be abandoned completely.

Nevertheless, some participants of the programme and some specialists outside the programme are trying to find alternative approaches such as residence time concepts, percolation theory, natural analogues, etc.

These techniques are good tools in static and dynamic (filtration) experiments to determine such migration parameters as diffusion/dispersion coefficients, sorption capability and capacity. Retardation phenomena is observed on the column flow-through regime directly.

Column techniques are closer to dynamic field conditions. But here too, the question arises of how to transfer laboratory (batch, column) data into environmental systems. It has been shown that natural (stable, radiogenic, cosmogenic) isotopes allow at regional, and sometimes at global level, the estimation of migration characteristics.

It has also been emphasized that multi-tracer techniques (tritium or other conservative tracer plus a tracer of a given pollutant) present a good basis to compare and distinguish water movement and pollutant movement, especially on a long time and large space scale, which is absolutely necessary in waste management and water assessment.

Some participants of the CRP deal with uranium-thorium isotopes as long-term and regional analogs of pollutant transport.

An approach based on tracer studies of residence time of water (as carrier) and pollutants was considered in more detail. This approach has been generalized and a principle scheme of tracer determination of these residence times has been developed. Their interconnection with retardation and other fundamental migration characteristics seems to be a good bridge between laboratory and field tracer measurements. Also, it has been shown that there exists a one-to-one correspondence between migration characteristics (diffusion coefficient, distribution coefficient, hydraulic velocity, sorption and decay kinetic parameters) and residence times as noted above. Perhaps it will develop into a key for more adequate processing and interpretation of tracer information for the problem under discussion.

It can also be expected that such a complex of nuclear techniques and residence time concepts combined with conventional methods provide information for constructing and validating models of migration of pollutants including radionuclides in geological media. Such work has to be carried out on the basis of a multi-disciplinary approach.

Investigations are continuing.

REFERENCES

[1] KIM, J.I., Chemical behaviour of transuranic elements in natural aquatic systems. In Handbook on the Physics and Chemistry of the Actinides (A.J. Freeman and C. Keller, eds). Elsevier Science Publishers B.V. Amsterdam pp. 413-455 (1986)

[2] SAITO, A. and CHOPPIN, G.R., Separation of Actinides in Different Oxidation States from Natural Solutions by Solvent Extraction, Anal. Chem., 55, 2454 (1983)

[3] BERTHOUD, T., MAUCHIEN, P., OMENETTO, N. and ROSSI, G., Determination of Low Levels of Uranium(VI) in Water Solutions by Means of the Laser-Induced Thermal Lensing Effect, Anal. Chim. Acta, 153, 265 (1983)

[4] SCHREPP, W., STUMPE, R., KIM, J.I., WALTHER, H., Oxidation-State-Specific detection of Uranium in Aqueous Solution by Photoacoustic Spectroscopy, Appl. Phys., B32, 207 (1983)

[5] STUMPE, R., KIM, J.I., SCHREPP, W. and WALTHER, H. Speciation of Actinide Ions in Aqueous Solution by Laser-Induced Pulsed Photoacoustic Spectroscopy, Appl. Phys., B34(4), 203 (1984)

[6] GORDON, J.P., LEITE, R.C.C., MOORE, R.S., PORTO, S.P. and WHINNERY, J.R., Long Transient Effects in Lasers with Inserted Liquid Samples, J. Appl. Phys., 36, 3 (1965)

[7] STUMPE, R. and KIM, J.I., Gepulste Photoakustische Laserspectroskopie zum oxidationsspezifischen Nachweis von Aktinoiden in Lösungen, Report: RCM 20284, TU München, (1984)

[8] SCOTT, R.D., MacKENZIE, A.B., HOUSTON, C.M., HOOKER, P.J., BEN-SHABAN, Y.A., Uranium transport and retardation at the Needle's Eye natural analogue site, southwest Scotland. Proceedings of the "Migration 89", Int. Conf. Monterey, Nov 6-10 1989 Radiochimica Acta (in press)

[9] BASHAM, I.R., MILODOWSKI, A.E., HYSLOP, E.K., PEARCE, J.M., The location of uranium in source rocks and sites of secondary deposition at the Needle's Eye natural analogue site, Dumfries and Galloway. British Geological Survey Technical Report WE/89/56 (1990)

[10] HOOKER, P.J., An overview and assessment of the British Geological Survey's research work on natural analogue studies in Great Britain. Proc. 'Migration 89 Meeting, Monterey, CA, U.S.A., 6-10 Nov. 1989 Radiochimica Acta (in press)

[11] HOOKER, P.J., IVANOVICH, M., MILODOWSKI, A.E., BALL, T.K., DAWES, A., READ, D., Uranium migration at the South Terras mine, Cornwall. British Geological Survey Technical Report WE/89/13(1990)

[12] LIEW, S.K., READ, D., Development of the CHEMTARD coupled process simulator for use in radiological assessment, DOE Report DOE/RW/88.051 (1987)

[13] BREWARD, N., PEACHEY, D., The development of portable equipment to study physical and chemical phases in natural water. British Geological Survey Technical Report WE/88/25 (1988)

[14] WILLLIAMS, G.M., HOOKER, P.J., BRIGHTMAN, M.A., Field studies about radionuclide migration, natural analogues and faults in clays. CEC Report EUR 13022, CEC Luxembourg (1990)

[15] LONGWORTH, G., WILKINS, M.A., IVANOVICH, M., Role of geocolloids in transport of naturally occurring radionuclides, Mat. Res. Loc. Symp. Proc. 127, 755-61 (1989)

[16] HAIGH, D.G., WILLIAMS, G.M., HOOKER, P.J., ROSS, C.A.M., ALLEN, M.R., WARWICK, P., The effect of organics on the sorption of cobalt by glacial sand in laboratory batch experiments. British Geological Survey Technical Report, WE/88/20 (1988)

[17] HAIGH, D.G., HIGGO, J.J.W., WILLIAMS, G.M., HOOKER, P.J., ROSS, C.A.M., FALCK, W.E., ALLEN, M.R., WARWICK, P., The effect of organics on the sorption of strontium, caesium, iodine, neptunium, uranium and europium by glacial sand. British Geological Survey Technical Report WE/89/16 (1989)

[18] WARWICK, P., SHAW, P., WILLIAMS, G.M., HOOKER, P.J., Preliminary studies of cobalt complexation in groundwater, Radiochimica Acta 44/45, 59 - 63 (1988)

[19] HIGGO., J.J.W., et.al., Iodine speciation and diffusion in a sand groundwater system, British Geological Survey Technical Report WE/89/44 (1989)

[20] MacKENZIE, A.B., SHIMMIELD, T.M., SCOTT, R.D., HOUSTON, C.M., Development of an analytical method for the analysis of I^- and Br ion concentrations in lacustrine sediment interstitial water. British Geological Survey Technical Report WE/89/65 (1989)

[21] MacKENZIE, A.B., SHIMMIELD, T.M., SCOTT, R.D., DAVIDSON, C.M., HOOKER, P.J., Chloride, bromide and iodide distributions in Loch Lomond sediment interstitial water. British Geological Survey Technical Report WE/90/2 (1990)

[22] TICKNOR, K.V., CHO, Y-H., Interactions of iodide and iodate with granitic fracture-filling minerals, J. of Radioanal. Nucl. Chem., Articles, 140, 1 (1990)

[23] TICKNOR, K.V., VANDERGRAAF, T.T., KAMINENI, D.C., Radionuclide sorption on primary and fracture-filling minerals from the East Bull Lake pluton, Massey, Ontario, Applied Geochemistry, 4, 163-76 (1989)

[24] FALCK, W.E., HOOKER, P.J., Quantitative interpretation of chloride, bromide and iodide porewater concentration profiles in lake sediments of Loch Lomond, Scotland, British Geological Survey Technical Report WE/90/3 (1990)

[25] Proceedings of International Conference on Disposal of Radioactive Waste on Seabed Sediments, Oxford, 20-21- Sept. 1988

[26] FLORKOWSKI, T., MORAWSKA, L., ROZANSKI, K., Natural production of radionuclides in geological formations Nucl. Geophys., 2, 1-14 (1988)

[27] FABRYKA-MARTIN, J., e.al., Plutonium geochemistry: Plutonium production in Uraniferous Rock, Los Alamos National Laboratory, Report LA-UR-90-2134 (1990)

[28] CURTIS, D.B., Geochemical Controls on ^{99}Tc transport and retention, Chemical Geology, 55, 227-31 (1986)

[29] CURTIS, D.B., et.al., Plutonium geochemistry in a redox front, Chemical Geology (to be published 1991)

[30] GOBLET, P., Developpment du code METIS. Rapport final METIS 2. Ecole des Mines de Paris, Report LHM/RD/86/77, Fontainebleau (1986)

[31] de MARSILY, G., Calculation tools. CEC project MIRAGE- Second phase on migration of radionuclides in the geosphere. First summary progress report (work period 1986-87) edited by B. Come. CEC EUR 11589 EN, 119-152 (1988)

[32] PARKHURST, D.L., THORSTENSON, D.C., PLUMMER, L.N.,: PHREEQE - A Computer programme for geochemical calculations. U.S. Geol. Surv., Water Resources Investigations 80-96, NTIS Tech. Report PB 81-167801, 1980, revised 1985

[33] READ, D., BROYD, T.W., Verification and validation of predictive computer programs describing the near and far field chemistry of radioactive waste disposal systems. Radiochimica Acta 44/45, 407-415 (1988)

[34] FALCK, W.E., Two modified versions of the speciation code PHREEQE for modelling macromolecule-proton/cation interaction. British Geological Survey Technical Report WE/89/57 (1990)

[35] DUERDEN, P., Alligator Rivers Analogue Project: Review of research and its implications for Model Validation, Symp. on Natural Analogues in Radioactive Waste Disposal, Brussels, 28-30 April 1987, CEC Report EUR-11037 (1987)

[36] INTRAVAL Ad Hoc Group, June 1987, "Geosphere Transport Model Validation - A Status Report", SKI 87:4, Swedish Nuclear Power Inspectorate, Stockholm, Sweden (1987)

[37] FABRYKA-MARTIN, J.T. et.al., Redistribution of natural ^{129}I among mineral phases and groundwater in the Koongarra uranium ore deposit, N.T., Australia, Symposium on Natural Analogues in Radioactive Waste Disposal, Brussels, 28-30 April 1987, CEC Report No. EUR 11037, 1987

[38] FABRYKA-MARTIN, J.T., DAVIS, S.N., ROMAN, D., AIREY, P.L., and KUBIK, P.W., Iodine-129 and chlorine-36 in uranium ores, 2, Discussion of AMS measurements, Chem. Geol. (Isot. Geosci. Sect.) 72, 7-16 (1987)

[39] FLORKOWSKI, T., Estimation of the natural production of radionuclides in geological formations from reactions with fast neutrons, Nucl. Geophys., 4, 281-7 (1989)

[40] SUNDER, S., TAYLOR, P. and CRAMER, J.J., XPS and XRD studies of uranium rich minerals from Cigar Lake, Saskatchewan. Mat. Res. Soc. Symp. Proc., 112, 465-472 (1988)

[41] VILKS, P., and DEGUELDRE, C., Sorption behaviour of ^{85}Sr, ^{131}I, and ^{137}Cs on colloids from the Grimsel Test Site, Switzerland. Submitted to Applied Geochemistry (1990)

[42] LEMIRE, R.J. and GARISTO, F., The Solubility of U, Np, Pu, Th and Tc in a Geological Disposal Vault for Used Nuclear Fuel, AECL Report No. AECL-10009 (1989)

[43] READ, D., Geochemical modelling of the Broubster natural analogue site, Caithness, Scotland, British Geological Survey Technical Report WE/88/43 and U.K, DOE report DOE/RW/89.005 (1988)

[44] READ, D., HOOKER, P.J., The speciation of uranium and thorium at the Broubster natural analogue site, Caithness, Scotland. Mat. Res. Soc. Symp. Proc. 127, 763-770 (1989)

[45] JAMET, Ph., LACHASSAGNE, P., DOUBLET, R., LEDOUX, E., Modelling of the Needle's Eye natural analogue. Ecole des Mines de Paris, Fontainebleau, CIG Report LHM/RD/89/81 (in English) 43 pp. (1989) and as BGS Technical Report WE/89/64

[46] READ, D., HOOKER, P.J., IVANOVICH, M., MILODOWSKI, A.E., A natural analogue study of an abandoned uranium mine in Cornwall, England, Radiochimica Acta (in press)

[47] QIN, Fei et al., 1980, "Present exploration status of the Lianshanguan uranium deposit, Northeast China", Uranium in the Pine Creek Geosyncline (Proc. Int. Symp. Sydney, 1979), IAEA, Vienna (1980) 655-661