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Sorption Studies of Radioelements on Geological Materials

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Batch sorption experiments have been carried out to study the sorption of uranium, technetium, curium, neptunium, actinium, protactinium, polonium, americium and plutonium onto bentonite, granodiorite and tuff. Mathematical modelling using the HARPHRQ program and the HATCHES database was carried out to predict the speciation of uranium and technetium in the equilibrated seawater, and neptunium, americium and plutonium in the rock equilibrated water. Review of the literature for thermodynamic data for curium, actinium, protactinium and polonium was carried out. Where sufficient data were available, predictions of the speciation and solubility were made.

This report is a summary report of the experimental work conducted by AEA Technology during April 1991～March 1998, and the main results have been presented at Material Research Society Symposium Proceedings and published as proceedings of them.

Keywords : Sorption, Bentonite, Tuff, Granodiorite, Reducing Condition

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鉱物への放射性元素の収着研究

日本原子力研究開発機構
地層処分研究開発部門地層処分基盤研究開発ユニット
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ベントナイト，花崗閃緑岩及び凝灰岩への U，Tc，Cm，Np，Ac，Pa，Po，Am 及び Pu の収着を研究するためにバッチ収着試験を行った。溶液は蒸留水及び人工海水(U，Tc のみ)を使用し，温度は 25 及び 60℃で行った。人工海水についての U と Tc の化学種及び岩石平衡水についての Np，Am と Pu の化学種を予測するために HARPHRQ プログラムと HATCHES データベースを使用した数学的モデリングを行った。Cm，Np，Ac，Pa 及び Po についての熱力学データの文献調査を行った。ここでは幾つかのデータを入手でき，化学種及び溶解度の予測を行っていた。

この報告書は 1991 年 4 月～1998 年 3 月の間に AEA Technology によって行われた試験結果をまとめたものであり，主な結果は Material Research Society Proceedings で公開されている。

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1. Introduction

Movement of radionuclides away from a radioactive waste repository, through the backfill and host rock formation towards the biosphere, will be retarded to a significant degree if sorption processes occur. Data concerning sorption behaviour of radionuclides on geological media are, therefore, needed in order to predict nuclide migration. This information is essential for the radiological assessment of potential repository sites.

The research programme described here has investigated major chemical parameters that govern the migration behaviour of important radioelements (uranium, technetium, curium, neptunium, actinium, protactinium, polonium, plutonium, americium). The philosophy underlying the research strategy is that the water flow rates will be slow at all points on the flow path, compared with the rates of the chemical reactions, so that chemical equilibrium may be assumed. Such a strategy has been used in the UK Nirex Ltd Safety Assessment Research Programme for the vault and the geosphere regions. The approach and the supporting research programme have been peer reviewed under the auspices of the IAEA and approved[1].

The research programme has obtained measurements of the sorption of the radioelements onto bentonite that will be used as a backfill material, tuff and granodiorite. Strongly reducing conditions (Eh $\backsim -400$mV vs SHE at pH 8) chosen, as standard conditions, because it is expected to occur in the repository in deep underground. The experiments under non-reducing conditions (Eh >+200mV at pH8) were also carried out for comparison for some elements.

The measurement of the Eh value of a solution is not straightforward and requires the presence of a redox couple at a sufficiently high concentration. Control of the Eh of a solution is similarly difficult and can only be effected by complex electrolytic means or by the addition of a holding reductant such as sodium hydrosulphite (sodium dithionite, $Na_2S_2O_4$, see Appendix 1). Although this introduces a small concentration of a chemical species to the system, there is still a distinct possibility that the alternative electrochemical reduction[2] will also produce chemical species which are not representative of the natural situation, and which could lead to undesirable side reactions.

Work under strongly-reducing conditions was carried out using sodium hydrosulphite, electrolytic methods not being practicable in view of the large number of individual experiments. This approach has been used successfully in other work by AEA Technology at Harwell[3]. These conditions are suitable for this study.

Work carried out has involved the preparation of solutions by equilibrating samples of bentonite, granodiorite and tuff with de-ionised water and seawater (only for U and Tc) at room temperature and 60℃ for one month. Batch sorption experiments were carried out on the three rock types with the appropriate synthetic solutions at room temperature and at 60℃.

Mathematical modelling using the geochemical speciation code HARPHRQ[4] and

HATCHES[5] database has been used to interpret the experimental results. Modelling has been undertaken with the aim to assess the chemical speciation of the radionuclides in the bentonite-, tuff- and granodiorite-equilibrated groundwaters under both strongly-reducing and non-reducing conditions.

The HATCHES[5] thermodynamic database underpins these geochemical modelling studies. This database has been specifically developed for the investigation of radioactive waste management problems and has been supplied to the Nuclear Energy Agency for use by member countries in nuclear waste studies, and is updated annually. The HATCHES database contains data for approximately 70 elements, 1100 aqueous species and over 800 mineral phases.

2. Batch Sorption Experiment of Important Radioelements on Bentonite, Tuff and Granodiorite

2.1 Materials

The bentonite sample used in this study is Kunigel V1 which is commercially available. Major composition of this bentonite is Na-montmorillonite and its content is about 50wt%[6]. The tuff sample consists mainly of volcanic glass, zeolite and quartz[7]. The granodiorite sample consists mainly plagioclase, alkali feldspar and quartz with minor amounts of biotite and apatite. The composition of minerals is shown in Table 1. The tuff and granodiorite were each ground in an automatic mortar and pestle until the entire sample passed through a 250 μm sieve in a nitrogen-atmosphere glove-box.

2.2 Solution

De-ionised water and synthetic seawater were equilibrated for four weeks with sample of the bentonite, tuff and granodiorite at a water : rock ratio of 5 : 1 (20 : 1 for bentonite) in a nitrogen-atmosphere glove box. The analytical results for these solutions and the original synthetic seawater are shown in Table 2 ～ 4.

Aliquots of de-ionised water were equilibrated at 60℃ with samples of tuff and granodiorite at a water : rock ratio of 5 : 1 for a period of four weeks, and the resulting solutions analysed following centrifugation and filtration (0.45μm followed by 10000MWCO). Equilibration, centrifugation and filtration were performed at 60℃ in order to reduce the risk of precipitating species which may be significantly soluble at 60℃, but not at lower temperatures. For bentonite, aliquots of synthetic seawater and de-ionised water were each equilibrated at 60℃ with samples of the bentonite at a water ratio of 20 : 1. No problems were encountered with the seawater, but in the case of the equilibrated de-ionised water, phase separation was extremely difficult. Therefore, it was decided to use the synthetic bentonite-equilibrated de-ionised water 'recipe' obtained following equilibration at room temperature for the experiments at 60℃, but with the pH value adjusted to that measured at the higher temperature (See Table 5). This approach is justified since the concentrations of ions in bentonite-equilibrated seawater are very similar for the two temperatures, so a similarity in concentrations at each temperature for de-ionised water might be expected.

Table 5 shows the concentration of cations and anions present after four weeks equilibration with de-ionised water and seawater with bentonite, tuff and granodiorite at 60℃.

2.3 Preparation of Solutions for Batch Sorption Studies

2.3.1 Uranium

Uranium-233 was obtained as a calibrated acidic stock solution from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

A solution of uranium-233 as uranium(IV) was prepared by first reducing a uranium(VI) solution with sodium hydrosulphite. After a few minutes, sodium hydroxide solution was added to precipitate "hydrous uranium(IV) oxide". After washing and centrifuging three times, this precipitate was dissolved in 1M hydrochloric acid to provide a uranium(IV) solution for use in the sorption experiments.

At room temperature experiments, an appropriate volume of this solution, to give a uranium concentration in the range 1.35×10^{-7}M to 1.9×10^{-7}M, was added to aliquots of either synthetic equilibrated seawater or synthetic equilibrated de-ionised water mixed with the appropriate weight of bentonite, tuff and granodiorite, together with sodium hydrosulphite at an initial concentration of 2.5×10^{-3}M. This acted as a "holding" reductant to maintain the +4 oxidation state.

At 60℃ experiments, an appropriate volume of this solution, giving an initial uranium concentration of 1.1×10^{-7}M and 1.2×10^{-7}M was added to volumes of synthetic equilibrated seawater and synthetic equilibrated de-ionised water respectively. Following filtration (0.45μm), aliquots were counted to determine the initial uranium (IV) concentration, and 30 cm^3 portions were then taken. A small volume of sodium hydrosulphite solution was added to each portion to give an initial concentration of 2.5×10^{-3}M. These portions were each mixed with appropriate weight of bentonite.

The concentrations of uranium were chosen to be within the constraints of the solubility limit and detection limit in each case.

For work with uranium(VI), no reducing agent was needed. The Eh values were in the range +280 to +360mV for seawater, and +200 to +360mV for de-ionised water. Only minor adjustment of pH was required. The initial uranium concentration at room temperature was 1.5×10^{-7}M for bentonite and tuff, and 1.4×10^{-7}M for granodiorite. At 60℃, initial concentration was 1.5×10^{-7}M.

Analysis of uranium-233 was by α-spectrometry (Canberra System 100).

2.3.2 Technetium

Tc-95m was obtained as a calibrated acidic stock solution from Actinide Chemistry and Analysis Department, AEA Technology, Harwell and obtained as a calibrated acidic stock solution from Los Alamos National Laboratory, USA.

Technetium-95m, received as pertechnetate, was purified by electrodeposition onto a platinum electrode. The hydrated technetium dioxide formed on the electrode was then dissolved in hot hydrogen peroxide and evaporated to a small volume to give a solution containing Tc(VII). Some of this was diluted with dilute hydrochloric acid to give a Tc(VII) stock solution for "spiking" the experiments using non-reducing conditions. A further fraction of the more concentrated Tc(VII) solution was reduced with sodium hydrosulphite to give a solution containing Tc(IV). This solution on dilution was used for spiking the experiments employing strongly reducing conditions.

The total technetium molarity (Tc-95m + Tc-97m) in each experiment under strongly reducing conditions was less than 1×10^{-10}M, well below the solubility of Tc(IV) which is about 1×10^{-8}M[9]. For the experiments under non-reducing conditions, the Tc concentration was 2×10^{-10}M or less, many orders of magnitude lower than the Tc(VII) solubility[10]. Following spiking, experiments were carried out as described in the previous reactions.

Analysis of technetium-95m was by γ-spectrometry (Canberra).

2.3.3 Curium

Curium-244 were obtained as calibrated acidic stock solutions from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

An appropriate volume of curium(III) solution to give an initial curium concentration of 1.7×10^{-10}M was added to volumes of synthetic bentonite-, tuff-, and granodiorite-equilibrated water, and sufficient sodium hydrosulphite added to give a concentration of 2.5×10^{-3}M. The solutions filtered using 0.45μm filters. Although hydrosulphite does not reduce Cm(III), it was added to enable accurate comparison to be made with the redox-sensitive radioelements studied in the programme. Aliquots of 30 cm^3 were then taken and mixed with rock at the appropriate water-to-rock ratio.

Analysis of curium-244 was by α-spectrometry (Canberra System 100).

2.3.4 Neptunium

Neptunium-237 were obtained as calibrated acidic stock solutions from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

In the case of neptunium experiments, since the starting concentration (6×10^{-9} M), dictated by the low solubility, was so low and the anticipated R_D quite high, intermediate sampling, which would have required a large volume of sample, was considered inappropriate. Intermediate sampling of neptunium experiments was therefore not performed. This preserved the maximum redioactivity for counting after 4 months equilibration. In addition, our previous experience was suggesting that the neptunium remaining in solution for counting at the end of the equilibration period may be below the α-spectrometry detection limit. Neptunium-237 is relatively long-lived (half-life 2.14×10^6 years), but no alternative shorter-lived isotope was available. Since the original standard-scale experiments were established using 30 cm^3 of solution and either 1.5 or 6 g solid, it was decided to do a small number of additional experiments in order to ensure that actual values for R_D, rather than lower limits, were obtained.

Two ways to conduct experiments so that the maximum amount of neptunium is present in solution at the end of the experiment are to increase the liquid-to-solid ratio, or to increase the volume of liquid and mass of solid using significantly, but preserving the same liquid-to-solid ratio. To this end, the following extra experiments were carried out:

(i) Three experiments (utilising respectively bentonite, tuff and granodiorite) using 300 cm^3 of the appropriate rock-equilibrated water at room temperature and at the same water-to-solid ratio as the smaller scale duplicate experiments.

(ii) Three experiments as (i) above, but at 60℃.

(iii) One experiment at room temperature using bentonite and 300 cm^3 bentonite-equilibrated water at the increased liquid-to-solid ratio of 100 : 1.

(iv) One experiment as (iii) above, but 60℃.

A solution of neptunium(V) was reduced to neptunium(IV) using a small amount of sodium hydrosulphite solution, at initial concentration of 2.5×10^{-3}M. An appropriate volume of this solution was then added to each type of rock-equilibrated water to give an initial neptunium concentration of 6.0×10^{-9}M. Addition of reducing agent, pH adjustment, and other experimental procedure is as described in the previous sections.

For the analysis of neptunium, following the phase separations, each of which yielded typically 50 ～ 100 cm^3 liquid, each sample was acidified and a known activity of ^{239}Pu(IV) added in order to determine the radiochemical yield. Each solution was evaporated to near-dryness and a small volume of concentrated nitric acid added. Heating with this acid destroyed sulphur oxy-anions such as hydrosulphite and its decomposition products which might have interfered with the subsequent electro-deposition. Following evaporation to dryness, each residue was dissolved, and the plutonium and neptunium elector-deposited onto stainless steel counting discs prior to counting for 48 hours. The radiochemical yield, based on ^{239}Pu recovery, was typically in excess of 70%.

The extra time taken to perform these experiments was approximately equivalent to the time saved by omitting the intermediate sampling of the main 30 cm^3 experiments.

Analysis of neptunium-237 was by α-spectrometry (Canberra System 100).

2.3.5 Actinium

Actinium-227 were obtained as calibrated acidic stock solutions from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

An appropriate volume of actinium(III) solution to give an initial actinium concentration in the range 1×10^{-9}M to 3×10^{-9}M was added to the appropriate synthetic bentonite-, tuff- and granodiorite-equilibrated water, and sufficient sodium hydrosulphite was then added to give a concentration of 2.5×10^{-3}M. The solutions filtered using 0.45μm filters. The filtrates were then diluted by a factor of 2 in order to minimize any risk that the solubility limit for actinium was exceeded. Each diluted filtrate was then sampled in order to determine the initial concentration of Ac-227. This was found to vary by about a factor of two for the six different filtrations performed (two temperatures and three geological materials). Aliquots of 30 cm^3 were then taken and mixed with rock at the appropriate water-to-rock ratio.

Determination of the initial activities of Ac-227 by γ-spectrometry was straightforward. The stock solution as supplied had been stored for a considerable period, and it was in radioactive equilibrium with its daughters, whose γ-emission could then be counted. Half-life corrections were made for both isotopes. However, the final activities were so low that only γ-counting times in the region of 24 hours per sample (and there were a total of 60 counts to be performed) would be sufficient, and even then the counting statistics would have been poor. Consequently, liquid scintillation counting was used to count aliquots from the final sampling. A 'Quantalus' liquid scintillation counter, which is specially designed for counting very low activities, was used. The counter was calibrated using diluted aliquots of the standard, calibrated solution, looking at the scintillations produced by the α-emitters at equilibrium with the Ac-227. Count times of only two hours were sufficient to provide good counting statistics.

2.3.6 Protactinium

Protactinium-233 were obtained as calibrated acidic stock solutions from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

An appropriate volume of calibrated protactinium solution was added to each type of rock-equilibrated water to give an initial protactinium concentration of 1.3×10^{-11}M for the bentonite experiments, and 3.8×10^{-11}M in the case of granodiorite and tuff experiments. Hydrosulphite was then added, the pH adjusted to the appropriate value, and a sample γ-counted in order to determine the initial concentration. This solution of protactinium was not filtered because of the known "polymeric" behaviour of protactinium in solution[11]. Weighed amounts of geological material were then added to 30 cm^3 aliquots of the solution. Due to the relatively short half-life of Pa-233(27days), equilibration was for one month, not four months.

Analysis of Pa-233 was straightforward, by the γ-spectrometry of the isotope Pa-233 itself.

2.3.7 Polonium

Po-210 was obtained as a calibrated acidic stock solution from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

Polonium-210 solution was added to appropriate volumes of synthetic rock-equilibrated water, and sodium hydrosulphite added. The solutions filtered using 0.45μm filters. The corresponding activities were 382 Bq cm^{-3} for experiments using bentonite, 190 Bq cm^{-3} for those using granodiorite, and 267 Bq cm^{-3} for those using tuff. Aliquots of 40 cm^3 were then taken and mixed with rock at the appropriate water-to-rock ratio.

A 'Quantalus' liquid scintillation counter was used to count the Po-210. This instrument is specially designed for counting very low activities. The counter was calibrated using diluted aliquots of a standard, calibrated solution obtained as an acidic stock solution from Actinide Chemistry and Analysis Department, AEA Technology, Harwell.

Final concentrations used in the calculation of R_D values were decay-corrected to the starting data.

2.3.8 Plutonium

The batch sorption methodology, preparation of solutions and execution of batch experiments involving plutonium were similar to those involving other elements.

Analysis for Plutonium-238 was by α-spectrometry. A known amount of a calibrated plutonium-236 solution was then added to enable determination of the electrochemical yield following electro-deposition for 2 hours onto a stainless steel counting tray. The software controlling the α-spectrometry counting equipment automatically made a small correction (approximately 7%) for the decay of Pu-236 (half-life 2.85 years) following separation from its daughters (U-232, Th-228 and Ra-224).

Initial plutonium-238 concentrations correspond to 6.53, 5.66, and 6.46 Bq cm^{-3} for bentonite, granodiorite and tuff experiments respectively.

2.3.9 Americium

Americium experiments were carried out in a similar manner to those involving other elements, except that a known amount of a calibrated americium-243 solution was added prior to electro-deposition and counting by α-spectrometry.

Initial americium-241 concentrations correspond to 3.59, 3.58, and 3.13 Bq cm^{-3} for bentonite, granodiorite and tuff experiments respectively.

2.4 Batch Sorption Methodology

Sorption experiments were carried out in a nitrogen-atmosphere glovebox suite with an oxygen level of less than 1 ppm. Experiments under both strongly-reducing and non-reducing conditions were carried out under such a nitrogen atmosphere to allow direct comparison to be made between the two redox conditions. Solutions for experiments under strongly-reducing conditions were de-oxygenated by bubbling an argon (96%)/hydrogen (4%) mixture through them. Nitrogen was bubbled through solutions for experiments under non-reducing conditions.

Samples of bentonite, tuff and granodiorite were mixed with the appropriate solution. The highly-reducing conditions required were achieved using sodium hydrosulphite. The pH of the solutions, which was measured at 60℃ or room temperature, was maintained at the value of the bentonite-, tuff- or granodiorite-equilibrated de-ionised water/seawater as appropriate.

Sodium hydrosulphite decomposes over a period of days, and this causes a small decrease in pH and an increase in Eh. In order to combat these related effects, Eh was monitored(every 4 ～ 5 day for U and Tc onto bentonite, every 10 ～ 15 day for U and Tc onto tuff and granodiorite, every7 day for Cm, Np, Ac, Pa, Po, Am and Pu), and when it increased, more hydrosulphite was added and the pH adjusted back to the appropriate value.

Batch sorption experiments were carried out in triplicate (uranium and technetium at room temperature) or in duplicate (uranium and technetium at 60℃, curium, neptunium, actinium, protactinium, polonium, americium and plutonium at room temperature). One tube was monitored regularly to test for a steady-state concentration of radionuclide, except in the case of neptunium. After four months, the contents of the remaining two tubes (all tubes in the case of duplicate) were analysed and the results used in the calculation of distribution coefficients, except protactinium. Due to the relatively short half-life of Pa-233 (27 days), equilibration for protactinium was for one month, not four months.

All tubes were gently agitated continuously at 60℃ or room temperature in a shaker/incubator. This is the large dome-shaped structure which can be seen inside the glove box.

Water : rock ratio of 5 : 1 was used in the case of tuff and granodiorite. For bentonite, water : bentonite ratio of 20 : 1 was used. Because of the swelling properties of bentonite, water : bentonite ratios were increased from the water : rock ratios normally used in experiments at Harwell. The lowest water : bentonite ratio which could be used in sorption experiments with equilibrated de-ionised water was found to be 20 : 1. At lower ratios (e.g. 10 : 1), insufficient water was left after the bentonite swelled to allow samples of water to be taken for analysis. The bentonite swelled to a smaller extent with seawater, but for reasons of comparison between de-ionised water and seawater, the same water : bentonite ratios were used.

In the case of uranium and technetium at room temperature, higher water : solid ratios (100 : 1 for bentonite, 50 : 1 for tuff and granodiorite) were also used.

The geological materials were weighted in room humidity and weight of adsorbed water was not corrected.

The vessel used were previously-washed polypropylene centrifuge tubes, except that the vessels used were previously-washed screw-top polythene bottles for neptunium with large amount of solution (300cm^3).

Three liquid/solid separation techniques were employed:

(i) centrifugation at 1100g with aliquots being removed from near the surface of the supernatant liquid;

(ii) centrifugation followed by filtration through a 0.45μm filter;

(iii) centrifugation followed by filtration first through a 0.45μm filter, and then through a 10000MWCO filter.

All filters were washed and pre-conditioned prior to use [8].

For those sorption experiments carried out at 60℃, all of the above phase separation techniques were also carried out at 60℃. In the case of bentonite, the centrifugation was carried out for 2.5 hours at 1100 g following the rapid transfer of experimental tubes to a heated centrifuge inside another glove box. Past experience with bentonite has demonstrated that shorter centrifugation times give poorer phase separation and result in blockage of pores in the membranes of filters used subsequently. Each tube was then placed in a heating block at 60℃, and an aliquot of liquid quickly removed and pipetted into 1 cm^3 dilute acid. This ensured that, on cooling, there was no precipitation onto the vessel walls which would interfere with the subsequent analysis. The remainder of the centrifuged liquid was quickly returned to the other glove box, and the supernatant liquid transferred to a centrifuge tube inside the incubator/shaker. It was then filtered through a Millipore 'Millex HV' 0.45μm filter which had been pre-heated, washed and pre-conditioned at 60 ℃ prior to use[8]. Whenever possible, the transparent lid of the shaker/incubator was kept in place, in order to minimize any temperature drop. Aliquots of the filtrate were then pipetted into dilute acid as above, and then analysed. The remaining solution which had passed through the 0.45μm filter was then filtered using Millipore 'TGC' (10000MWCO) filters. These were pre-treated in a similar manner to the 0.45μm filters used earlier. Aliquots of filtrate were then pipetted into dilute acid and analysed. Room temperature phase separations were carried out in a similar manner, except that no heating was used.

In addition, "blank" tubes, containing no solid phase were established to monitor the solution behaviour of the radioelement. Where there was significant sorption on vessel walls in the "blank" tubes, the vessel walls were subsequently investigated for sorption in the corresponding tubes containing geological materials (bentonite, tuff and granodiorite). This was in order to confirm that sorption was genuinely onto the geological materials and not onto the vessel walls.

In order to determine the vessel wall sorption, following removal of residual liquid, a small amount of the appropriate rock-equilibrated water was gently mixed with the residual geological material. The resulting slurry was carefully poured away, and the vessel walls carefully washed with two 5 cm^3 volumes of rock-equilibrated water. The vessel walls were then washed with strong acid solution, the aliquots of the solution were removed for counting. For curium, neptunium and actinium, 5.0 cm^3 4M nitric acid was used, 10.0 cm^3 4M nitric acid was used for polonium, plutonium and americium, and 5.0 cm^3 9M HCl/0.1M HF in the case of protactinium. In the case of protactinium, the tubes were placed in the shaker/incubator at 60℃ to ensure dissolution of protactinium, if present.

The distribution coefficient, R_D, was calculation as follows：

$$R_D = \frac{Ai - Ae}{Ai} \times \frac{V}{W} \qquad (1)$$

A_i：initial activity in solution (M)

A_e：activity in solution at the end of the sorption (M)

V: volume of the liquid phase (cm^3)

M: weight of the solid phase (g)

No allowance was made for the small degree of wall sorption in the R_D calculations, is this factor is small by comparison with errors based on the statistics of counting.

The experimental workflow is shown in Fig 1.

3. Results and Discussion

3.1 Batch Sorption Studies of Uranium

3.1.1 Sorption of Uranium on Bentonite at Room Temperature

The results of sorption of uranium are presented in Tables 6 and 7.

The final values obtained for R_D after 4 months equilibration under strongly-reducing conditions are shown in Table 6. The values of pH and Eh are also indicated. The results show that sorption of uranium onto bentonite under strongly-reducing conditions is strong at both water：bentonite ratios and for both solutions, R_D values being in the range 1.8×10^4～6.7×10^5 $cm^3\ g^{-1}$ after filtration using 10000MWCO filters. Sorption appears to be unaffected by the solution ionic strength but there is a small dependence on water：bentonite ratio, sorption being slightly greater at the 100：1 ratio. There is a small variation with liquid/solid separation method, R_D values being slightly greater after 10000MWCO filtration.

The data obtained for uranium sorption under non-reducing conditions are presented in Table 7. Sorption is much weaker than under strongly-reducing conditions with R_D values lying in the range 30 ～ 250 $cm^3\ g^{-1}$. There is very little difference between the results from the equilibrated seawater experiments and those carried out with equilibrated de-ionised water. There is also no significant variation with liquid：solid separation technique. Sorption appeared to depend to a small extent on water：bentonite ratio, with R_D values being approximately a factor of five higher for the experiments at a 100：1 ratio than for those at a ratio of 20：1.

Under strongly-reducing conditions, considerable sorption onto the vessel walls occurred in the "blank" tubes (Table 8). However, very little uranium was found on vessel walls when bentonite had been present. One tube from each set of experiments was selected and the results are shown in Table 9. Under non-reducing conditions, no drop in uranium concentration in any of the "blank" tubes was recorded, thus showing that no wall sorption had occurred.

3.1.2 Sorption of Uranium on Tuff at Room Temperature

The results of sorption of uranium are presented in Tables 10 and 11.

The final values obtained for R_D after 4 months equilibration under strongly-reducing conditions are shown in Table 10, The values of final pH and Eh are also included. The results show that sorption of uranium onto tuff under strongly-reducing conditions is strong at both water : rock ratios, and for both solutions, R_D values being in the range $5 \times 10^4 \sim 1.2 \times 10^6$ cm^3 g^{-1} after filtration using 10000MWCO filters. R_D values are higher at a water : rock ratio of 50 : 1 for both solutions.

The data obtained for uranium sorption under non-reducing conditions are shown in Table 11. Sorption is much weaker than under strongly-reducing conditions, with R_D values lying in the range 30 ～ 150 cm^3 g^{-1}. Sorption of uranium in the case of equilibrated seawater is weaker than in the case of equilibrated de-ionised water at a water : rock ratio of 5 : 1, but R_D values for a ratio of 50 : 1 are similar for both types of water. There is no significant difference in R_D with liquid : solid phase separation technique.

Under strongly reducing conditions, considerable sorption onto the vessel walls occurred in the "blank" tubes (Table 12). However, very little uranium was found on vessel walls when tuff had been present (Table 13). Under non-reducing conditions, only a small decrease in uranium concentration was found in the "blank" tubes (Table 12), showing that wall sorption had not occurred to any significant extent even in the absence of tuff.

3.1.3 Sorption of Uranium on Granodiorite at Room Temperature

The results of sorption of uranium are presented in Tables 14 and 15.

The final values obtained for R_D after 4 months equilibration under strongly-reducing conditions are shown in Table 14. The values of final pH and Eh are also included. The results show that sorption of uranium onto granodiorite under strongly-reducing conditions is strong at both water : rock ratios, and for both solutions, R_D values being in the range $6.3 \times 10^3 \sim 2.8 \times 10^5$ cm^3 g^{-1} after filtration using 10000MWCO filters. R_D values are significantly higher after filtration.

The data obtained for uranium sorption under non-reducing conditions are shown in Table 15. Sorption is much weaker than under strongly-reducing conditions, with R_D values lying in the range 1 ～ 120 cm^3 g^{-1}. Sorption of uranium in the case of equilibrated seawater is weaker than in the case of equilibrated de-ionised water at both water : rock ratios. There is no significant difference in R$_D$ value with liquid : solid separation technique, except in the second of the seawater experiments at a water : rock ratio of 50 : 1, where the R$_D$ value was less than 1 cm^3 g^{-1} after centrifugation and 0.45μm filtration, increasing to 86 cm^3 g^{-1} after 10000MWCO filtration. This is attributed to the presence of colloids whose particle size is less than 0.45μm.

Under strongly-reducing conditions, considerable sorption onto the vessel walls occurred in the "blank" tubes (Table 16). However, very little uranium was found on vessel walls when granodiorite had been present (Table 17). Under non-reducing conditions, only a small decrease in uranium concentration was found in the "blank" tubes containing de-ionised water, and no decrease at all in the case of seawater (Table 16), showing that wall sorption had not occurred to any significant extent even in the absence of granodiorite.

3.1.4 Sorption of Uranium on Bentonite at 60℃

The results of sorption of uranium onto bentonite at 60℃ are shown in Tables 18 and 19.

Table 18 shows the results obtained under strongly-reducing conditions. In the case of bentonite-equilibrated seawater, sorption was strong, but not as strong as that previously measured at room temperature for the same water-to-bentonite ratio (Section 3.1.1). R$_D$ values were in the range 7.9×10^3 cm^3 g^{-1} ～ 1.8×10^4 cm^3 g^{-1} following 0.45μm and 10000MWCO filtration. For bentonite-equilibrated de-ionised water, sorption was slightly stronger than it was in the case of bentonite-equilibrated seawater, R$_D$ values ranging from 2.7×10^4 cm^3 g^{-1} ～ 5.2×10^4 cm^3 g^{-1} following 0.45μm and 10000MWCO filtration, very similar to the values obtained for the same water-to-bentonite ratio at room temperature.

Table 19 shows the R$_D$ values obtained under non-reducing conditions. Sorption was weaker than under strongly-reducing conditions. In bentonite-equilibrated seawater, R$_D$ values are in the range 720 cm^3 g^{-1} ～ 870 cm^3 g^{-1} following 0.45μm and 10000MWCO filtration. This range is up to a factor of twenty higher than that measured for the same water-to-bentonite ratio at room temperature. In the case of bentonite-equilibrated de-ionised water, R$_D$ values are in the range 60 cm^3 g^{-1} ～ 120 cm^3 g^{-1}, which is up to a factor of about four higher than the values obtained for the same water-to-bentonite ratio at room temperature (Section 3.1.1).

Table 20 shows the amount of uranium remaining in solution in the "blank" experiments i.e. in the absence of bentonite. Wall sorption was observed in all cases except bentonite equilibrated de-ionised water under non-reducing conditions. Vessel wall sorption was therefore examined in all of the experimental centrifuge tubes containing bentonite. The results, which show a maximum of 1.1 % of uranium on the vessel walls, are shown in Table 21.

3.2 Batch Sorption Studies of Technetium

3.2.1 Sorption of Technetium on Bentonite at Room Temperature

The results of sorption of technetium are presented in Tables 22 and 23.

Table 22 lists the final values obtained for R_D after 4 months equilibration under strongly-reducing conditions, together with the final values of pH and Eh. In the case of seawater, sorption is moderately strong at both water : bentonite ratios ($R_D = 4\times10^3$ cm^3 g^{-1} ～ 1×10^3 cm^3 g^{-1}). R_D is almost independent of water : bentonite ratios and filtration methods. For bentonite equilibrated with de-ionised water, sorption is slightly less (R_D values are a factor of 3 ～ 5 lower) at a water : bentonite ratio of 20 : 1 than in the case of seawater at either ratio. At a ratio of 100 : 1, R_D values decrease by about a factor of 2 relative to the 20 : 1 case to about 600 cm^3 g^{-1}.

The final values obtained for R_D after 4 months equilibration under non-reducing conditions are shown in Table 23. In all cases sorption is much less than that under strongly-reducing conditions. Sorption is stronger from seawater than from de-ionised water.

Under strongly-reducing conditions, Considerable sorption onto vessel walls occurred in the "blank" tubes, especially those containing seawater (Table 24). However very little technetium was found on vessel walls when bentonite had been present. The results shown (Table 25) are the average of two tubes studied in each case. Under non-reducing conditions, only a small drop in technetium concentration was observed in the "blank" tubes (Table 24) in contrast to the experiments under strongly-reducing conditions. Since there had only been a small amount of wall sorption in the presence of bentonite under strongly-reducing conditions, wall sorption under non-reducing conditions was not investigated further.

3.2.2 Sorption of Technetium on Tuff at Room Temperature

The results of sorption of technetium are presented in Tables 26 and 27.

Table 26 lists the final values obtained for R_D after 4 months equilibration under strongly-reducing conditions, together with the final values of Eh and pH. Sorption was strong in both equilibrated seawater and equilibrated de-ionised water. For equilibrated seawater, R_D values obtained following filtration were in the range 2×10^4 ～ 4×10^5 cm^3 g^{-1}, and for equilibrated de-ionised water, 1×10^4 ～ 3×10^4 cm^3 g^{-1}. In general, R_D values were slightly higher at a water : rock ratio of 50 : 1 than at a ratio of 5 : 1 in both types of water.

Table 27 lists the final values obtained for R_D after 4 months equilibration under non-reducing conditions, together with the final values of Eh and pH. Sorption was very weak under all conditions, not exceeding 5 cm^3 g^{-1}.

Under strongly-reducing conditions, considerable sorption onto vessel walls occurred in the "blank" tubes (Table 28). However, very little technetium was found on vessel walls where tuff had been present (Table 29). Under non-reducing conditions, in the "blank" tubes (Table 28), there was no wall sorption in the case of equilibrated seawater, but with equilibrated de-ionised water, just over half of the technetium was sorbed on the vessel walls.

3.2.3 Sorption of Technetium on Granodiorite at Room Temperature

The results of sorption of technetium are presented in Tables 30 and 31.

Table 30 lists the final values obtained for R_D after 4 months equilibration under strongly-reducing conditions, together with the final values of Eh and pH. Sorption was strong in both equilibrated seawater and equilibrated de-ionised water. For equilibrated seawater, R_D values obtained following filtration were in the range $1.9\times10^4 \sim 2.0\times10^5$ $cm^3\ g^{-1}$, and for equilibrated de-ionised water, $2.8\times10^4 \sim 1.8\times10^5$ $cm^3\ g^{-1}$. In general, R_D values were slightly higher at a water : rock ratio of 50 : 1 than at a ratio of 5 : 1 in both types of water.

Table 31 lists the final values obtained for R_D after 4 months equilibration under non-reducing conditions, together with the final values of Eh and pH. Sorption was weak under all conditions, not exceeding 70 $cm^3\ g^{-1}$.

Under strongly-reducing conditions, considerable sorption onto vessel walls occurred in the "blank" tubes (Table 32). However, very little technetium was found on vessel walls where granodiorite had been present (Table 33). Under non-reducing conditions, in the "blank" tubes (Table 32), there was very little wall sorption in the case of either equilibrated de-ionised water or seawater.

3.2.4 Sorption of Technetium on Bentonite at 60℃

The results of sorption of technetium onto bentonite at 60℃ are shown in Tables 34 and 35.

Table 34 shows the final R_D values obtained after 4 months equilibration under strongly-reducing conditions. Sorption was strong or very strong in the case of bentonite-equilibrated seawater, R_D values being in the range 5.8×10^4 to 2.6×10^5 $cm^3\ g^{-1}$ following 0.45μm and 10000MWCO filtration. In bentonite-equilibrated de-ionised water, sorption was strong, but not as strong as from seawater, R_D values being in the range 8.0×10^3 to 2.1×10^4 $cm^3\ g^{-1}$ following 0.45μm and 10000MWCO filtration. These R_D values are about an order of magnitude greater than those obtained at the same water-to-bentonite ratio at room temperature (Section 3.2.1).

Table 35 shows the results obtained under non-reducing conditions. Sorption was relatively weak from bentonite-equilibrated seawater, R_D values being in the range 88 $cm^3\ g^{-1}$ to 280 $cm^3\ g^{-1}$ following 0.45μm and 10000MWCO filtration. Sorption was slightly stronger than that measured for the same water-to-bentonite ratio at room temperature in Section 3.1.1. In bentonite-equilibrated de-ionised water, R_D values are somewhat high, ranging from 1.6×10^3 $cm^3\ g^{-1}$ to 2.3×10^3 $cm^3\ g^{-1}$ after 0.45μm and 10000MWCO filtration. The high R_D values in the case of de-ionised water under non-reducing conditions cannot yet be fully explained, since there is very little information in the literature about technetium behaviour at higher temperatures. However, these high R_D values are supported by the work of Lieser[12], who found that when working in various groundwater/sediment systems in the pH range 5.8 to 7.4, there was a change in speciation at an Eh value of +100mV, the distribution ratio changing from 10^3 cm^3 g^{-1} below +100mV to less than 1 cm^3 g^{-1} above +200mV. This suggests that the increased sorption under non-reducing de-ionised water conditions at the higher temperature may be caused by a reduction in oxidation state of technetium from that present at 20℃.

Table 36 shows the amount of technetium remaining in solution in the "blank" experiments i.e. in the absence of bentonite. Under non-reducing and strongly-reducing conditions, there was strong wall sorption in the case of seawater, but relatively weak wall sorption in the case of de-ionised water. However, in the actual sorption experiments where bentonite was present, wall sorption of technetium was never greater than 4.3% (See Table 37).

3.3 Batch Sorption Studies of Curium

3.3.1 Sorption of Curium on Bentonite

The results of sorption of curium onto bentonite are shown in Table 38.

The results for sorption of curium onto bentonite at room temperature and 60℃ are shown in Table 38. Sorption was strong for both temperatures, R_D values following 10000MWCO filtration being in the range 6×10^4 to 5×10^5 cm^3 g^{-1}.

3.3.2 Sorption of Curium on Tuff

The results of sorption of curium onto tuff are shown in Table 39.

Sorption was strong at both temperatures, R_D values being in the range 4×10^4 to 2×10^5 cm^3 g^{-1} after 10000MWCO filtration. Differences in R_D value with phase separation technique suggest possible colloid formation.

3.3.3 Sorption of Curium on Granodiorite

The results of sorption of curium onto granodiorite are shown in Table 40.

Sorption is not quite so strong as in the case of bentonite, R_D values following 10000MWCO filtration all exceeding 1×10^4 cm^3 g^{-1}. Differences in R_D value with phase separation technique suggest possible colloid formation.

Table 41 shows the amount of curium remaining in solution in the "blank" experiments in the absence of rock. Since in all cases, only a small fraction of the initial curium concentration remained in solution at the end of the equilibration period, experiments were performed to determine the degree of wall sorption in the batch experiments in the presence of geological material (See Table 42).

Table 42 shows the results of vessel wall sorption experiments. For curium sorption, the maximum amount sorbed onto the vessel walls, which was in the case of bentonite at 60℃, was 3.13 %. Although the "blank" experiments showed considerable sorption onto the vessel walls, when geological material was present, the curium sorbed primarily onto this, rather than the vessel walls. No allowance was made for this small degree of wall sorption when calculating R_D values.

3.4 Batch Sorption Studies of Neptunium

The results of sorption of neptunium onto bentonite, granodiorite and tuff are shown in Tables 43.

Since activities in the 'centrifuged' samples were at background level in normal scale experiments, no attempt was made to analyze any filtered samples. Results for the larger scale neptunium experiments can be found in Table 43, which shows the R_D values obtained for the experiments performed on a 300 cm^3 scale (water : rock ratio of 300 cm^3 : 15 g for bentonite, 300 cm^3 : 6 g for tuff and granodiorite). Note that bentonite sorbs more strongly than granodiorite or tuff at both temperatures ($R_D = 10^3$ to 10^4 $cm^3\ g^{-1}$). Tuff is significantly less sorbing than the other materials, particularly at 60℃, when the R_D value is only 210 $cm^3\ g^{-1}$ after 10000MWCO filtration.

The degree of sorption of neptunium onto granodiorite is intermediate between that for bentonite and that for tuff.

Due to the very small amount of neptunium present in the experiments, it was not considered practicable to measure wall sorption in the case of neptunium.

3.5 Batch Sorption Studies of Actinium

3.5.1 Sorption of Actinium on Bentonite

The results for sorption of actinium onto bentonite at room temperature and 60℃ are shown in Table 44.

Sorption was strong for both temperatures, R_D values following 10000MWCO filtration being approximately 1×10^5 $cm^3\ g^{-1}$. The effect of temperature was not significant on R_D values obtained following filtration, although values were apparently higher at room temperature for centrifuged samples.

3.5.2 Sorption of Actinium on Tuff

The results for sorption of actinium onto tuff at room temperature and 60℃ are shown in Table 45.

All of the phase separation techniques used, sorption was relatively strong at room temperature, but less so at 60℃. At room temperature, R_D values following filtration were in the range 5.5×10^3 to 8.9×10^4 cm^3 g^{-1}, and at 60℃, 5.9×10^2 to 4.2×10^3 cm^3 g^{-1}. There was relatively poor agreement between the room temperature R_D values for 10000MWCO filtrates, there being up to a factor of seven differences, instead of the usual agreement to within a factor of about two.

3.5.3 Sorption of Actinium on Granodiorite

The results for sorption of actinium onto granodiorite at room temperature and 60℃ are shown in Table 46.

Sorption was strong, R_D values following 10000MWCO filtration being in the range 2.0×10^4 to 4.8×10^4 cm^3 g^{-1}. As in the case of bentonite, the effect of temperature was insignificant on R_D values obtained after filtration. After centrifuging only, sorption appeared to be much stronger at room temperature.

3.5.4 Discussion of Actinium Sorption Behaviour

Actinium sorption is strong at room temperature, particularly in the case of bentonite. R_D values from centrifuged samples from experiments at 60℃ were lower, however, particularly in the case of tuff, where this was also the case after filtration.

There is, however, some evidence for particulate formation, as is known to be the case for protactinium. The changes in R_D values with temperature may be explained if actinium polymers are present and are less stable at 60℃ than at room temperature. If they broke down into smaller particles at 60℃, which could stay in suspension, then the apparent solution concentrations would be higher and R_D values lower.

Table 47 shows the amount of actinium remaining in solution in the "blank" experiments i.e. in the absence of rock. Since in all cases, only a small fraction of the initial actinium concentration remained in solution at the end of the equilibration period, experiments were performed to determine the degree of wall sorption in the batch experiments i.e. in the presence of geological material (See Table 48).

For the Ac-227 experiments, vessel wall sorption was determined in a similar manner with the case of protactinium, except that 4M HNO_3 was used instead of 9M HCl / 0.1M HF, Table 48 also shows the results of vessel wall sorption experiments for actinium. For actinium sorption, the maximum amount sorbed onto the vessel walls, (bentonite and granodiorite at 60℃), was about 0.8 %. Although the "blank" experiments showed considerable sorption onto the vessel walls, when geological material was present, the actinium sorbed primarily onto this, rather than the vessel walls. No allowance was considered necessary for this small degree of wall sorption when calculating R_D values.

3.6 Batch Sorption Studies of Protactinium

3.6.1 Sorption of Protactinium on Bentonite

The results for sorption of protactinium onto bentonite at room temperature and 60℃ are shown in Table 49.

The R_D values following 10000MWCO filtration were all in excess of 2×10^5 cm^3 g^{-1}.

Values obtained after 0.45μm filtration were similar, except for a single result of 8.1×10^3 cm^3 g^{-1} at 60℃. The R_D values obtained after centrifugation only were significantly lower at 60℃ than at room temperature.

3.6.2 Sorption of Protactinium on Tuff

The results for sorption of protactinium onto tuff at room temperature and 60℃ are shown in Table 50.

Again, the values obtained after 10000MWCO filtration are greater than 10^5 cm^3 g^{-1}, except for a single value of 1.2×10^4 cm^3 g^{-1} at 60℃. The values obtained at room temperature following centrifuging only and 0.45μm filtration were also in excess of 10^5 cm^3 g^{-1}, but sorption was apparently much less strong at 60℃ in both cases.

3.6.3 Sorption of Protactinium on Granodiorite

The results for sorption of protactinium onto granodiorite at room temperature and 60℃ are shown in Table 51.

The R_D values obtained after 10000MWCO filtration were again in excess of 2×10^5 cm^3 g^{-1}. Following 0.45μm filtration, similar values were obtained at room temperature, but sorption at 60℃ was two orders of magnitude less strong. Sorption was also apparently less strong after centrifuging only.

3.6.4 Discussion of Protactinium Sorption Behaviour

Sorption was generally very strong onto all three geological materials. Lower R_D values were obtained at 60℃ (except for one result of $>3.2\times10^5$ cm^3 g^{-1} for bentonite at 60℃). However, values of R_D after centrifuging only are variable. These results can be interpreted in terms of the known "polymeric" behaviour of protactinium in aqueous systems[11], assuming that the polymers are less stable at 60℃.

Baes and Mesmer[13] have summarized the difficulty of studying the solution chemistry of protactinium thus:

'The great difficulty of maintaining Pa(V) in aqueous solution without hydrolytic precipitation or, at the very low concentrations that have been studied, loss of a large portion by adsorption on container surfaces or particulate impurities is perhaps the best known feature of the aqueous chemistry of this element'.

The results obtained are consistent with those obtained by Berry et al. [11] for the sorption of protactinium onto sandstone, granite and clay in the pH range 6 ～ 9. They do, however differ from those obtained by Nakayama et al. [14] who studied sorption of protactinium onto Ohya tuff in the pH range 7 ～ 11, and whose R_D values following 0.1μm filtration were 52 cm^3 g^{-1} at pH 7 and 65 cm^3 g^{-1} at pH 11. In the work of Nakayama et al. a neptunium-237 spike solution was used as the source of protactinium. Neptunium-237 and its daughter protactinium-233 were therefore studied simultaneously. Detailed comparisons between this work and the present AEA Technology study are complicated by the fact that Nakayama et al. used such a source of protactinium and do not report an initial concentration of protactinium nor any description of the neptunium-protactinium equilibrium in their analysis.

For each temperature, "blank" tubes containing no rock had also been established to monitor the solution behaviour of protactinium. Since there was significant sorption on vessel walls in the "blank" tubes (see Table 52), the vessel walls were subsequently investigated for sorption in the corresponding tubes containing rock. This was in order to confirm that sorption was genuinely onto rock and not onto the vessel walls.

The maximum amount of Pa-233 adhering to the vessel walls in the experiments containing geological material (see Table 53) was less than 3 %, often much less. The maximum amount sorbed onto the vessel walls was 2.68 % for granodiorite at room temperature. In other words, in the presence of polypropylene and geological material, the Pa-233 is preferentially sorbed onto the geological material.

3.7 Batch Sorption Studies of Polonium

The results for sorption of polonium onto bentonite, granodiorite and tuff at room temperature are shown in Table 54.

Sorption was strong, R_D values following 10000MWCO filtration being in the region of 8×10^4 cm^3 g^{-1} in the case of bentonite, 1.7×10^4 cm^3 g^{-1} to 3.2×10^4 cm^3 g^{-1} in the case of granodiorite, and in the region of 3 ～ 4×10^4 cm^3 g^{-1} tuff. These is evidence for colloid formation in the cases of all three geological materials, since R_D generally increases in the order：

Centrifugation < 0.45μm < 10000MWCO

This is most significant in the case of granodiorite, and minimal in the case of bentonite.

Table 55 shows the results obtained for polonium redionuclides studied.

3.8 Batch Sorption Studies of Plutonium

The results for sorption of plutonium onto bentonite, granodiorite and tuff at 60℃ are shown in Table 56.

As for polonium, sorption is strongest in the case of bentonite ($R_D = 2.7\times10^4$ cm^3 g^{-1} to 8.7×10^3 cm^3 g^{-1} after 10000MWCO filtration). For granodiorite, R_D values are in the range 9.8×10^3 to 5.7×10^4 cm^3 g^{-1}, and for tuff, 6.7×10^3 to 1.2×10^4 cm^3 g^{-1}. These are evidence of colloid formation in the cases of granodiorite and tuff, but not in the case of bentonite.

Table 57 shows the results obtained for plutonium redionuclides studied.

The maximum amount of radionuclide adhering to the vessel walls in the experiments containing geological material (see Table 57) was 5.7 % in the case of plutonium. In order words, in the presence of polypropylene and geological material, the radionuclides are preferentially sorbed onto the geological material.

3.9 Batch Sorption Studies of Americium

The results for sorption of americium onto bentonite, granodiorite and tuff at 60℃ are shown in Table 58.

They are very similar to those obtained for polonium and plutonium. Sorption is strongest onto bentonite. R_D values after 10000MWCO filtration are 3.0×10^4 to 1.1×10^5 cm^3 g^{-1}, 2.0×10^4 to 6.2×10^4 cm^3 g^{-1} and $\sim 2.2\times10^4$ cm^3 g^{-1} in the cases of bentonite, granodiorite and tuff respectively. As in the case of plutonium, these are evidence for colloid formation for granodiorite and tuff, but for bentonite.

Table 59 shows the results obtained for americium redionuclides studied.

4. Thermodynamic Modelling for Sorption of the Adsorbate Elements in Batch Sorption Experiments

4.1 Introduction

In this section, thermodynamic data used in solubility and speciation calculation are discussed these studies are conducted in 1990s during 7 years. Therefore the discussion is based on the knowledge at that time, and the thermodynamic database version is different for each element.

4.1.1 Uranium at Room Temperature

There has been considerable debate over the thermodynamic data to be used for uranium. The data in HATCHES (Version 4.0 and 5.0) are based on the 1990 published dataset of the Nuclear Energy Agency (NEA) [15].

The compilation is the result of detailed work by a number of world experts in the field and reviews all available data on the topic. The HATCHES uranium database has been used successfully in an extensive experimental programme on U(IV) and U(VI) solubility undertaken at Harwell[16].

Modelling work at Harwell has predicted the stability of U(VI) compared with U(IV) at pH values above 8, under oxidizing and mildly reducing conditions. The presence of carbonate has the effect of stabilizing further the U(VI) state, such that extreme reducing conditions (e.g. the presence of sodium hydrosulphite) are required for U(IV) to be stable.

4.1.2 Uranium at 60℃

The thermodynamic aqueous speciation program HARPHRQ (version 1.41)[4, 21] was used in conjunction with the HATCHES database (version 7.0)[5]. This version of HATCHES includes an extended range of enthalpy data for uranium species, necessary for more realistic predictions at elevated temperatures. For simulations at room temperature, there are no significant changes to the database from versions used in earlier modelling work for uranium sorption onto bentonite, tuff and granodiorite at room temperature. A sample of earlier calculations was repeated with the new database to confirm consistency.

4.1.3 Technetium at Room Temperature

For technetium, the data in HATCHES (Version 4.0 and 5.0) are taken directly from a compilation by Rard[17], which has been shown to be in close agreement with the experimental data of Meyer[18] and Pilkington[19].

4.1.4 Curium and Neptunium

The thermodynamic aqueous speciation code HARPHRQ (version 1.41)[4][20], was used in conjunction with the HATCHES database (version NEA8)[5], in the modelling studies described below.

The aqueous thermodynamic speciation data from a literature review of curium compounds are discussed in Section 4.2.3 together with the predicted speciation from HARPHRQ.

Section 4.2.4 describes the predicted aqueous speciation of neptunium under the experimental conditions.

4.1.5 Actinium, Protactinium, Polonium, Plutonium and Americium

Thermodynamic modelling has been carried out in support of the batch sorption experiments using the aqueous speciation code HARPHRQ (version 1.41) [4, 21] in conjunction with the HATCHES database (version NEA9 and NEA10)[5].

For actinium and protactinium, the extent of thermodynamic data available in HATCHES NEA 9 was limited. No data for polonium were available. The modelling study for these three elements were therefore restricted to a review of the data available in the literature and, where possible, predictions of the speciation and solubility.

4.2 Calculations of the Speciation of Elements

4.2.1 Speciation of Uranium

The predicted speciation of uranium in bentonite-, Tuff- and Granodiorite-equilibrated de-ionised water under the two sets of experimental conditions is shown in Table 60.

The results for bentonite-equilibrated de-ionised solution predict that under non-reducing conditions (Eh = +200mV), uranium is present exclusively in the U(VI) oxidation state and that uranyl carbonate complexes dominate the speciation. The predicted solubility-limiting solid phase under these conditions is a hydrated U(VI) oxide. This phase is significantly undersaturated under the experimental conditions and so any observed reduction in aqueous uranium concentration may be attributed to a sorption process.

Under the strongly-reducing conditions used, (Eh ~ −400mV) uranium is predicted to be almost exclusively present in the U(IV) oxidation state. The dominant complex is the neutral $U(OH)_4(aq)$ species. Amorphous UO_2 is the solid-phase most likely to control the solubility under the experimental conditions and this phase is significantly undersaturated.

It is noteworthy that very low uranium solubilities are predicted under a range of experimental conditions if the literature value for $CaUO_4$ is adopted as the solubility-limiting phase. This prediction is not supported by experimental observations[16] and Lemire[21] states that this phase is not found in natural systems. Therefore, this phase was not considered in the current modelling study.

U(V) species were not included in these thermodynamic calculations as U(V) is known to disproportionate rapidly to U(IV) and U(VI) in aqueous solution under these conditions[22].

Regarding the granodiorite-equilibrated de-ionised water system, for these preliminary calculations the uranium concentration used in the modelling was 1.5×10^{-7}M for the non-reducing conditions and 1.9×10^{-7}M under the strongly-reducing conditions, these values being chosen as they were consistent with the concentrations used in the bentonite/de-ionised water batch experiments. The value of CO_3^{2-} concentration used in the simulations was 10 ppm, the upper limit of the range measured experimentally.

The results predict that under non-reducing conditions (Eh = +200mV vs SHE), uranium is present exclusively in the uranium(VI) oxidation state and uranyl carbonate and hydroxycarbonate species dominate the speciation.

Under the strongly-reducing conditions used (Eh ~ −400mV), the U(IV) oxidation state dominates, the neutral $U(OH)_4(aq)$ complex being the major species present. About 0.1 % of the uranium is predicted to be present in the uranium(VI) oxidation state, again as a carbonate complex.

Regarding the tuff-equilibrated de-ionised water system, for these preliminary calculations the uranium concentration used in the modelling was 1.5×10^{-7}M for the non-reducing conditions and

1.9×10^{-7}M under the strongly-reducing conditions, these values being chosen as they were consistent with the concentrations used in the bentonite/de-ionised water batch experiments and are similar to the concentrations used in the tuff experiments which were set up after the calculations had been carried out.

The results predict that under non-reducing conditions (Eh = +200 mV), uranium is present exclusively in the U(VI) oxidation state and that uranyl carbonate complexes dominate the speciation. The predicted solubility-limiting solid phase under these conditions is a hydrated U(VI) oxide. This phase is significantly undersaturated under the experimental conditions and so any observed reduction in aqueous uranium concentration may be attributed to a sorption process.

Under the strongly-reducing conditions used, (Eh ～ −400 mV) uranium is predicted to be almost exclusively present in the U(IV) oxidation state. The dominant complex is the neutral $U(OH)_4(aq)$ species. Amorphous UO_2 is the solid phase most likely to control the solubility under the experimental conditions and this phase is significantly undersaturated.

Speciation calculations have been performed for uranium in bentonite-, Tuff- and Granodiorite-equilibrated and granodiorite-equilibrated seawater under both non-reducing and strongly-reducing conditions. The results are shown in Tables 61.

As is the case for the de-ionised water experiments reported above, uranium speciation in these three groundwaters under non-reducing conditions is dominated by carbonate complexes. However, under strongly-reducing conditions the dominant species is predicted to be $U(OH)_4(aq)$.

Modelling of uranium speciation at 60℃ was performed for both the de-ionised-equilibrated and seawater-equilibrated systems under each set of the redox conditions. The effect of temperature, on each equilibrium, is incorporated into the model by application of the van't Hoff equation (with the assumption that ΔH^0 is independent of temperature)：

$$\frac{d\ln K}{dt}=\frac{\Delta H^{0}}{RT^{2}} \qquad (2)$$

where：

K= Equilibrium constant (−)

T= Temperature (K)

ΔH^0= Standard molar enthalpy for the reaction (J mol^{-1})

R= Universal gas constant (J mol^{-1} K^{-1})

For the groundwater ions and for uranium, extensive enthalpy data are available. These data allow predictions of the uranium speciation at 60℃ (Table 62).

4.2.2 Speciation of Technetium

The predicted speciation of technetium in de-ionised water equilibrated with bentonite, granodiorite and tuff is shown in Table 63.

The modelling predicts that under the chosen experimental conditions, the behaviour of two oxidation states of technetium can be studied. Under non-reducing conditions, technetium is predicted to be present in solution in the +7 oxidation state, as TcO_4^-. This species has a very high solubility. In the three system under strongly-reducing conditions, Tc(IV) is present as a neutral complex, $TcO(OH)_2(aq)$. The predicted solubility-limiting solid phase is amorphous TcO_2, which is undersaturated under the conditions employed in the experiments performed in this study.

The technetium concentrations used for these preliminary modelling were 2×10^{-10}M for the case of non-reducing conditions and 8×10^{-11}M for the case of strongly-reducing conditions.

Speciation calculations have been performed for technetium in bentonite-equilibrated and granodiorite- and tuff-equilibrated seawater under both non-reducing and strongly-reducing conditions. The results are shown in Table 64.

As is the case for uranium, for technetium no strong affinity for chloride is predicted; the major species in the seawater-equilibrated samples are the same as those in the de-ionised water-equilibrated samples.

4.2.3 Speciation of Curium

A literature review was carried out to determine the aqueous thermodynamic speciation data available for curium compounds. The data were compared to those already in the HATCHES database. The existing data in HATCHES version NEA8 were based on data from Katz et al. [23], for aqueous species and from various sources for curium solids[24][25][26]. Additional data were found in the literature for curium hydrolysis products[27][28][29], and for sulphate[28][30], fluoride[28], and carbonate[27], complexes. Data for curium solids were also revised. Where applicable, data were added to the database. The amended version of HATCHES was then used to predict the aqueous speciation of curium under the experimental conditions of this work. Details of the data for curium used in this work are given in Table 65. Aqueous speciation calculations were modelled assuming equilibration of the solid $Cm(OH)_3(s)$ phase. The predicted solubility of $Cm(OH)_3(s)$ in pure water, de-ionised water equilibrated with bentonite, and seawater equilibrated with bentonite is shown in Figure 1. Below pH 7, the $Cm(OH)_3(s)$ solubility is predicted to increase above $l0^{-3}$ mol dm^{-3}. In this region, the concentration of curium is likely to become inventory limited.

A lack of experimental data for $Cm(OH)_3(s)$ necessitated the estimation of its solubility product (Ksp) as that of $Am(OH)_3(s)$[31]. This approach is taken due to the similar chemistry of curium and americium, but quantitative predictions based on this analogy should be treated with caution.

The solubility of the hydroxides is also dependent upon the quantities of aqueous hydrolysis products formed. As shown in Table 66, there are some differences between the aqueous hydrolysis constants for curium and americium. Therefore the predicted dissolution of $Cm(OH)_3(s)$ differs from that predicted for $Am(OH)_3(s)$. Moreover, the lack of any data for the $Cm(OH)_3(aq)$ species means that at high pH, the predicted solubility of $Cm(OH)_3(s)$ drops more rapidly than for $Am(OH)_3(s)$[32].

The $Cm(OH)_3(s)$ solubility enhancement in the de-ionised and seawaters is a result of carbonate complexation. The elemental concentrations used in these waters were given in Table 2. However precipitation of solid $CmOHCO_3(s)$ is not considered in these calculations. Figure 2 shows the effect of allowing precipitation of this carbonate. In this case, the system has been equilibrated with atmospheric carbon dioxide. The curium solubility is reduced in the intermediate pH range. At high pH, carbon dioxide becomes very soluble. However, if the level of carbonate is limited, the $Cm(OH)_3$ solid again limits the solubility in this high pH region.

Figure 3 shows the predicted curium speciation in pure water. Here, the Cm^{3+} species is predicted to dominate below pH ～ 7.5, $CmOH^{2+}$ between pH ～ 7.5 and ～ 8.5, and $Cm(OH)_2^+$ above pH ～ 8.5. In de-ionised water equilibrated with bentonite (Figure 4), carbonate availability now ensures the $CmCO_3^+$ species dominates between pH ～ 6 to ～ 10. With seawater equilibrated with bentonite (Figure 5), $CmCO_3^+$ dominates over the range pH ～ 6.5 to ～ 9.5. In the region below pH 6.5, the high concentration of chloride ions causes the proportion of $CmCl_2^+$ to become significant. In these low pH conditions, the curium concentration is likely to be inventory limited.

4.2.4 Speciation of Neptunium

The predicted speciation of neptunium in de-ionised water equilibrated with bentonite, granodiorite and tuff is shown in Table 67, under strongly-reducing and non-reducing experimental conditions. Under the strongly-reducing conditions, $Np(OH)_4(aq)$ is predicted to be the only significant aqueous neptunium species. Under non-reducing conditions, neptunium (V) carbonate species are predicted to form for bentonite-and tuff equilibrated waters, whereas NpO_2^+ dominates the speciation for granodiorite-equilibrated waters in the absence of carbonate.

4.2.5 Speciation of Actinium

A literature search was carried out to determine the available thermodynamic data for actinium compounds. These data were compared with those already in the HATCHES database [5] (version NEA9). Data for new species were added to the database and where appropriate the data in HATCHES were refined (Refinements included in version NEA10). The revised database was used in conjunction with the speciation program HARPHRQ version 1.41 to predict the speciation and solubility of actinium under a range of chemical conditions. However, very few enthalpy data for aqueous species were available and therefore no predictions at 60℃ could be made as the dataset was incomplete.

The existing HATCHES data for actinium were extremely limited and are based on data from Baes and Mesmer[13]. The review highlighted further data for hydroxy complexes[30] and carbonate complexes[33], and for complexes with a range of other inorganic ligands[30][34][35][36]. The data for carbonate complexes were estimated based on a correlation between oxalate and carbonate stability constants[37] and reported data for oxalate complexes[38]. The data for solid compounds of actinium were limited to those for the hydroxide[37][39]. No data for carbonate solids were available. A summary of the data for actinium is given in Table 68.

The predicted speciation of actinium in pure water is shown in Figure 6. The hydrolysis of the Ac^{3+} ion occurs at high pH, above pH 10. Figure 7 shows the speciation in bentonite-equilibrated de-ionised water. At low pH, some complexation by sulphate is predicted, whilst above pH 8, carbonate complexes dominate. However, it emphasised that the thermodynamic data for carbonate have been estimated. The prediction for tuff-equilibrated water (Figure 8) is similar, but the higher sulphate concentration leads to an increase in the concentration of sulphate complexes, at low pH. For the granodiorite-equilibrated water, the sulphate and carbonate concentrations were below the detection limit and were assumed to be zero in these calculations. The resulting prediction was the same as for the pure water case.

Figure 9 shows the predicted solubility of $Ac(OH)_3(s)$ in pure water. The solubility drops rapidly from around 10^{-2}M at pH 8 to 10^{-13}M at pH 12. The solubility curves in bentonite-equilibrated de-ionised water (Figure 10) and in tuff-equilibrated de-ionised water (Figure 11) show similar trends. However, the solubility above pH 8 is predicted to be enhanced by up to two orders of magnitude due to carbonate complexation. The prediction for the granodiorite case in the same as that for pure water as no additional complexes are present.

4.2.6 Speciation of Protactinium

A literature search was carried out to determine the available thermodynamic data for protactinium compounds. These data were compared with those already in the HATCHES database[5] (version NEA9). Data for new species were added to the database and where appropriate the data in HATCHES were refined (Refinements included in version NEA10). The revised database was used in conjunction with the speciation program HARPHRQ version 1.41 to predict the speciation and solubility of protactinium under a range of chemical conditions. However, very few enthalpy data for aqueous species were available and therefore no predictions at 60℃ could be made as the dataset was incomplete.

At the start of this task, thermodynamic data in HATCHES for Pa(IV) were limited to those for hydroxy complexes taken from Baes and Mesmer[13]. Further data for carbonate complexes[40] and a range of complexes with other inorganic ligands have been added. The carbonate data were estimated by Berner, based on an analogy with other actinide(IV) complexes[40]. Data for Pa(V) were limited to hydrolysis products[14] and data for sulphate complexes[39] have been added. The thermodynamic data for Pa(V) species have been refined due to a change in the interpretation of the electrode potential data between Pa(IV) and Pa(V) species. The refined HATCHES data are now consistent with reported data for the formation of the $PaOOH^{2+}$ from Pa^{4+} as given by Fuger and Oetting[41]. Data for Pa(IV) and Pa(V) oxides are included, however no data for solid carbonates were available. A summary of the data for protactinium is given in Table 69.

The hydrolysis data for Pa(IV) are consistent with those selected in reference[42]. For Pa(V) hydrolysis products there are some discrepancies. However it is likely that these are largely due to differences in the interpretation of hydrolysis species of the same charge. It is likely that the selected value for PaO_2^+ ($\log K = 2.36$) is an alternative representation of the $PaO(OH)_2^+$ ($\log K = 0.85$) species selected in reference[42]. Similarly, PaO_2OH ($\log K = -2.14$) is probably equivalent to $PaO(OH)_3$ ($\log K = -3.6$). In both cases, the $PaOOH^{2+}$ species has been selected with $\log K = 1.86$ (1.9 in reference[42]). Whilst it is difficult to conclude which of the representations is correct in the absence of spectroscopic data, it is not necessary to make this distinction for example in predicting solubilities. However, it is important to ensure that both sets of species are not specified simultaneously. The differences in the numerical values selected are not large compared to the general uncertainties in the Pa dataset.

The speciation of protactinium in pure water is given in Figure 12. The speciation is predicted to be very simple but this probably reflects a lack of data for higher hydrolysis products at the higher pH values. Pa(V) is the predicted stable oxidation state under most redox conditions, however, predictions carried out at the lower water stability boundary show that Pa(IV) may become important under very strongly-reducing conditions (Figure 13). All predictions for rock-equilibrated waters were carried out at under fixed redox conditions determined by the pH and redox potential measured in the sorption experiments. The redox potential was converted into the appropriate value for the pe parameter and the calculations were performed under the condition : pH(expt) + pe(expt) = a constant, as summarized in Table 70. The resulting predicted speciation in bentonite and tuff-equilibrated de-ionised waters was the same as that for the pure water case. This may reflect a lack of data for Pa(V)-carbonate complexes. In granodiorite-equilibrated de-ionised water, the speciation is similar but a small percentage of the Pa(IV) species $Pa(OH)_4$ is predicted, due to the low measured redox potential in this water (see Figure 14).

The solubility of $Pa_2O_5(s)$ in pure water (Figure 15) is predicted to be the same as that in bentonite and tuff-equilibrated de-ionised waters and is very similar to that in granodiorite-equilibrated de-ionised water (Figure 16). In each case, a decrease in solubility is predicted between pH 3 and pH 5. Above pH 6, the solubility is predicted to be around 3×10^{-7}M. This value is significantly higher than reported solubilities[12] and suggests that the solubility product for $Pa_2O_5(s)$ may be too high.

Given the uncertainties in the protactinium dataset there is some doubt as to whether protactinium will be present as Pa(IV) or Pa(V) under the experimental conditions.

4.2.7 Speciation of Polonium

No thermodynamic data for polonium were available in HATCHES version NEA 9 or NEA 10. A literature review therefore carried out. Data from standard compilations[30][39][43][44][45][46] were collated and original sources were obtained where this was considered necessary, particularly for redox reactions[46][47][48][49]. This review was supported by a computer search for further published data on polonium.

The extent of published thermodynamic data for polonium is very limited. In addition, measurements of the redox potential of systems containing polonium may be inaccurate due to possible problems of irreversibility[43] and oxidation due to radiolytic effects[47].

Data for redox equilibria are shown in Table 71 are either based on redox measurements or have been calculated from tables of free energy of formation[43][44]. The redox potential for Po^{4+}/Po(s) (reaction 1 in Table 71) was measured in nitric acid by Bagnall and Freeman[47]. This should give a reasonable value provided that nitrate complexation of Po(IV) is not strong. The authors calculate that even if only around 10 % of Po(IV) is present as Po^{4+}, the measured potential would still be accurate to a few millivolts. Measurements of this potential in 1M HCl solution give rise to thermodynamic data for Po(II) and Po(IV) chloride complexes. Discrepancies in the measured potential for between the chloride complexes of these two oxidation states (reaction 3)[47][48][49] give rise to a wide range of log$K$ values for reaction 4. These discrepancies may be caused by oxidation due to the effects of radiolysis[47][48].

No reliable data were found for the redox potential between Po^{2+}/Po(s). The value selected is based on data for the free energies of formation[43][44] but the original source of these data could not be traced. Values for the other redox reactions 5 and 6 are reported[46] as having been estimated in earlier work. The calculated value for reaction 8 was found to lead to unrealistic results (with the Po(VI) species dominating the speciation even at low redox potentials).

Thermodynamic data for the complexation of the bare metal ion could only be found for Po^{4+}. The data for hydrolysis products and chloride complexes were taken from Högfeld and Martell[39]. These data were in reasonable agreement with the stepwise equilibrium constants between the second, third and fourth hydrolysis constants reported by Hataye et al.[50]. The value for the sixth chloride complex is in good agreement with that obtained from the redox measurements of

Bagnall and Freeman[47] (from reactions 1 and 2 in Table 71). Nitrate and sulphate complexation data were taken from the IUPAC compilation[29].

The data selected for speciation and solubility calculations are given in Table 72. During the course of performing these calculations it became clear that some of the values were unrealistic and these have been indicated in Table 72. No enthalpy data for polonium species were available and therefore predictions were made only at 25℃.

The prediction of the speciation and solubility of polonium under the experimental conditions was hindered by a lack of thermodynamic data for Po(II) complexes. Meaningful predictions of the Po^{4+}/Po^{2+} transition could only be made at low pH. Figure 17 shows the predicted speciation of polonium in 1M HCl as a function of Eh. The transition between the chloride complexes at an Eh value of around 720 mV arises from the Bagnall and Freeman data selected[47]. The presence of Po^{2+} as the dominant species at lower Eh values is questionable due to the uncertainty in reaction 6 in Table 71.

The speciation of polonium in each of the groundwaters was predicted under the experimental pH and pe (Eh) conditions. In addition, the speciation was calculated across the pH range 0 to 12 for the condition that the sum of the pH and the pe is held constant at the values determined in the sorption experiments. In each case, Po^{2+} was predicted to dominate the speciation across the pH range studied. The predicted concentration of Po^{2+} in equilibrium with Po(s) is shown in Figure 18 for each redox condition. These results suggest that Po(II) is the likely oxidation state of the aqueous polonium, however no prediction of the solubility could be made due to the lack of data for the formation of Po(II) complexes. Po(s) is likely to be the solubility-limiting phase under reducing conditions although Po(II) solids, such as PoS(s) could also be important.

The predicted solubility and speciation of Po(IV) is given in Figure 19 where PoO_2(case b) has been selected as the solubility-limiting phase. The predicted solubility above pH 3 was 2×10^{-10}M. When the solubility product for PoO_2 (case c) was selected a solubility of 4×10^{-16}M was predicted. Hataye et al.[51] have reported studies of aged polonium solutions. They report final aqueous concentrations after ageing for seven months for a range of pH values 0 ～ 8. A large proportion of the polonium was lost from solution by deposition, although formation of colloids and wall sorption were reported to be significant. The final solution concentrations for systems above pH 3 were reported as 200 cpm/20 μl. Assuming a specific activity of 1.662×10^{14} Bq g^{-1}, this corresponds to a concentration of around 5×10^{-12}M.

4.2.8 Speciation of Plutonium

The predicted speciation of plutonium in de-ionised water equilibrated with bentonite, granodiorite and tuff is shown Table 73 under the strongly-reducing conditions. The predictions at 25℃ were carried out at the reported Eh values for the room temperature neptunium sorption experiments reported in Section 3.4.

The major aqueous species were predicted to be $Pu(CO_3)_3^{2-}$ in the bentonite and tuff waters and $Pu(OH)_4(aq)$ in the granodiorite water. The Pu(IV) oxidation state is predicted to be stabilised by carbonate complexation, however, in the granodiorite case the measured redox potential was very close to the Pu(III)/Pu(IV) boundary and around 9 % of Pu(III) species was predicted.

Predications at 60℃ were hindered by a lack of enthalpy data for Pu(III) species and for Pu(IV) carbonate species.

4.2.9 Speciation of Americium

The predicted speciation of americium in de-ionised water equilibrated with bentonite, granodiorite and tuff is shown in Table 74 under the strongly-reducing conditions. The predictions at 25℃ were carried out at the reported Eh values for the room temperature neptunium sorption experiments reported in Section 3.4.

The major aqueous species was predicted to be $Am(OH)_2^+$ in each of the bentonite, granodiorite and tuff waters studied. A small amount of carbonate complexation was predicted for the bentonite and tuff waters.

Predictions at 60℃ indicate that $Am(OH)_2^+$ is again the major aqueous species.

5. Conclusions

Batch sorption experiments for some actinide elements, such as U, Cm, Np, Ac, Pa, Po, Am, Pu and Tc were conducted under strongly-reducing conditions onto bentonite, granodiorite and tuff. For some elements experiments under not-reducing conditions and/or at higher temperature (60℃) were also conducted.

The results, in general, show that these elements are strongly sorbed onto these three geological medias under strongly-reducing conditions, and the sorption under strongly-reducing conditions are significantly greater than that under non-reducing conditions, as shown for U, and Tc.

These observations are consistent with a change in oxidation state of the elements between the two sets of experimental conditions.

The measured R_D values are higher than 10^3 cm^3 g^{-1} for all elements under strongly reducing conditions (except for part of Tc, Np).

For U, Tc, Cm, Np, Ac and Pa, the effect of temperature (room temperature and 60℃) were not significantly observed. In the case of uranium sorption onto bentonite under non-reducing conditions, sorption is less strong at 60℃ than room temperature. In the case of technetium sorption onto bentonite under non-reducing conditions, sorption is less strong at room temperature than 60℃.

Sorption data under strongly-reducing conditions are essential information for safety assessment of geological disposal, however the data had not been sufficient. These data obtained by this study have enhanced the information in this aspect.

The speciation calculations were also conducted, and for some elements, such as Ac, Pa and Po, literature survey and discussion for relevant thermodynamic data were conducted. These must help further understanding of sorption mechanism.

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Table 1

Composition of Kunigel V1[6], Tuff[7] and Granodiorite

Mineral	Content(wt%)		
	Kunigel V1	Tuff	Granodiorite
Na–montmorillonite	46–49	–	–
Quartz	0.5–0.7	9.5	30.8
Feldspar	–	0.5	24.5
Plagioclase	2.7–5.5	5	39.2
Calcite	2.1–2.6	–	–
Zeolite	–	34.6	–
Dolomite	2.0–2.8	–	–
Pyrite	0.5–0.7	–	–
Volcanic glass	–	47.1	–
Biotite	–	–	4.2
Appatite	–	–	<0.1
Analcime	3.0–3.5	–	–
Chalcedony	37–38	–	–
Chlorite	–	–	1.3

Table 2

Analysis of Synthetic Seawater and De–ionised Water after Equilibration with Bentonite

Speciation	Synthetic Seawater^{*1}	Concentration/μg cm^{-3}	
		Seawater after equilibration with Bentonite at room temperature^{*3}	De–ionised water after equilibration with Bentonite at room temperature^{*3}
Al	<0.3	<0.3	<0.3
B	4.1	3.9	<0.02
Ca	390	400	0.49
Fe	0.11	0.19	0.04
K	35	320	0.66
Mg	1500	1400	0.07
Na	10200	10500	110
Si	1.7	5.1	5.3
Sr	4.3	6.1	0.005
Cl^-	22000	21000	<0.1
Br^-	60	60	<0.5
S as SO_4^{2-}	2800	2900	9.2
TIC as CO_3^{2-}	108	111	28
Final pH	7	8	10.1^{*2}

*1 Based on compositions of seawater in the following:–

1 "Handbook of Chemistry and Physics" 71st Edition (1990–91), CRC Press, p14–10

2 B Mason "Principles of Geochemistry" John Wiley and Sons, 3rd Edition 1966, p194

3 P Henderson "Inorganic Chemistry" Permagon Press, 1st Edition 1982, p280

*2 pH of solution measured at 60°C was 9.4, so this pH was used in batch sorption experiments at 60°C

*3 Sample were filtered using a 10000MWCO filter period to analysis.

TIC = Total Inorganic Carbon

Table 3

Analysis of Synthetic Seawater and De-ionised Water after Equilibration with Tuff at room temperature

Speciation	Concentration/μg cm^{-3}	
	Seawater	De-ionised water
Al	0.24	0.07
B	3.9	0.23
Ca	1020	10.2
Fe	0.39	0.08
K	148	0.6
Mg	1170	0.42
Na	10200	75
Si	7	6.8
Sr	12	0.02
Cl^-	18000	4
Br^-	74	<0.04
S as SO_4^{2-}	2500	115
TIC as CO_3^{2-}	29	37
Final pH	8.1	9.4

All values measured after 4 weeks eqilibration at a water/rock ratio of 5:1 in a nitrogen-atmosphere glove box. Sample were filtered using a 10000MWCO filter prior to analysis

Table 4

Analysis of Synthetic Seawater and De-ionised Water after Equilibration with Granodiorite at room temperature

Speciation	Concentration/μg cm^{-3}	
	Seawater	De-ionised water
Al	0.3	0.6
B	3.4	<0.1
Ca	380	4.1
Fe	0.2	0.2
K	380	11
Mg	1300	2.4
Na	9900	29
Si	4.7	6.2
Sr	4.7	0.02
F^-	0.64	0.41
Cl^-	18000	20
Br^-	0.82	0.13
PO_4^{3-}	ND	ND
SO_4^{2-}	2100	ND
CO_3^{2-}	140	<10
Final pH	8.4	10.1

ND = Not Detected

All values measured after 4 weeks eqilibration at a water/rock ratio of 5:1 in a nitrogen-atmosphere glove box. Sample were filtered using a 10000MWCO filter prior to analysis.

Table 5
Analysis of Seawater and De−ionised Water after Equilibration with Bentonite, Tuff and Granodiorite at 60℃

Speciation	Concentration/μg cm^{-3}			
	De−ionised with Bentonite*	De−ionised with Tuff	De−ionised with Granodiorite	Seawater with Bentonite*
Al	<0.3	0.36	1.6	0.17
B	<0.02	0.33	0.03	4.5
Ca	0.49	5	2.8	407
Fe	0.04	0.08	<0.003	0.09
K	0.66	9	11	363
Mg	0.07	<0.05	<0.05	1210
Na	110	97	11	10890
Si	5.3	10	14	4.4
Sr	0.005	0.01	<0.002	8.3
F−	<0.1	2.6	0.78	−
Cl−	<0.1	8.7	1.2	21000
Br−	<0.05	<0.02	<0.02	88
PO43−	<0.1	<0.05	<0.05	−
SO42−	9.2	160	0.55	3000
CO32−	28	47	<10	<30
Final pH	9.4	9.2	9.6	8.1

Sample were filtered using a 10000MWCO filter prior to analysis.

* Analysis from 20℃ equilibration used, only pH values are measured at 60℃

All values measured after 4 weeks eqilibration at a water/rock ratio of 20:1 for bentonite and 5:1 for tuff and granodiorite in a nitrogen−atmosphere glove box.

Table 6

Uranium Sorption onto Bentonite under Strong–Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45•m	10000MWCO
Seawater (Nominal pH 8)	20:1	8	−410	$2.2\text{x}10^4 \pm 5.9\text{x}10^3$	$5.2\text{x}10^4 \pm 1.4\text{x}10^4$	$1.0\text{x}10^5 \pm 3.0\text{x}10^4$
		8	−400	$2.5\text{x}10^4 \pm 7.7\text{x}10^3$	$7.8\text{x}10^4 \pm 2.1\text{x}10^4$	$2.3\text{x}10^5 \pm 7.3\text{x}10^4$
	100:1	8	−400	$5.0\text{x}10^4 \pm 1.3\text{x}10^4$	$1.8\text{x}10^5 \pm 4.7\text{x}10^4$	$1.5\text{x}10^5 \pm 4.0\text{x}10^4$
		8.1	−410	$3.5\text{x}10^4 \pm 9.0\text{x}10^3$	$1.6\text{x}10^5 \pm 4.5\text{x}10^4$	$1.7\text{x}10^5 \pm 4.5\text{x}10^4$
De−ionised water (Nominal pH 10.1)	20:1	10.1	−450	$2.6\text{x}10^4 \pm 6.8\text{x}10^3$	$3.9\text{x}10^4 \pm 1.0\text{x}10^4$	$2.8\text{x}10^4 \pm 7.4\text{x}10^3$
		10.1	−470	$1.3\text{x}10^4 \pm 3.4\text{x}10^3$	$1.7\text{x}10^4 \pm 4.5\text{x}10^3$	$1.8\text{x}10^4 \pm 4.8\text{x}10^3$
	100:1	10.2	−440	$7.6\text{x}10^4 \pm 2.1\text{x}10^3$	$5.9\text{x}10^5 \pm 1.7\text{x}10^5$	$6.7\text{x}10^5 \pm 1.9\text{x}10^5$
		10.2	−440	$7.6\text{x}10^4 \pm 2.0\text{x}10^4$	$1.5\text{x}10^5 \pm 4.9\text{x}10^4$	$5.2\text{x}10^5 \pm 1.4\text{x}10^5$

Initial U−233 concentration = $1.9 \text{ x } 10^{-7}$M

Errors quoted are 2σ and are based on counting statistics alone

Table 7

Uranium Sorption onto Bentonite under Non−Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45•m	10000MWCO
Seawater (Nominal pH 8)	20:1	8.2	+310	37±7	42±8	35±7
		8.1	+310	35±7	53±10	36±7
	100:1	8.2	+310	150±31	190±38	160±33
		8.2	+300	150±30	200±40	150±31
De−ionised water (Nominal pH 10.1)	20:1	10.2	+350	47±9	47±9	32±7
		10.1	+350	30±6	49±10	23±5
	100:1	10.2	+330	250±48	230±45	180±36
		10.2	+330	230±45	240±47	190±39

Initial U−233 concentration = $1.5 \text{ x } 10^{-7}$M

Errors quoted are 2σ and are based on counting statistics alone

Table 8

Uranium Remaining in Solution under Strongly-Reducing Conditions in the Absence of Bentonite

Solution	Initial U-233 Concentration /Bq cm^{-3}	U-233 Concentration in Solution after 4 Months/Bq cm^{-3}		
		Centrifuged	0.45μm Filtered	10000MWCO Filtered
Seawater	15.64+0.23	3.53+0.02 (22.6%)	0.112+0.004 (0.7%)	0.122+0.011 (0.8%)
De-ionised water	15.64+0.23	1.20+0.02 (7.7%)	0.172+0.08 (1.1%)	0.092+0.005 (0.6%)

Table 9

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly-Reducing Conditions

Radioelement	Solution	Water:Bentonite Ratio	Amount Sorbed on Vessel Walls
Uranium	Seawater	100:1	2.6%
Uranium	De-ionised water	100:1	3.4%
Uranium	Seawater	20:1	1.5%
Uranium	De-ionised water	20:1	1.2%

Table 10

Uranium Sorption onto Tuff under Strongly-Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R$_D$(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	5:1	8.3	-350	2.8x10^{4}±0.5x10^{4}	6.3x10^{4}±1.6x10^{4}	5.6x10^{4}±1.5x10^{4}
		8.1	-340	1.1x10^{4}±0.2x10^{4}	5.6x10^{4}±1.1x10^{4}	1.4x10^{5}±1.2x10^{5}
	50:1	8.3	-340	5.6x10^{4}±0.9x10^{4}	2.8x10^{5}±0.8x10^{5}	2.8x10^{5}±0.7x10^{5}
		8.1	-330	5.1x10^{4}±0.8x10^{4}	2.8x10^{5}±0.8x10^{5}	1.2x10^{6}±0.5x10^{6}
De-ionised water (Nominal pH 9.4)	5:1	9.4	-410	5.1x10^{3}±0.7x10^{3}	1.9x10^{4}±0.3x10^{4}	5.6x10^{4}±1.0x10^{4}
		9.4	-400	9.4x10^{3}±1.2x10^{3}	5.6x10^{4}±1.5x10^{4}	5.6x10^{4}±0.9x10^{4}
	50:1	9.5	-410	1.1x10^{4}±0.1x10^{4}	6.2x10^{4}±0.9x10^{4}	2.8x10^{5}±0.5x10^{5}
		9.5	-420	1.5x10^{4}±0.2x10^{4}	9.4x10^{4}±1.2x10^{4}	5.6x10^{5}±1.2x10^{5}

Initial uranium concentration = 1.35 x 10^{-7}M

Errors quoted are 2σ and are based on counting statistics alone

Table 11

Uranium Sorption onto Tuff under Non-Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	5:1	8.3	+310	32±4	33±4	33±4
		8.2	+300	35±4	35±4	36±4
	50:1	8.1	+300	110±14	100±14	110±14
		8.1	+300	96±13	97±13	110±14
De-ionised water (Nominal pH 9.4)	5:1	9.4	+350	92±11	97±12	98±12
		9.4	+330	110±13	110±13	110±13
	50:1	9.4	+320	100±14	110±14	110±15
		9.4	+360	130±17	150±19	140±18

Initial uranium concentration = 1.5 x 10^{-7}M

Errors quoted are 2σ and are based on counting statistics alone

Table 12

Uranium Remaining in Solution in the Absence of Tuff

Conditions	Solution	Initial U-233 Concentration /Bq cm^{-3}	U-233 Concentration in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly-Reducing	Seawater	11.25	0.11 (0.98%)	0.03 (0.27%)	0.03 (0.27%)
	De-ionised water	11.25	0.6 (5.33%)	0.14 (1.24%)	0.05 (0.44%)
Non-Reducing	Seawater	12.78	10.08 (78.9%)	10.75 (84.1%)	10.93 (85.5%)
	De-ionised water	12.78	11.6 (90.8%)	11.84 (92.6%)	12.38 (96.9%)

Table 13

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly-Reducing Conditions

Radioelement	Solution	Water:Tuff Ratio	Amount Sorbed on Vessel Walls
Uranium	Seawater	50:1	2.05%
Uranium	De-ionised water		0.80%
Uranium	Seawater	5:1	0.28%
Uranium	De-ionised water		0.18%

Table 14

Uranium Sorption onto Granodiorite under Strongly-Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm Filtered	10000MWCO Filtered
Seawater (Nominal pH 8.4)	5:1	8.5	−420	$1.2\times10^3\pm0.3\times10^3$	$1.9\times10^4\pm0.8\times10^4$	$>10^4$
		8.4	−430	840±220	$>10^4$	$>10^4$
	50:1	8.5	−420	$2.6\times10^3\pm0.7\times10^3$	$4.1\times10^4\pm1.5\times10^4$	$8.1\times10^4\pm2.5\times10^4$
		8.4	−460	480±90	$7.1\times10^4\pm2.1\times10^4$	$2.8\times10^5\pm1.0\times10^5$
De-ionised water (Nominal pH 10.1)	5:1	10.1	−450	540±90	$6.3\times10^3\pm1.6\times10^3$	$2.8\times10^4\pm0.6\times10^4$
		10.1	−450	360±70	$4.7\times10^3\pm1.6\times10^3$	$6.3\times10^3\pm2.0\times10^3$
	50:1	10.1	−440	$1.1\times10^3\pm0.2\times10^3$	$6.9\times10^3\pm3.6\times10^3$	$1.2\times10^4\pm0.6\times10^4$
		10.2	−440	950±160	$9.1\times10^3\pm5.5\times10^3$	$1.8\times10^4\pm1.1\times10^4$

Initial uranium concentration = 1.4×10^{-7}M

Errors quoted are 2σ and are based on counting statistics alone

Table 15

Uranium Sorption onto Granodiorite under Non-Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.4)	5:1	8.3	+330	5±1	5±1	4±1
		8.4	+330	7±2	7±2	8±2
	50:1	8.4	+310	<14	<18	<13
		8.5	+280	<1	<1	86±17
De-ionised water (Nominal pH 10.1)	5:1	10.1	+200	50±9	37±7	48±10
		10.1	+300	27±5	31±6	29±5
	50:1	10	+280	93±18	49±12	47±11
		10.1	+270	120±20	86±16	86±16

Initial U-233 concentration = 1.4×10^{-7}M

Errors quoted are 2σ and are based on counting statistics alone

Table 16

Uranium Remaining in Solution in the Absence of Granodiorite

Conditions	Solution	Initial U−233 Concentration/Bq cm^{-3}	U−233 Concentration in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly−Reducing	Seawater	11.38	0.008 (0.07%)	0.012 (0.11%)	0.099 (0.87%)
	De−ionised water	11.4	0.573 (5.03%)	0.062 (0.54%)	0.032 (0.28%)
Non−Reducing	Seawater	12.29	13.82* (100%)	13.15* (100%)	13.92* (100%)
	De−ionised water	12.21	8.82 (72.2%)	9.28 (76.0%)	9.22(75.5%)

＊ These values are close to the 2σ counting errors on the initial U−233

Table 17

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly−Reducing Conditions

Radioelement	Solution	Water:Granodiorite Ratio	Amount Sorbed on Vessel Walls
Uranium	Seawater	50:1	0.42%
Uranium	De−ionised water	50:1	0.07%
Uranium	Seawater	5:1	0.06%
Uranium	De−ionised water	5:1	0.06%

Table 18

Uranium Sorption onto Bentonite at 60℃ under Strongly−Reducing Conditions

Bentonite Equilibrated with :	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	8.2	−360	～10^4	$1.3\text{x}10^4 \pm 0.4\text{x}10^4$	$1.8\text{x}10^4 \pm 0.9\text{x}10^4$
	8.1	−370	$2.0\text{x}10^4 \pm 1.0\text{x}10^4$	$9.5\text{x}10^3 \pm 2.7\text{x}10^3$	$7.9\text{x}10^3 \pm 2.1\text{x}10^3$
De−ionised water (Nominal pH 9.4)	9.4	−400	$7.1\text{x}10^3 \pm 1.6\text{x}10^3$	$2.7\text{x}10^4 \pm 0.7\text{x}10^4$	$5.2\text{x}10^4 \pm 1.8\text{x}10^4$
	9.4	−410	$7.6\text{x}10^3 \pm 1.8\text{x}10^3$	$3.3\text{x}10^4 \pm 1.0\text{x}10^4$	$3.8\text{x}10^4 \pm 1.2\text{x}10^4$

Initial U−233 concentration = 1.1 x 10^{-7}M for seawater and 1.2 x 10^{-7}M for de−ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 19

Uranium Sorption onto Bentonite at 60℃ under Non-Reducing Conditions

Bentonite Equilibrated with :	Final pH	Final Eh/mV vs SHE	$R_D(cm^3\ g^{-1})$		
			Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	8.1	+240	780±350	720±330	720±510
	8.1	+200	780±340	870±490	720±720*
De-ionised water (Nominal pH 9.4)	9.4	+270	27±7	110±25	120±36
	9.4	+280	60±13	61±16	92±39

* Very low yield after electrodeposition results in the high 2σ error shown

Initial U-233 concentration = 1.3 x 10^{-7}M for seawater and de-ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 20

Uranium Remaining in Solution at 60℃ in the Absence of Bentonite

Conditions	Solution	Initial U-233 Concentration /Bq cm^{-3}	U-233 Concentration in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly-Reducing	Seawater	9.14	0.068 (0.74%)	0.023 (0.25%)	0.027 (0.30%)
	De-ionised water	9.8	2.33 (23.8%)	1.46 (14.9%)	0.16 (1.60%)
Non-Reducing	Seawater	11.16	7.8 (69.9%)	6.9 (61.8%)	6.9 (61.8%)
	De-ionised water	11.16	11.16 (100%)	8.1 (72.6%)	8.1 (72.6%)

Table 21

Results of Analysis of Vessel Walls after Batch Sorption Experiments at 60℃ under Non- Reducing and Strongly-Reducing Conditions

Radioelement	Solution	Amount Sorbed on Vessel Walls Under Non-Reducing Conditions	Amount Sorbed on Vessel Walls Under Strongly-Reducing Conditions
Uranium	Seawater	0.59%	1.1%
		0.58%	0.41%
	De-ionised water	0.30%	0.54%
		0.33%	0.76%

Table 22

Technetium Sorption onto Bentonite under Strongly–Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8)	20:1	8.2	−420	4200±200	6900±300	6900±300
		8.2	−410	5200±200	8200±400	8800±400
	100:1	8.2	−430	6800±200	9800±300	9100±300
		8.2	−430	4600±200	1.0x10^4±400	1.0x10^4±400
De–ionised water (Nominal pH 10.1)	20:1	10	−460	1300±50	1400±60	1500±60
		10.1	−450	1400±60	1600±60	1700±70
	100:1	10.2	−460	680±20	640±20	620±20
		10.1	−460	640±20	640±20	590±20

Initial Tc−95m concentration = 4.0 x 10^{-11}M

Errors quoted are 2σ and are based on counting statistics alone

Table 23

Technetium Sorption onto Bentonite under Non–Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8)	20:1	8.1	+310	68±2	71±2	76±3
		8.2	+300	65±2	65±2	69±2
	100:1	8.1	+310	210±7	220±8	240±8
		8	+300	210±7	210±8	230±8
De–ionised water (Nominal pH 10.1)	20:1	10.1	+320	26±1	40±1	46±2
		10.1	+320	23±1	29±1	34±1
	100:1	10.2	+310	54±2	55±2	59±2
		10.1	+320	47±2	48±2	51±2

Initial Tc−95m concentration = 1.0 x 10^{-10}M

Errors quoted are 2σ and are based on counting statistics alone

Table 24

Technetium Remaining in Solution in the Absence of Bentonite

Conditions	Solution	Initial Tc−95m Concentration /Bq cm^{-3}	Tc−95m Concentration in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly−Reducing	Seawater	3.49 x 10^3	306 (8.7%)	62.8 (1.8%)	60.8 (1.7%)
	De−ionised water	3.29 x 10^3	2.39 x 10^3 (72.6%)	2.04 x 10^3 (62.0%)	1.92 x 10^3 (58.4%)
Non−Reducing	Seawater	9.53 x 10^3	7.54 x 10^3 (79.1%)	7.98 x 10^3 (83.7%)	7.90 x 10^3 (82.9%)
	De−ionised water	9.45 x 10^3	8.52 x 10^3 (90.2%)	8.28 x 10^3 (87.6%)	8.74 x 10^3 (92.5%)

Table 25

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly−Reducing Conditions

Radioelement	Solution	Water:Bentonite Ratio	Amount Sorbed on Vessel Walls
Technetium	Seawater	100:1	2.4%
Technetium	De−ionised water	100:1	0.03%
Technetium	Seawater	20:1	1.3%
Technetium	De−ionised water	20:1	0.35%

Table 26

Technetium Sorption onto Tuff under Strongly−Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	5:1	8.1	−390	$1.8x10^4 \pm 0.2x10^4$	$5.2x10^4 \pm 1.1x10^4$	$2.4x10^4 \pm 0.3x10^4$
		8.1	−380	$1.9x10^4 \pm 0.2x10^4$	$1.3x10^5 \pm 0.8x10^5$	$8.3x10^4 \pm 0.4x10^4$
	50:1	8.1	−370	$2.0x10^4 \pm 0.1x10^4$	$3.7x10^5 \pm 0.7x10^5$	$3.6x10^5 \pm 0.6x10^5$
		8.2	−360	$4.3x10^3 \pm 0.2x10^3$	$3.1x10^5 \pm 0.5x10^5$	$3.4x10^5 \pm 0.6x10^5$
De−ionised water (Nominal pH 9.4)	5:1	9.4	−400	$1.6x10^3 \pm 0.1x10^2$	$1.2x10^4 \pm 0.2x10^4$	$1.8x10^4 \pm 0.4x10^4$
		9.4	−400	$2.9x10^3 \pm 0.2x10^3$	$1.2x10^4 \pm 0.2x10^4$	$1.1x10^4 \pm 0.2x10^4$
	50:1	9.4	−400	960 ± 34	$2.6x10^4 \pm 0.2x10^4$	$2.9x10^4 \pm 0.2x10^4$
		9.5	−410	$1.3x10^3 \pm 0.1x10^3$	$2.2x10^4 \pm 0.1x10^4$	$2.2x10^4 \pm 0.1x10^4$

Initial Tc−95m concentration = 4.3 x 10^{-11}M for seawater and 1.5 x 10^{-11}M for de−ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 27

Technetium Sorption onto Tuff under Non-Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^{3}g $^{-1}$)		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	5:1	8.1	+350	1.5±0.2	1.7±0.2	1.9±0.2
		8.1	+320	1.5±0.2	1.6±0.2	1.8±0.2
	50:1	8.2	+340	<4	<4	3.9±1.7
		8.3	+340	<3	<3	4.9±1.7
De-ionised water (Nominal pH 9.4)	5:1	9.3	+450	1.0±0.2	1.2±0.2	1.4±0.2
		9.3	+390	1.1±0.2	1.2±0.2	1.5±0.2
	50:1	9.3	+400	<4	<4	4.0±1.7
		9.3	+390	<3	<4	3.7±1.7

Initial Tc-95m concentration = 5.6 x 10^{-11}M for seawater and 5.5 x 10^{-11}M for de-ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 28

Technetium Remaining in Solution in the Absence of Tuff

Conditions	Solution	Initial Tc-95m Concentration /Bq cm^{-3}	Tc-95m Concentration* in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly-Reducing	Seawater	3.44 x 10^3	6.70 x 10^2 (19.5%)	2.65 x 10^2 (7.7%)	1.61 x 10^2 (4.7%)
	De-ionised water	1.20 x 10^3	1.22 x 10^1 (1.0%)	1.60 x 10^0 (0.13%)	1.60 x 10^0 (0.13%)
Non-Reducing	Seawater	4.40 x 10^3	4.65 x 10^{3**} (100%)	4.60 x 10^{3**} (100%)	4.45 x 10^{3**} (100%)
	De-ionised water	4.50 x 10^3	2.18 x 10^3 (48.4%)	2.04 x 10^3 (45.3%)	1.80 x 10^3 (40.0%)

* All decay-corrected to the starting data

** Within counting errors (not incleded)

Table 29

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly-Reducing Conditions

Radioelement	Solution	Water:Tuff Ratio	Amount Sorbed on Vessel Walls
Technetium	Seawater	50:1	0.73%
Technetium	De-ionised water	50:1	1.35%
Technetium	Seawater	5:1	0.06%
Technetium	De-ionised water	5:1	0.06%

Table 30

Technetium Sorption onto Granodiorite under Strongly–Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.4)	5:1	8.4	−330	$1.6\text{x}10^3 \pm 0.9\text{x}10^3$	$1.9\text{x}10^4 \pm 0.3\text{x}10^4$	$2.2\text{x}10^4 \pm 0.4\text{x}10^4$
		8.5	−330	$2.1\text{x}10^3 \pm 0.2\text{x}10^3$	$2.4\text{x}10^4 \pm 0.5\text{x}10^4$	$2.7\text{x}10^4 \pm 0.5\text{x}10^4$
	50:1	8.4	−330	$1.5\text{x}10^4 \pm 0.1\text{x}10^4$	$1.7\text{x}10^5 \pm 0.3\text{x}10^5$	$2.0\text{x}10^5 \pm 0.3\text{x}10^5$
		8.5	−330	$1.1\text{x}10^4 \pm 0.1\text{x}10^4$	$1.5\text{x}10^5 \pm 0.2\text{x}10^5$	$1.6\text{x}10^5 \pm 0.2\text{x}10^5$
De–ionised water (Nominal pH 10.1)	5:1	10.2	−330	$4.9\text{x}10^3 \pm 0.4\text{x}10^3$	$3.5\text{x}10^4 \pm 0.7\text{x}10^4$	$3.8\text{x}10^4 \pm 0.9\text{x}10^4$
		10.1	−340	$1.8\text{x}10^3 \pm 0.1\text{x}10^3$	$2.8\text{x}10^4 \pm 0.5\text{x}10^4$	$3.3\text{x}10^4 \pm 0.6\text{x}10^4$
	50:1	10.2	−370	$1.2\text{x}10^3 \pm 0.06\text{x}10^3$	$4.3\text{x}10^4 \pm 0.3\text{x}10^4$	$9.0\text{x}10^4 \pm 0.9\text{x}10^4$
		10.2	−360	$7.7\text{x}10^3 \pm 0.5\text{x}10^3$	$1.6\text{x}10^5 \pm 0.2\text{x}10^5$	$1.8\text{x}10^5 \pm 0.2\text{x}10^5$

Initial Tc–95m concentration = 3.3 x 10^{-11}M for seawater and 4.5 x 10^{-11}M for de–ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 31

Technetium Sorption onto Granodiorite under Non–Reducing Conditions

Bentonite Equilibrated with :	Water:Bentonite Ratio	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
				Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.4)	5:1	8.4	+320	38±2	39±2	42±2
		8.3	+310	63±4	63±4	70±4
	50:1	8.5	+240	28±3	27±3	28±3
		8.5	+280	28±3	30±3	37±4
De–ionised water (Nominal pH 10.1)	5:1	10.2	+310	18±3	19±3	19±3
		10.2	+240	17±2	18±2	18±3
	50:1	10.2	+270	26±8	27±8	32±9
		10.1	+210	33±9	35±9	38±9

Initial Tc–95m concentration = 6.4 x 10^{-11}M for seawater and 5.5 x 10^{-11}M for de–ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 32

Technetium Remaining in Solution in the Absence of Granodiorite

Conditions	Solution	Initial Tc−95m Concentration /Bq cm^{-3}	Tc−95m Concentration* in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly−Reducing	Seawater	2.68×10^3	2.90×10^1 (1.08%)	2.73×10^0 (0.10%)	1.43×10^0 (0.05%)
	De−ionised water	3.60×10^3	2.00×10^2 (5.56%)	1.37×10^1 (0.38%)	1.19×10^1 (0.33%)
Non−Reducing	Seawater	5.14×10^3	4.95×10^3 (96.3%)	4.93×10^3 (95.9%)	4.60×10^3 (89.5%)
	De−ionised water	5.16×10^3	5.05×10^3(97.9%)	4.80×10^3 (93.0%)	4.55×10^3 (88.2%)

＊ All decay−corrected to the starting data

Table 33

Results of Analysis of Vessel Walls after Batch Sorption Experiments under Strongly−Reducing Conditions

Radioelement	Solution	Water:Granodiorite Ratio	Amount Sorbed on Vessel Walls
Technetium	Seawater	50:1	1.8%
Technetium	De−ionised water	50:1	0.35%
Technetium	Seawater	5:1	0.07%
Technetium	De−ionised water	5:1	0.02%

Table 34

Technetium Sorption onto Bentonite at 60℃ under Strongly−Reducing Conditions

Bentonite Equilibrated with :	Final pH	Final Eh/mV vs SHE	$R_D(cm^3\ g^{-1})$		
			Centrifuged	0.45μm	10000MWCO
Seawater (Nominal pH 8.1)	8.1	−390	$5.5x10^4 \pm 1.1x10^4$	$5.8x10^4 \pm 1.2x10^4$	$2.6x10^5 \pm 0.3x10^5$
	8.1	−380	$3.1x10^4 \pm 0.5x10^4$	$1.1x10^5 \pm 0.4x10^5$	$8.1x10^4 \pm 2.7x10^4$
De−ionised water (Nominal pH 9.4)	9.4	−390	$4.7x10^3 \pm 0.3x10^3$	$1.3x10^4 \pm 0.1x10^4$	$1.5x10^4 \pm 0.1x10^4$
	9.4	−390	$2.9x10^3 \pm 0.1x10^3$	$8.0x10^3 \pm 0.4x10^3$	$2.1x10^4 \pm 0.2x10^4$

Initial Tc−95m concentration = 1.2×10^{-11}M for seawater and 1.5×10^{-11}M for de−ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 35

Technetium Sorption onto Bentonite at 60℃ under Non-Reducing Conditions

Bentonite Equilibrated with :	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Seawater	8.1	+260	250±10	280±10	270±10
(Nominal pH 8.1)	8.1	+240	85±3	88±3	89±3
De-ionised water	9.4	+260	$1.6\times10^3 \pm 0.1\times10^3$	$2.3\times10^3 \pm 0.1\times10^3$	$2.0\times10^3 \pm 0.1\times10^3$
(Nominal pH 9.4)	9.4	+250	$1.5\times10^3 \pm 0.1\times10^3$	$1.7\times10^3 \pm 0.1\times10^3$	$1.6\times10^3 \pm 0.1\times10^3$

Initial Tc-95m concentration = 1.9×10^{-11}M for seawater and 1.6×10^{-11}M for de-ionised water

Errors quoted are 2σ and are based on counting statistics alone

Table 36

Technetium Remaining in Solution at 60℃ in the Absence of Bentonite

Conditions	Solution	Initial Tc-95m Concentration /Bq cm^{-3}	Tc-95m Concentration* in Solution after 4 Months/Bq cm^{-3}		
			Centrifuged	0.45μm Filtered	10000MWCO Filtered
Strongly-Reducing	Seawater	9.86×10^2	46.2 (4.7%)	5.1 (0.51%)	2.34 (0.24%)
	De-ionised water	1.24×10^3	900 (72.6%)	880 (71.0%)	660 (53.7%)
Non-Reducing	Seawater	1.49×10^3	9.96 (0.67%)	4.84 (0.32%)	3.86 (0.26%)
	De-ionised water	1.32×10^3	1152 (87.3%)	1084 (82.1%)	800 (60.6%)

* All decay-corrected to the starting data

Table 37

Results of Analysis of Vessel Walls after Batch Sorption Experiments at 60℃ under Non- Reducing and Strongly-Reducing Conditions

Radioelement	Solution	Amount Sorbed on Vessel Walls under Non-Reducing Conditions	Amount Sorbed on Vessel Walls under Strongly-Reducing Conditions
Technetium	Seawater	4.3%	0.91%
Technetium	Seawater	2.4%	1.1%
Technetium	De-ionised water	0.05%	0.68%
Technetium	De-ionised water	0.13%	1.0%

Table 38

Curium Sorption onto Bentonite at Room Temperature and 60℃ under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^{3} g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−400	2.3x10^{4}±0.3x10^{4}	3.5x10^{4}±0.5x10^{4}	6.5x10^{4}±1.2x10^{4}
	10.1	−410	2.9x10^{4}±0.4x10^{4}	5.2x10^{4}±0.8x10^{4}	2.1x10^{5}±0.4x10^{5}
60℃	9.4	−350	3.3x10^{4}±0.5x10^{4}	2.3x10^{4}±0.4x10^{4}	6.9x10^{4}±1.6x10^{4}
	9.4	−350	2.2x10^{4}±0.3x10^{4}	2.1x10^{5}±0.4x10^{5}	5.1x10^{5}±1.5x10^{5}

Initial curium-244 concentration = 1.7 x 10^{-10}M

Errors quoted are 2σ and are based on counting statistics alone

Table 39

Curium Sorption onto Tuff at Room Temperature and 60℃ under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^{3} g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	9.4	−430	7.1x10^{3}+1.0x10^{3}	3.0x10^{4}+0.5x10^{4}	4.5x10^{4}+1.0x10^{4}
	9.4	−440	5.8x10^{3}+0.8x10^{3}	2.9x10^{4}+0.5x10^{4}	1.1x10^{5}+0.3x10^{5}
60℃	9.2	−370	1.9x10^{4}+0.3x10^{4}	6.4x10^{4}+1.2x10^{4}	1.3x10^{5}+0.3x10^{5}
	9.2	−370	1.7x10^{4}+0.2x10^{4}	7.1x10^{4}+1.2x10^{4}	2.1x10^{5}+0.5x10^{5}

Initial curium-244 concentration = 1.7 x 10^{-10}M

Errors quoted are 2σ and are based on counting statistics alone

Table 40

Curium Sorption onto Granodiorite at Room Temperature and 60℃ under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−430	810±120	1.1x10^{4}±0.2x10^{4}	1.2x10^{4}±0.2x10^{4}
	10.1	−440	540±80	7.3x10^{3}±1.0x10^{3}	1.2x10^{4}±0.2x10^{4}
60℃	9.6	−390	40±6	3.2x10^{3}±0.5x10^{3}	4.0x10^{4}±0.4x10^{4}
	9.6	−400	43±7	2.1x10^{3}±0.3x10^{3}	2.3x10^{4}±0.5x10^{4}

Initial curium-244 concentration = 1.7 x 10^{-10}M

Errors quoted are 2σ and are based on counting statistics alone

Table 41

Curium Remaining in Solution in the Absence of Rock

Temperature	Cm−244 Concentration in Solution after 4 Months/Bq cm^{-3}								
	Bentonite			Tuff			Granodiorite		
	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO
Room Temperature	3.08 (2.4%)	3.85 (3.0%)	0.35 (0.3%)	10.73 (8.5%)	2.88 (2.3%)	1.89 (1.5%)	14.5 (11.4%)	9.9 (7.8%)	0.14 (0.1%)
60℃	3.07 (2.4%)	3.99 (3.1%)	0.8 (0.6%)	2.81 (2.2%)	0.8 (0.63%)	0.08(0.06%)	5.18 (4.1%)	3.09 (2.4%)	0.09 (0.07%)

Initial curium−244 concentration = 1.7 x 10^{-10}M

Table 42

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly−Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls (%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Curium	0.79	3.13	0.3	0.48	1.74	2.32

Table 43

Neptunium Sorption onto Bentonite, Granodiorite and Tuff at Room Temperature and 60℃ under Strongly−Reducing Conditions(Larger Scale Experiments)

Temperature	Geological Material	Final pH	Final Eh/mV vs SHE	Liquid−to−Solid ratio	R_D(cm^3 g^{-1})		
					Centrifuged	0.45μm	10000MWCO
Room Temperature	Bentonite	10.4	−440	20:1	$6.8x10^3 \pm 2.1x10^3$	$4.5x10^3 \pm 1.3x10^3$	$5.7x10^3 \pm 2.0x10^3$
		10.4	−380	100:1	$4.3x10^4 \pm 1.1x10^4$	$1.8x10^4 \pm 0.4x10^4$	$9.8x10^3 \pm 2.2x10^3$
	Tuff	9.4	−310	5:1	620+±20	810±170	680±150
	Granodiorite	10.1	−460	5:1	200±40	$1.3x10^3 \pm 0.3x10^3$	$3.2x10^3 \pm 1.1x10^3$
60℃	Bentonite	9.4	−320	20:1	$9.1x10^3 \pm 3.5x10^3$	$4.7x10^3 \pm 1.4x10^3$	$4.0x10^3 \pm 1.1x10^3$
		9.4	−380	100:1	$7.1x10^4 \pm 3.1x10^4$	$2.3x10^4 \pm 0.4x10^4$	$6.2x10^3 \pm 1.2x10^3$
	Tuff	9.2	−330	5:1	320±70	640±130	210±40
	Granodiorite	9.6	−470	5:1	47±13	790±190	$1.0x10^3 \pm 0.3x10^3$

Initial neptunium−237 concentration = 6.0 x 10^{-9}M

Errors quoted are 2σ and are based on counting statistics alone

Table 44

Actinium Sorption onto Bentonite at Room Temperature and 60°C under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−570	$5.4\text{x}10^{4}\pm0.2\text{x}10^{4}$	$5.8\text{x}10^{4}\pm0.2\text{x}10^{4}$	$9.4\text{x}10^{4}\pm0.3\text{x}10^{4}$
	10.1	−580	$3.4\text{x}10^{4}\pm0.1\text{x}10^{4}$	$5.9\text{x}10^{4}\pm0.2\text{x}10^{4}$	$1.3\text{x}10^{5}\pm0.1\text{x}10^{5}$
60°C	9.4	−500	$1.1\text{x}10^{4}\pm0.1\text{x}10^{4}$	$3.1\text{x}10^{4}\pm0.1\text{x}10^{4}$	$1.6\text{x}10^{5}\pm0.1\text{x}10^{5}$
	9.4	−510	$2.1\text{x}10^{3}\pm0.1\text{x}10^{3}$	$5.0\text{x}10^{4}\pm0.2\text{x}10^{4}$	$9.3\text{x}10^{4}\pm0.4\text{x}10^{4}$

Initial actinium-227 concentration = $2.2 \text{ x } 10^{-9}$M at room temperature and $2.4 \text{ x } 10^{-9}$M at 60°C

Errors quoted are 2σ and are based on counting statistics alone

Table 45

Actinium Sorption onto Tuff at Room Temperature and 60°C under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	9.4	−320	970 ± 40	$1.4\text{x}10^{4}\pm0.1\text{x}10^{4}$	$8.9\text{x}10^{4}\pm0.4\text{x}10^{4}$
	9.4	−320	$4.3\text{x}10^{3}\pm0.2\text{x}10^{3}$	$5.5\text{x}10^{3}\pm0.3\text{x}10^{3}$	$1.4\text{x}10^{4}\pm0.1\text{x}10^{4}$
60°C	9.4	−110	480+20	590 ± 30	$4.2\text{x}10^{3}\pm0.2\text{x}10^{3}$
	9.4	−110	700+30	890 ± 40	$7.1\text{x}10^{3}\pm0.3\text{x}10^{3}$

Initial actinium-227 concentration = $2.8 \text{ x } 10^{-9}$M at room temperature and $2.4 \text{ x } 10^{-9}$M at 60°C

Errors quoted are 2σ and are based on counting statistics alone

Table 46

Actinium Sorption onto Granodiorite at Room Temperature and 60°C under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−550	$2.0\text{x}10^{3}\pm0.1\text{x}10^{3}$	$3.9\text{x}10^{4}\pm0.1\text{x}10^{4}$	$4.8\text{x}10^{4}\pm0.2\text{x}10^{4}$
	10.1	−560	$1.9\text{x}10^{3}\pm0.1\text{x}10^{3}$	$1.9\text{x}10^{4}\pm0.1\text{x}10^{4}$	$3.6\text{x}10^{4}\pm0.1\text{x}10^{4}$
60°C	9.6	−570	150 ± 10	$1.5\text{x}10^{4}\pm0.1\text{x}10^{4}$	$4.0\text{x}10^{4}\pm0.2\text{x}10^{4}$
	9.6	−590	83 ± 3	$1.1\text{x}10^{4}\pm0.1\text{x}10^{4}$	$2.0\text{x}10^{4}\pm0.1\text{x}10^{4}$

Initial actinium-227 concentration = $1.4 \text{ x } 10^{-9}$M at room temperature and $2.8 \text{ x } 10^{-9}$M at 60°C

Errors quoted are 2σ and are based on counting statistics alone

Table 47

Actinium Remaining in Solution in the Absence of Rock

Temperature	Ac−227 Concentration in Solution after 4 Months/Bq cm^{-3}								
	Bentonite			Tuff			Granodiorite		
	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO
Room Temperature	30.15 (2.3%)	23.94 (1.8%)	4.29 (0.33%)	5.66 (0.33%)	3.36 (0.20%)	2.37 (0.14%)	94.48 (10.9%)	16.26 (1.9%)	9.28 (1.1%)
60℃	91.62 (6.3%)	40.33 (2.8%)	7.64 (0.52%)	181.88 (12.4%)	94.26 (6.4%)	6.4 (0.44%)	204.91 (11.9%)	103.14 (6.0%)	6.52 (0.38%)

For bentonite−equilibrated water, initial actinium−227 concentration = 2.2 x 10^{-9}M at room temperature and 2.4 x 10^{-9}M at 60℃

For granodiorite−equilibrated water, initial actinium−227 concentration = 1.4 x 10^{-9}M at room temperature and 2.8 x 10^{-9}M at 60℃

For tuff−equilibrated water, initial actinium−227 concentration = 2.8 x 10^{-9}M at room temperature and 2.4 x 10^{-9}M at 60℃

Table 48

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly−Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls*(%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Actinium	0.33	0.81	0.03	0.12	0.74	0.8

* Percentages are the average value for each duplicate pair

Table 49

Protactinium Sorption onto Bentonite at Room Temperature and 60℃ under Strongly−Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−330	$>2.1x10^5$	$>2.6x10^5$	$>3.5x10^5$
	10.1	−330	$>1.9x10^5$	$>1.9x10^5$	$>2.6x10^5$
60℃	9.4	−150	$7.6x10^3 \pm 0.5x10^3$	$8.1x10^3 \pm 0.6x10^3$	$>2.9x10^5$
	9.4	−150	$9.9x10^3 \pm 0.8x10^3$	$>3.2x10^5$	$>3.3x10^5$

Initial protactinium−233 concentration = 1.3 x 10^{-11}M

Errors quoted are 2σ and are based on counting statistics alone

Table 50

Protactinium Sorption onto Tuff at Room Temperature and 60°C under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	9.4	−180	$>1.2\times10^5$	$>1.9\times10^5$	$>2.1\times10^5$
	9.4	−180	$>1.6\times10^5$	$>2.1\times10^5$	$>1.2\times10^5$
60°C	9.2	−70	$2.9\times10^3\pm0.2\times10^3$	$9.4\times10^3\pm0.7\times10^3$	$>2.2\times10^5$
	9.2	−70	$2.7\times10^3\pm0.1\times10^3$	$8.2\times10^3\pm0.7\times10^3$	$1.2\times10^4\pm0.1\times10^4$

Initial protactinium-233 concentration = 3.8×10^{-11}M

Errors quoted are 2σ and are based on counting statistics alone

Table 51

Protactinium Sorption onto Granodiorite at Room Temperature and 60°C under Strongly-Reducing Conditions

Temperature	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})		
			Centrifuged	0.45μm	10000MWCO
Room Temperature	10.1	−480	$1.7\times10^3\pm0.1\times10^3$	$>1.6\times10^5$	$>3.0\times10^5$
	10.1	−480	750±40	$>1.4\times10^5$	$>2.1\times10^5$
60°C	9.6	−340	250±10	$2.0\times10^3\pm0.1\times10^3$	$>2.1\times10^5$
	9.6	−340	520±30	$7.8\times10^3\pm0.6\times10^3$	$>2.4\times10^5$

Initial protactinium-233 concentration = 3.8×10^{-11}M

Errors quoted are 2σ and are based on counting statistics alone

Table 52

Protactinium Remaining in Solution in the Absence of Rock

Temperature	Pa-233 Concentration in Solution after 1 Months/Bq cm^{-3}								
	Bentonite			Tuff			Granodiorite		
	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO	Centrifuged	0.45μm	10000MWCO
Room Temperature	181.6 (7.9%)	49 (2.1%)	<0.14 (<0.006%)	220 (3.2%)	4.7 (0.07%)	<0.38 (<0.006%)	31.6 (0.46%)	<0.26 (<0.004%)	<0.12 (<0.002%)
60°C	666 (29%)	224 (9.8%)	<0.15 (<0.006%)	1290 (19%)	210 (3.1%)	4.34 (0.06%)	167 (2.4%)	67.6 (0.98%)	8.38 (0.12%)

Initial protactinium-233 concentration = 1.3×10^{-11}M (2.28×10^3 Bq cm^{-3}) in the case of bentonite and 3.8×10^{-11}M (6.79×10^3 Bq cm^{-3}) in the case of granodiorite and tuff

Table 53

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly-Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls*(%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Protactinium	0.71	1.41	0.35	0.48	2.68	1.67

* Percentages are the average value for each duplicate pair

Table 54

Polonium Sorption onto Bentonite, Granodiorite and Tuff at Room Temperature under Strongly-Reducing Conditions

Geological material	Final pH	Final Eh/mV vs SHE	R_D(cm^3 g^{-1})*		
			Centrifuged	0.45μm	10000MWCO
Bentonite	10.1	−230	$2.7\text{x}10^4 \pm 0.1\text{x}10^4$	$5.5\text{x}10^4 \pm 0.3\text{x}10^4$	$8.2\text{x}10^4 \pm 0.5\text{x}10^4$
	10.1	−280	$3.2\text{x}10^4 \pm 0.1\text{x}10^4$	$7.5\text{x}10^4 \pm 0.4\text{x}10^4$	$8.5\text{x}10^4 \pm 0.5\text{x}10^4$
Granodiorite	10.1	−500	$1.0\text{x}10^2 \pm 0.02\text{x}10^2$	$2.1\text{x}10^4 \pm 0.2\text{x}10^4$	$3.2\text{x}10^4 \pm 0.4\text{x}10^4$
	10.1	−590	$2.3\text{x}10^2 \pm 0.1\text{x}10^2$	$4.0\text{x}10^3 \pm 0.2\text{x}10^3$	$1.7\text{x}10^4 \pm 0.1\text{x}10^4$
Tuff	9.4	−350	$1.8\text{x}10^3 \pm 0.04\text{x}10^3$	$5.1\text{x}10^3 \pm 0.2\text{x}10^3$	$3.9\text{x}10^4 \pm 0.4\text{x}10^4$
	9.4	−340	$1.1\text{x}10^3 \pm 0.03\text{x}10^3$	$3.7\text{x}10^3 \pm 0.1\text{x}10^3$	$3.4\text{x}10^4 \pm 0.3\text{x}10^4$

Initial polonium concentration = $1.1 \text{ x } 10^{-11}$M for bentonite, $5.5 \text{ x } 10^{-12}$M for granodiorite and $7.7 \text{ x } 10^{-12}$M for tuff

Water-to-rock ratio 20:1 for bentonite, and 5:1 for granodiorite and tuff

* Final concentration used in the calculation of R_D values was decay-corrected to the starting data. Errors quoted are 2σ and are based on counting statistics alone

Table 55

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly-Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls*(%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Polonium	0.1	N.S.	0.04	N.S.	0.06	N.S.

* Percentages are the mean value for each duplicate experiment

N.S. = Not studied

Table 56

Plutonium Sorption onto Bentonite , Granodiorite and Tuff at 60℃ under Strongly–Reducing Conditions

Geological material	Final pH	Final Eh/mV vs SHE	$R_D(cm^3\ g^{-1})$		
			Centrifuged	0.45μm	10000MWCO
Bentonite	9.4	–410	$1.3\times10^{4}\pm0.3\times10^{4}$	$1.1\times10^{4}\pm0.1\times10^{4}$	$8.7\times10^{4}\pm1.4\times10^{4}$
	9.4	–410	$1.6\times10^{4}\pm0.3\times10^{4}$	$2.1\times10^{4}\pm0.3\times10^{4}$	$2.7\times10^{4}\pm0.3\times10^{4}$
Tuff	9.2	–520	$8.4\times10^{2}\pm1.0\times10^{2}$	$1.4\times10^{3}\pm0.2\times10^{3}$	$6.7\times10^{3}\pm0.39\times10^{3}$
	9.2	–530	$7.6\times10^{2}\pm1.0\times10^{2}$	$8.3\times10^{2}\pm2.0\times10^{2}$	$1.2\times10^{4}\pm0.3\times10^{4}$
Granodiorite	9.6	–580	$1.7\times10^{2}\pm0.2\times10^{2}$	$1.2\times10^{3}\pm0.2\times10^{3}$	$5.7\times10^{4}\pm0.8\times10^{4}$
	9.6	–590	$2.2\times10^{2}\pm0.3\times10^{2}$	$1.3\times10^{3}\pm0.2\times10^{3}$	$9.8\times10^{3}\pm1.3\times10^{3}$

Initial plutonium concentration = 4.3×10^{-11}M for bentonite and tuff, and 3.8×10^{-11}M for granodiorite

Water–to–rock ratio 20:1 for bentonite, and 5:1 for granodiorite and tuff

Errors quoted are 2σ and are based on counting statistics alone

Table 57

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly–Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls*(%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Plutonium	N.S.	2.2	N.S.	1.4	N.S.	5.7

* Percentages are the mean value for each duplicate experiment

N.S. = Not studied

Table 58

Americium Sorption onto Bentonite, Granodiorite and Tuff at 60℃ under Strongly–Reducing Conditions

Geological material	Final pH	Final Eh/mV vs SHE	$R_D(cm^3\ g^{-1})$		
			Centrifuged	0.45μm	10000MWCO
Bentonite	9.4	–350	$1.2\times10^{4}\pm0.2\times10^{4}$	$1.0\times10^{5}\pm0.3\times10^{5}$	$1.1\times10^{5}\pm0.2\times10^{5}$
	9.4	–360	$3.0\times10^{4}\pm0.3\times10^{4}$	$4.6\times10^{4}\pm1.4\times10^{4}$	$3.0\times10^{4}\pm2.5\times10^{4}$
Tuff	9.2	–390	$3.5\times10^{3}\pm0.6\times10^{3}$	$6.8\times10^{3}\pm0.9\times10^{3}$	$2.3\times10^{4}\pm0.3\times10^{4}$
	9.2	–390	$3.6\times10^{3}\pm0.6\times10^{3}$	$5.8\times10^{3}\pm3.3\times10^{3}$	$2.2\times10^{4}\pm0.3\times10^{4}$
Granodiorite	9.6	–510	$1.5\times10^{2}\pm0.2\times10^{2}$	$3.3\times10^{3}\pm0.5\times10^{3}$	$2.0\times10^{4}\pm0.5\times10^{4}$
	9.6	–520	$1.6\times10^{2}\pm0.2\times10^{2}$	$2.7\times10^{3}\pm0.4\times10^{3}$	$6.2\times10^{4}\pm1.2\times10^{4}$

Initial americium concentration = 1.2×10^{-10}M for bentonite and granodiorite, and 1.0×10^{-10}M for tuff

Water–to–rock ratio 20:1 for bentonite, and 5:1 for granodiorite and tuff

Errors quoted are 2σ and are based on counting statistics alone

Table 59

Results of Analysis of Vessel Walls after Batch Sorption Experiments at Room Temperature and 60℃ under Strongly-Reducing Conditions

Radioelement	Amount Sorbed on Vessel Walls*(%)					
	Bentonite		Tuff		Granodiorite	
	Room Temperature	60℃	Room Temperature	60℃	Room Temperature	60℃
Americium	N.S.	2.3	N.S.	0.56	N.S.	3.4

* Percentages are the mean value for each duplicate experiment

N.S. = Not studied

Table 60

Predicted Speciation of Uranium in Bentonite-, Tuff- and Granodiorite-Equilibrated De-Ionised Water

Bentonite			Tuff			Granodiorite		
Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation	
pH = 10.1 Eh = +200mV	$UO_2(CO_3)_3^{4-}$	90.4%	pH = 9.4 Eh = +200mV	$UO_2(CO_3)_3^{4-}$	85.0%	pH = 10.1 Eh = +200mV	$(UO_2)_2(OH)_3CO_3^-$	46.0%
	$UO_2(CO_3)_2^{2-}$	6.9%					$UO_2(CO_3)_3^{4-}$	40.0%
	$(UO_2)_2(OH)_3CO_3^-$	2.4%		$UO_2(CO_3)_2^{2-}$	14.0%		$UO_2(CO_3)_2^{2-}$	9.5%
	$UO_2(OH)_2$	0.3%		$(UO_2)_2(OH)_3CO_3^-$	0.5%		$UO_2(OH)_2$	4.5%
pH = 10.1 Eh = -400mV	$U(OH)_4$	97.0%	pH = 9.4 Eh = -400mV	$U(OH)_4$	>99.9%	pH = 10.1 Eh = -400mV	$U(OH)_4$	~99.9%
	$UO_2(CO_3)_3^{4-}$	2.8%						
	$UO_2(CO_3)_2^{2-}$	0.2%					$UO_2(CO_3)_3^{4-}$	~0.1%

Table 61

Predicted Speciation of Uranium in Bentonite-, Tuff- and Granodiorite-Equilibrated Seawater

Bentonite			Tuff			Granodiorite		
Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation	
pH = 8.0 Eh = +200mV	$UO_2(CO_3)_3^{4-}$	88.9%	pH = 8.1 Eh = +200mV	$UO_2(CO_3)_3^{4-}$	70.0%	pH = 8.4 Eh = +200mV	$UO_2(CO_3)_3^{4-}$	96.0%
				$UO_2(CO_3)_2^{2-}$	27.0%			
	$UO_2(CO_3)_2^{2-}$	11.0%		$(UO_2)_2(OH)_3CO_3^-$	2.0%		$UO_2(CO_3)_2^{2-}$	4.0%
pH = 8.0 Eh = -350mV	$U(OH)_4$	>99.9%	pH = 8.1 Eh = -350mV	$U(OH)_4$	>99.0%	pH = 8.4 Eh = -350mV	$U(OH)_4$	93.0%
							$UO_2(CO_3)_3^{4-}$	7.0%

Table 62

Predicted Speciation of Uranium in Bentonite–Equilibrated Seawater and De–Ionised Water at 60℃

Bentonite–Equilibrated Seawater			Bentonite–Equilibrated De–Ionised Water		
Experimental Condition	Predicted Uranium Speciation		Experimental Condition	Predicted Uranium Speciation	
pH = 8.1 Eh = +200mV	$UO_2(CO_3)_2^{2-}$	65.8%	pH = 9.4 Eh = +275mV	$UO_2(CO_3)_2^{2-}$	59.1%
	$UO_2(CO_3)_3^{4-}$	29.4%		$UO_2(CO_3)_3^{4-}$	35.7%
	$UO_2(OH)_2$	4.8%		$UO_2(OH)_2$	5.1%
pH = 8.1 Eh = −365mV	$U(OH)_4$	99.9%	pH = 9.4 Eh = −405mV	$U(OH)_4$	97.9%
				$UO_2(CO_3)_2^{2-}$	1.3%
	$UO_2(CO_3)_2^{2-}$	0.1%		$UO_2(CO_3)_3^{4-}$	0.8%

Table 63

Predicted Speciation of Technetium in Bentonite–, Tuff– and Granodiorite–Equilibrated De–Ionised Water

Bentonite			Tuff			Granodiorite		
Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation	
pH = 10.1 Eh = +200mV	TcO_4^-	>99.9%	pH = 9.4 Eh = +200mV	TcO_4^-	>99.0%	pH = 10.1 Eh = +200mV	TcO_4^-	>99.0%
pH = 10.1 Eh = −400mV	$TcO(OH)_2$	99.0%	pH = 9.4 Eh = −400mV	$TcO(OH)_2$	>99.0%	pH = 10.1 Eh = −400mV	$TcO(OH)_2$	>99.0%

Table 64

Predicted Speciation of Technetium in Bentonite–, Tuff– and Granodiorite–Equilibrated Seawater

Bentonite			Granodiorite			Tuff		
Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation	
pH = 8.0 Eh = +200mV	TcO_4^-	>99.0%	pH = 8.1 Eh = +200mV	TcO_4^-	>99.0%	pH = 8.4 Eh = +200mV	TcO_4^-	>99.0%
pH = 8.0 Eh = −350mV	$TcO(OH)_2$	99.0%	pH = 8.1 Eh = −350mV	$TcO(OH)_2$	>99.0%	pH = 8.4 Eh = −350mV	$TcO(OH)_2$	99.0%

Table 65

Thermodynamic Equilibrium Constants for Aqueous and Solid Cm Species

(Given in Terms of HATCHES Master Species, Corrected to Zero Ionic Strength)

Aqueous Species	HATCHS NEA8	Amended HATCHES	Other data
CmF^{2+}	4.13[23]	4.13[23]	3.41*[28], 4.30**[28]
CmF_2^+	7.50[23]	7.50[23]	7.60**[28]
CmF_3	10.7[23]	10.7[23]	10.90**[28]
$CmCl^{2+}$	0.98[23]	0.98[23]	
$CmCl_2^+$	−0.05**[23]	−0.05**[23]	
$CmNO_3^{2+}$	1.13*[23]	1.13*[23]	
$Cm(NO_3)_2^+$	1.4*[23]	1.4*[23]	
$CmSO_4^+$	2.92*[23]	2.92*[23]	3.47[28], 3.73[30], 4.94*[28], 3.66*[28], 3.60**[28], 2.12**[28]
$Cm(SO_4)_2^-$	4.0*[23]	4.0*[23]	4.84[28], 4.46*[28], 8.86*[28], 4.30**[28], 5.60**[28]
Citrate 1:1	12.58[23]	12.58[23]	
Citrate 1:2	13.82[23]	13.82[23]	
Oxalate 1:1	7.45[23]	7.45[23]	
Oxalate 1:2	12.14[23]	12.14[23]	
EDTA 1:1	18.9[23]	18.9[23]	
Cm^{4+}	−52.4[23]	−52.4[23]	
$CmOH^{2+}$	−5.3[23]	−7.56[29]	−5.46[28], −4.98[28], −3.20[28], −5.50[28], −5.60**[28], −6.69[27]
$Cm(OH)_2^+$		−15.7[29]	−9.00**[28], −14.87[27]
$CmCO_3^+$		7.93[27]	
$CmH_2PO_4^{2+}$		21.95*[28]	
$Cm(H_2PO_4)_2^+$		42.7*[28]	
$Cm(H_2PO_4)_3$		64.26*[28]	
$Cm(H_2PO_4)_4^-$		84.4*[28]	
$CmPO_4$		20.2*[28]	
$Cm(PO_4)_2^{3-}$		36.8*[28]	
Solid			
CmO_2	46.2[24]	46.2[24]	
$CmOHCO_3$	−8.5[25]	−7.03[32]	
$Cm(OH)_3$	17.5[26]	17.5[26]	24.77[23]
Cm2O3***		53.94[23]	
CmOCl		9.33[23]	
$CmCl_3$		16.2[23]	15.24[28]

* Value taken from experiment where original ionic strength I>0.5mol dm^{-3}. The use of the truncated Davies correction to allow for ionic strength effects may introduce error in these values.

** Value taken from experiment where original ionic strength is not given.

*** Solid only forms at high temperature.

Table 66

Comparison of the Thermodynamic Equilibrium Constants for Aqueous and Solid Cm and Am Species (Given in Terms of HATCHES Master Species, Corrected to Zero Ionic Strength)

Aqueous	Cm		Am
	HATCHS NEA8	Amended HATCHES	HATCHS NEA8
OH−	−5.3[23]	−7.56[29]	−8.0[31]
		−15.7[29]	−16.9[31]
			−29[31]
Solid			
$X(OH)_3$	17.5[26]	17.5[26]	17.5[31]
$XOHCO_3$	−8.5[25]	−7.03[32]	−7.03[32]
XO_3	46.2[24]	46.2[24]	33.9[31]

X : Cm or Am

Table 67

Predicted Speciation of Neptunium in Bentonite−, Tuff− and Granodiorite−Equilibrated De−Ionised Water at Room Temperature under Experimental Conditions

Bentonite			Tuff			Granodiorite		
Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation		Experimental Condition	Predicted Speciation	
pH = 10.4 Eh = −440mV	$Np(OH)_4$	>99.9%	pH = 9.4 Eh = −310mV	$Np(OH)_4$	>99.9%	pH = 10.1 Eh = −460mV	$Np(OH)_4$	>99.9%
pH = 10.1 Eh = +320mV	$NpO_2CO_3^-$	90.7%	pH = 9.4 Eh = +375mV	$NpO_2CO_3^-$	84.0%	pH = 10.1 Eh = +260mV	NpO_2^+	94.5%
	NpO_2^+	6.2%		NpO_2^+	14.8%			
	$NpO_2(CO_3)_2^{3-}$	2.7%		$NpO_2(CO_3)_2^{3-}$	1.1%		NpO_2OH	4.5%

Table 68

Comparison of HATCHES and Literature Data for Thermodynamic Equilibrium Constants of Actinium Species

Aqueous Species	HATCHES NEA9	Amended HATCHES	Other data(literature reference)
$Ac(OH)^{2+}$	(<) −10.4[13]	−10.4	−8.07[30]
$AcNO_3^{2+}$		0.9	0.9[35]
$Ac(NO_3)_2^+$		1.34	1.34[35]
$AcH_2PO_4^{2+}$		21.94	21.94[30][35]
$AcCO_3^+$		5.91*	5.91*[33]
$Ac(CO_3)_2^-$		9.14*	9.14*[33]
$AcSO_4^+$		3.36	3.36[30][34], 2.81[35]
$Ac(SO_4)_2^-$		4.78	4.78[30][34], 3.99[35]
AcF^{2+}		3.52	3.52[30][8][35]
AcF_2^+		6.56	6.56[30][8][35]
AcF_3		9.51	9.51[30][8][35]
$AcCl^{2+}$		0.76	0.76[30], 1.24[36], 0.70[35]
$AcCl_2^+$		0.3	0.30[30], 1.65[36], 0.74[35]
$AcCl_3$		0.35	0.35[30]
$AcBr^{2+}$		0.6	1.22[36], 0.60[35]
$AcBr_2^+$		0.84	1.63[36], 0.84[35]
$AcOX^+$		5.64	6.08[34], 5.64[38]
$Ac(OX)_2^-$		8.79	10.14[34], 8.79[38]
Solid			
$Ac(OH)_3$	21.1[20]	21.1	fresh:23.3[13][39] ; aged:21.1[13][39]

1)All data are expressed as log(equilibrium constant) at 25℃ for the formation of aqueous complexes from HATCHES Master Species or for the dissolution of solids to give HATCHES Master Species. The Master Species are : Ac^{3+}, H^+, H_2O, NO_3^-, PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Br^- and OX^{2-}, where OX represents the oxalate ligand.

2)All data have been corrected to zero ionic strength by applying the Truncated Davies approach.

3)Values marked ＊ have been estimated.

Table 69

Comparison of HATCHES and Literature Data for Thermodynamic Equilibrium Constants of Protactinium Species

Aqueous Species	HATCHES Nirex91	Amended HATCHES	Other data(literature reference)
Pa(IV)			
$Pa(OH)^{3+}$	0.84[13]	0.84	1.11[35], 0.8[35], −0.5*[40]
$Pa(OH)_2^{2+}$	−0.02[13]	−0.02	1.72[35], 0.0[35]
$Pa(OH)_3^+$	−1.5[13]	−1.5	1.11[35]
$Pa(OH)_4$		1.92	−1.92[35], −12*[40]
$PaCO_3^{2+}$		11*	11*[40]
$Pa(CO_3)_5^{6-}$		34*	34*[40]
$Pa(OH)_3CO_3^-$		−1*	−1*[40]
$PaSO_4^{2+}$		5.22	5.22[39]
$Pa(SO_4)_2$		8.3	8.30[39]
PaF^{3+}		5.8	9.10[35], 5.80[39]
PaF_2^{2+}		10.14	16.74[35], 10.14[39]
$PaCl^{3+}$		1.07	10.7[35]
Pa(V)			
PaO_2^+	1.90[36]	2.36	2.36[13]
$PaO(OH)^{2+}$	1.40[13]	1.86	1.86[41]
$PaO_2(OH)$	−2.60[13]	−2.14	−2.14[13]
$PaOSO_4^+$		5.68	5.68[39]
$PaO(SO_4)_2^-$		8.89	8.89[39]
Solid			
PaO_2	0.6[13]	4	4[40]
Pa_2O_5	<−8.72[13]	−8.72	<−8.72[13] but <−4.0 in terms of PaO_2^+

1)All data are expressed as log(equilibrium constant) at 25℃ for the formation of aqueous complexes from HATCHES Master Species or for the dissolution of solids to give HATCHES Master Species. The Master Species are : Pa^{4+}, H^+, H_2O, e^-, CO_3^{2-}, SO_4^{2-}, F^- and Cl^-.

2)All data have been corrected to zero ionic strength by applying the Truncated Davies approach.

3)Values marked * have been estimated.

Table 70

Summary of Redox Conditions for Pa Calculations

Water Sample	pH(expt)	Eh(expt)/mV	pe(expt)	pH+pe*
Bentonite	10.1	−330	−5.6	4.5
Tuff	9.4	−180	−3	6.4
Granodiorite	10.1	−480	−8.1	2
Llower stability boundary	−	−	−	0

* Stepped pH calculations were performed whilst keeping the appropriate pH + pe value constant.

Table 71

Summary of Polonium Redox Reactions

Reaction		Eh/V	log *K*	log *K*(I=0)[a]
1) $Po^{4+} + 4e^{-} = Po(s)$	a)Bagnall and Freeman[47] in HNO_3	0.76	51.4	53.5
	b)NBS[44], Bard et al.[43]		51.3	
2) PoCl62− + 4e− = Po(s) + 6Cl−	a)Bagnall and Freeman[47]	0.55	37.2	37.5
3) $PoCl_6^{2-} + 2e^{-} = PoCl_4^{2-} + 2Cl^{-}$	a)Bagnall and Freeman[47]	0.72	24.3	
	b)Haïssinsky and Pluchet[48]	0.36	12.2	
	c)Eichelberger et al.[49]	0.71	24.0	
4) $PoCl_4^{2-} + 2e^{-} = Po(s) + 4Cl^{-}$	a)Bagnall and Freeman[47] b	0.38	12.8	12.8
	b)Haissinsky and Pluchet[48] b	0.73	24.7	
	c)Eichelberger et al.[49]	0.51	17.2	
5) $Po^{2+} + 2H^{+} + 4e^{-} = H_2Po(g)$	a)Charlot et al.[46] c	<−1	<−33.8	−33.8
6) $Po^{2+} + 2e^{-} = Po(s)$	a)Charlot et al.[46] c	∽0.6	∽20.3	
	b)NBS[44], Bard et al.[43]		12.4	12.4
7) $PoO_2(s) + 4H^{+} + 2e^{-} = Po^{2+} + 2H_2O$	a)Charlot et al.[46] c	0.8	27.0	27.0
8) $Po(OH)_2^{4+} + 2H^{+} + 2e^{-} = Po^{4+} + 2H_2O$	a)NBS[44], Bard et al.[43]		51.9	51.9

Values in italics have been calculated from values of free energy of formation of the species in the given reaction. The original sources of these data are not given in the references quoted.

a : Corrected to zero ionic strength using the truncated Davies method.

b : Values estimated from data for reactions (2) and (3).

c : Quoted as an estimated value in Charlot et al.[46] compilation.

Table 72

Summary of Thermodynamic Data for Polonium Using in Calculations

Equilibrium	log *K* (I=0)[a]	Reference or calculated value[b]
Aqueous		
$Po^{4+} + 2e^{-} = Po^{2+}$	41.1	reactions)1a and 6)a
$Po^{4+} + 4Cl^{-} + 2e^{-} = PoCl_4^{2-}$	40.7	reactions 1)a and 4)a
$Po^{4+} + H_2O = Po(OH)^{3+} + H^{+}$	−0.46	42
$Po^{4+} + 2H_2O = Po(OH)_2^{2+} + 2H^{+}$	−1.13	42
$Po^{4+} + 3H_2O = Po(OH)_3^{+} + 3H^{+}$	−1.78	42
$Po^{4+} + 4H_2O = Po(OH)_4 + 4H^{+}$	−3.52	42
[c] $Po^{4+} + 3H_2O = PoO_3^{2-} + 6H^{+}$	0.78	46
$Po^{4+} + Cl^{-} = PoCl^{3+}$	3.63	42
$Po^{4+} + 2Cl^{-} = PoCl_2^{2+}$	6.68	42
$Po^{4+} + 3Cl^{-} = PoCl_3^{+}$	9.29	42
$Po^{4+} + 4Cl^{-} = PoCl_4$	11.53	42
$Po^{4+} + 5Cl^{-} = PoCl_5^{-}$	13.28	42
$Po^{4+} + 6Cl^{-} = PoCl_6^{2-}$	14.73	42
$Po^{4+} + NO_3^{-} = PoNO_3^{3+}$	1.63	33
$Po^{4+} + 2NO_3^{-} = Po(NO_3)_2^{2+}$	3.03	33
$Po^{4+} + 3NO_3^{-} = Po(NO_3)_3^{+}$	3.71	33
$Po^{4+} + SO_4^{2-} = PoSO_4^{2+}$	3.64	33
[c] $Po^{4+} + 2H_2O = Po(OH)_2^{4+} + 2H^{+} + 2e^{-}$	51.1	46
Solids		
$Po(s) = Po^{4+} + 4e^{-}$	−53.5	48
$PoS(s) = Po^{2+} + S_2^{-}$	−26.9	45
$Po(OH)_4(s) + 4H^{+} = Po^{4+} + 4H_2O$	19.6	45
[c] $PoO_2(a) + 4H^{+} = Po^{4+} + 2H_2O$(case a)	−128.0	44
$PoO_2(b) + 4H^{+} = Po^{4+} + 2H_2O$ (case b)	−6.2	reaction 1)a), 6)a), 7)a)
$PoO_2(c) + 4H^{+} = Po^{4+} + 2H_2O$ (case c)	−11.9	reaction 1)b), 6)a), 7)a)
$PoO_3(s) + 4H^{+} = Po(OH)_2^{4+} + H_2O$	100.2	44
Gas		
$H_2Po(g) = Po_{2+} + 2H^{+} + 4e^{-}$	>33.8	47

a : Corrected to zero ionic strength using the truncated Davies method.

b : Calculated values are based on data for reactions given in Table 71.

c : Species removed from calculations. Using these reported values gave results that were very inconsistent with reported experimental data.

Table 73

Predicted Speciation of Plutonium in Bentonite–, Tuff– and Granodiorite–Equilibrated De–Ionised waters at Room Temperature under Strongly–Reducing Conditions

Equilibrated Water	Eh/mV	pH	Predicted Speciation	
Bentonite	−440	10.4	$Pu(CO_3)_3^{2-}$	80.2%
			$Pu(CO_3)_4^{4-}$	12.0%
			$Pu(OH)_4$	7.3%
			$Pu(OH)_3$	0.2%
Tuff	−310	9.4	$Pu(CO_3)_3^{2-}$	93.3%
			$Pu(CO_3)_4^{4-}$	6.6%
Granodiorite	−460	10.1	$Pu(OH)_4$	91.1%
			$Pu(OH)_3$	4.7%
			$Pu(OH)_4^-$	1.9%
			$Pu(OH)_2^+$	1.2%

Table 74

Predicted Speciation of Americium in Bentonite–, Tuff– and Granodiorite–Equilibrated De–Ionised waters at Room Temperature and 60℃ under Strongly–Reducing Conditions

a) Room temperature

Equilibrated Water	Eh/mV	pH	Predicted Speciation	
Bentonite	−440	10.1	$Am(OH)_2^+$	92.5%
			$Am(CO_3)_2^-$	3.1%
			$Am(OH)_3$	2.8%
			$AmCO_3^+$	0.7%
			$Am(CO_3)_3^{3-}$	0.6%
			$AmOH^{2+}$	0.4%
Tuff	−310	9.4	$Am(OH)_2^+$	80.7%
			$Am(CO_3)_2^-$	10.4%
			$AmCO_3^+$	5.8%
			$AmOH^{2+}$	2.0%
			$Am(CO_3)_3^{3-}$	0.9%
			$Am(OH)_3$	0.5%
Granodiorite	−460	10.1	$Am(OH)_2^+$	96.8%
			$Am(OH)_3$	2.9%
			$AmOH^{2+}$	0.4%

b) 60℃

Equilibrated Water	Eh/mV	pH	Predicted Speciation	
Bentonite	−355	9.4	$Am(OH)_2^+$	95.1%
			$Am(CO_3)_2^-$	1.2%
			$Am(OH)_3$	2.0%
			$AmCO_3^+$	0.6%
			$Am(CO_3)_3^{3-}$	0.1%
			$AmOH^{2+}$	1.0%
Tuff	−515	9.2	$Am(OH)_2^+$	91.5%
			$Am(CO_3)_2^-$	3.8%
			$AmCO_3^+$	1.7%
			$AmOH^{2+}$	1.5%
			$Am(CO_3)_3^{3-}$	0.2%
			$Am(OH)_3$	1.2%
Granodiorite	−390	9.6	$Am(OH)_2^+$	96.0%
			$Am(OH)_3$	3.3%
			$AmOH^{2+}$	0.6%

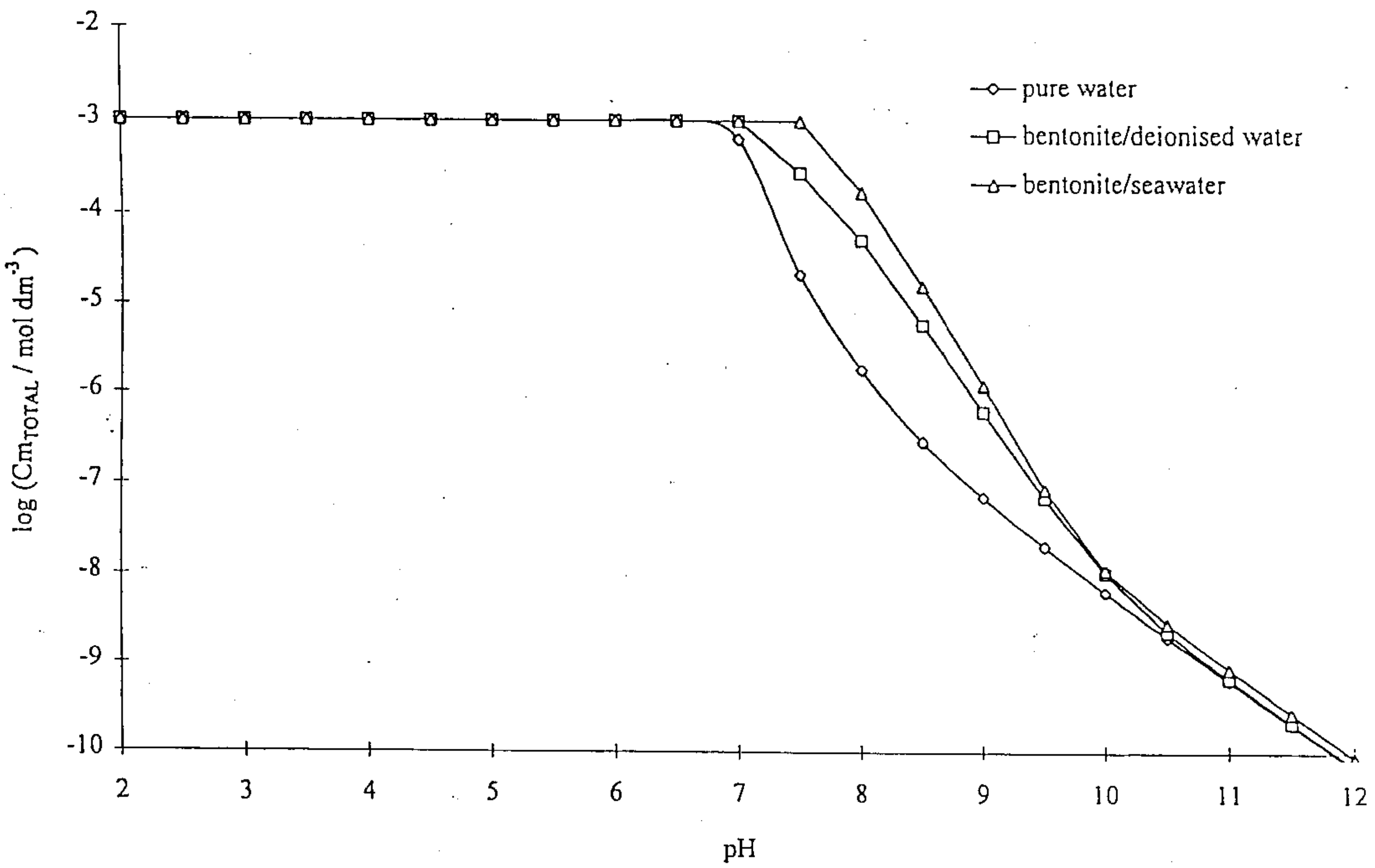

Figure 1

Predicted Solubility of Cm(OH)$_3$(s) at 25°C(Water compositions from Table 4, CmOHCO$_3$(s) not included)

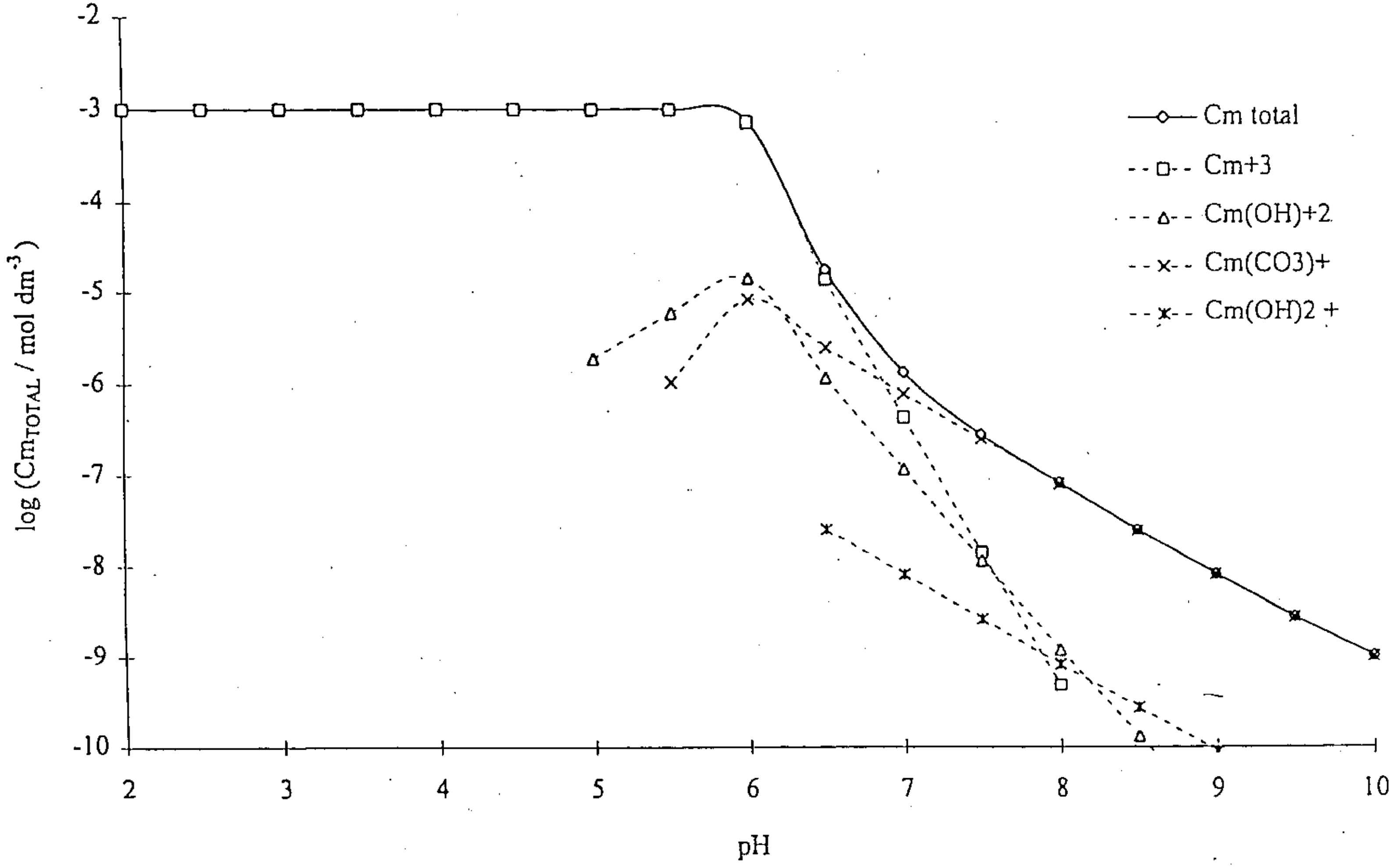

Figure 2
Predicted Solubility and Speciation of $CmOHCO_3(s)$ in Pure Water at 25℃ Equilibrated with Atmospheric $CO_2(g)$

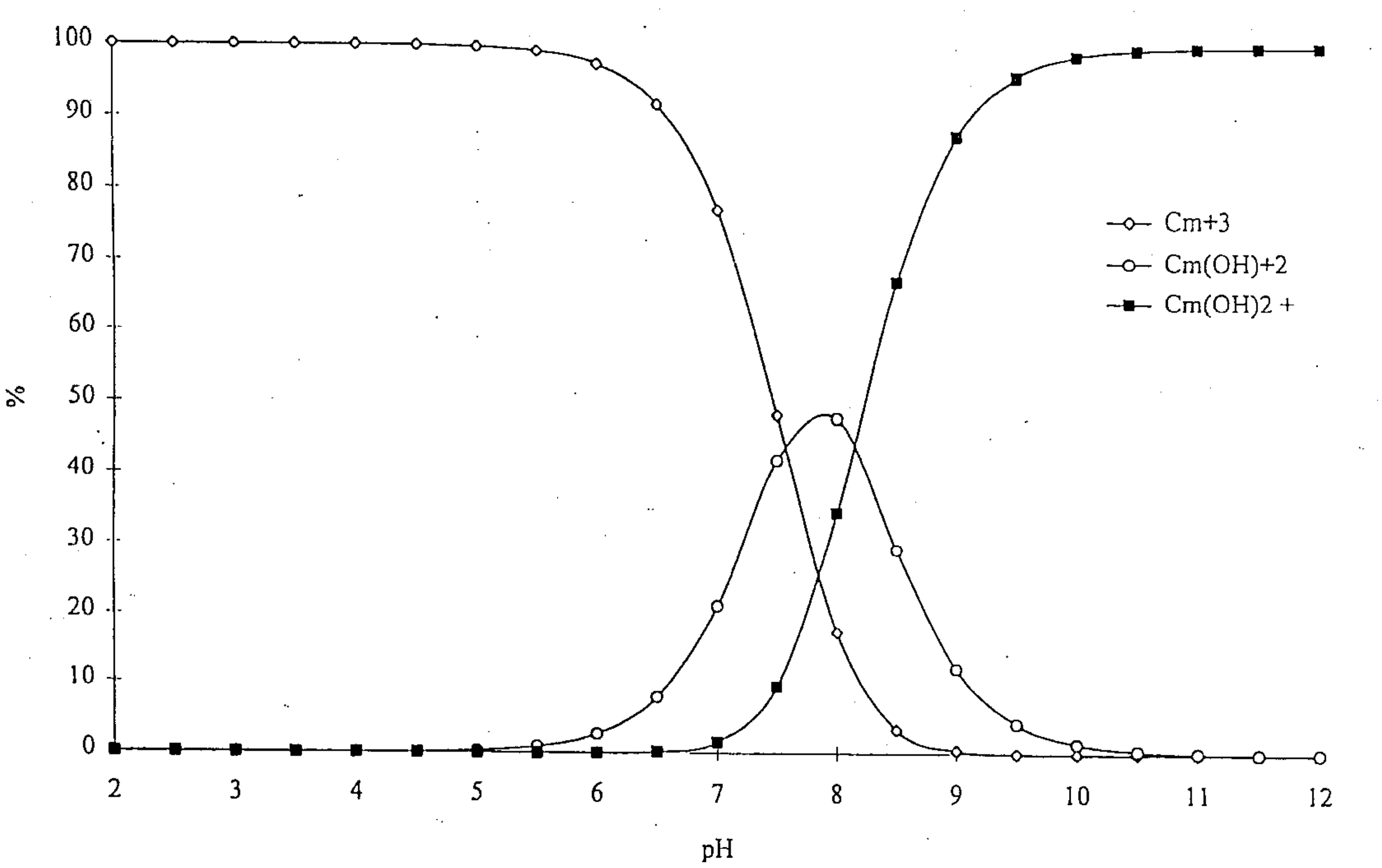

Figure 3
Predicted Speciation of 6 x 10^{-9} mol dm^{-3} Curium in Pure Water (25°C)

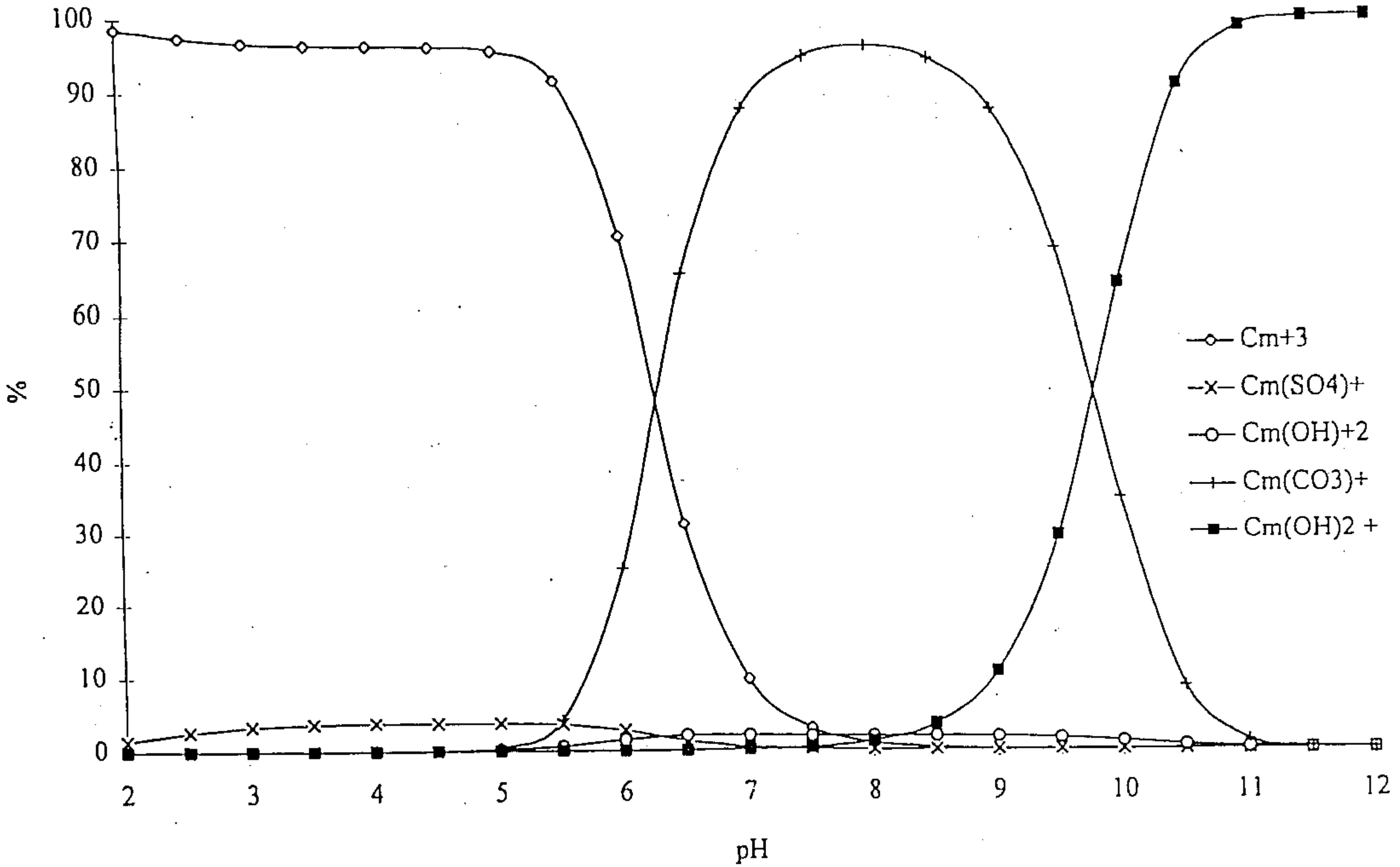

Figure 4
Predicted Speciation of 6 x 10^{-9} mol dm^{-3} Curium in Bentonite Equilibrated De-ionised Water (25°C)

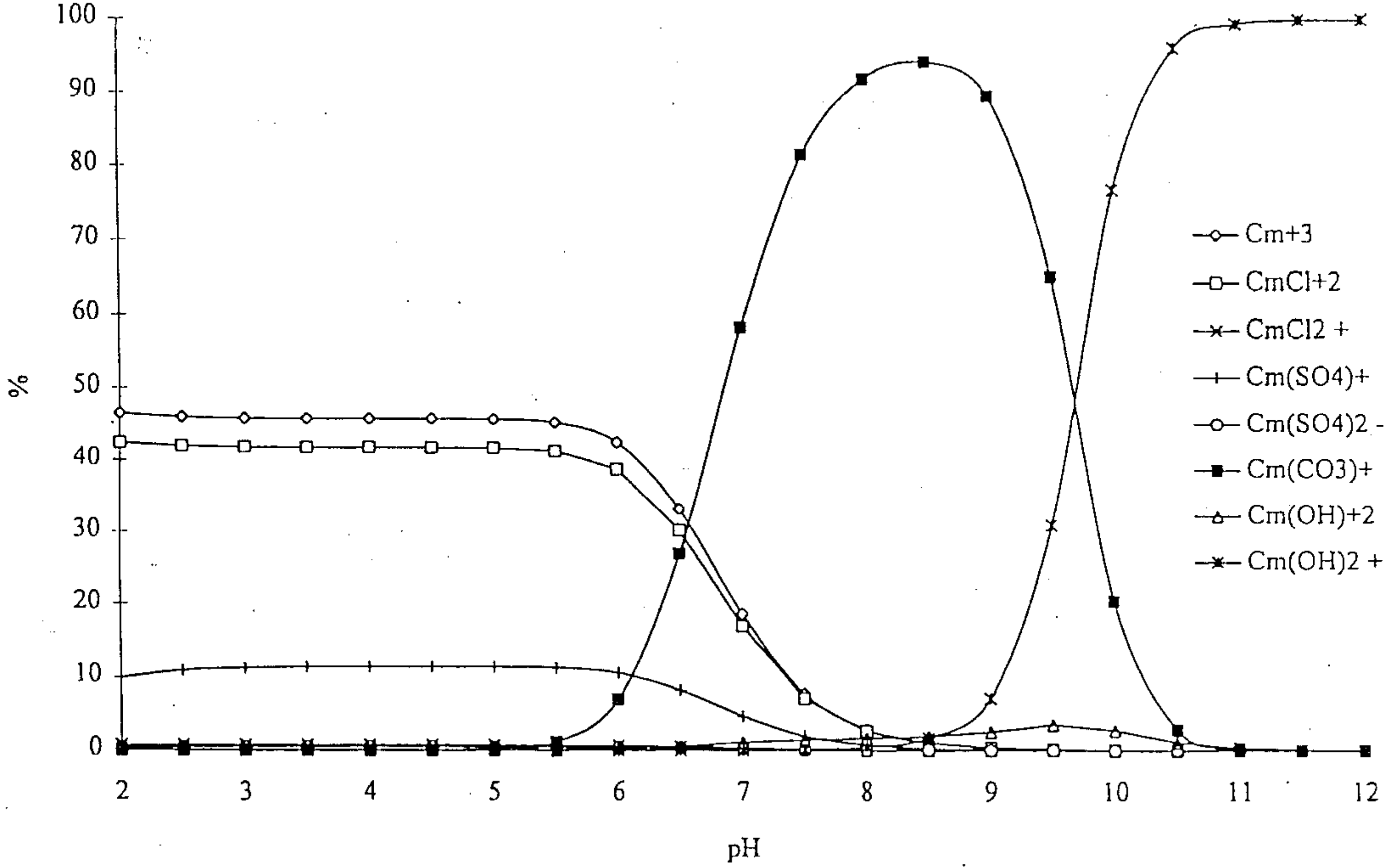

Figure 5
Predicted Speciation of 6 x 10^{-9} mol dm^{-3} Curium in Bentonite Equilibrated Seawater (25°C)

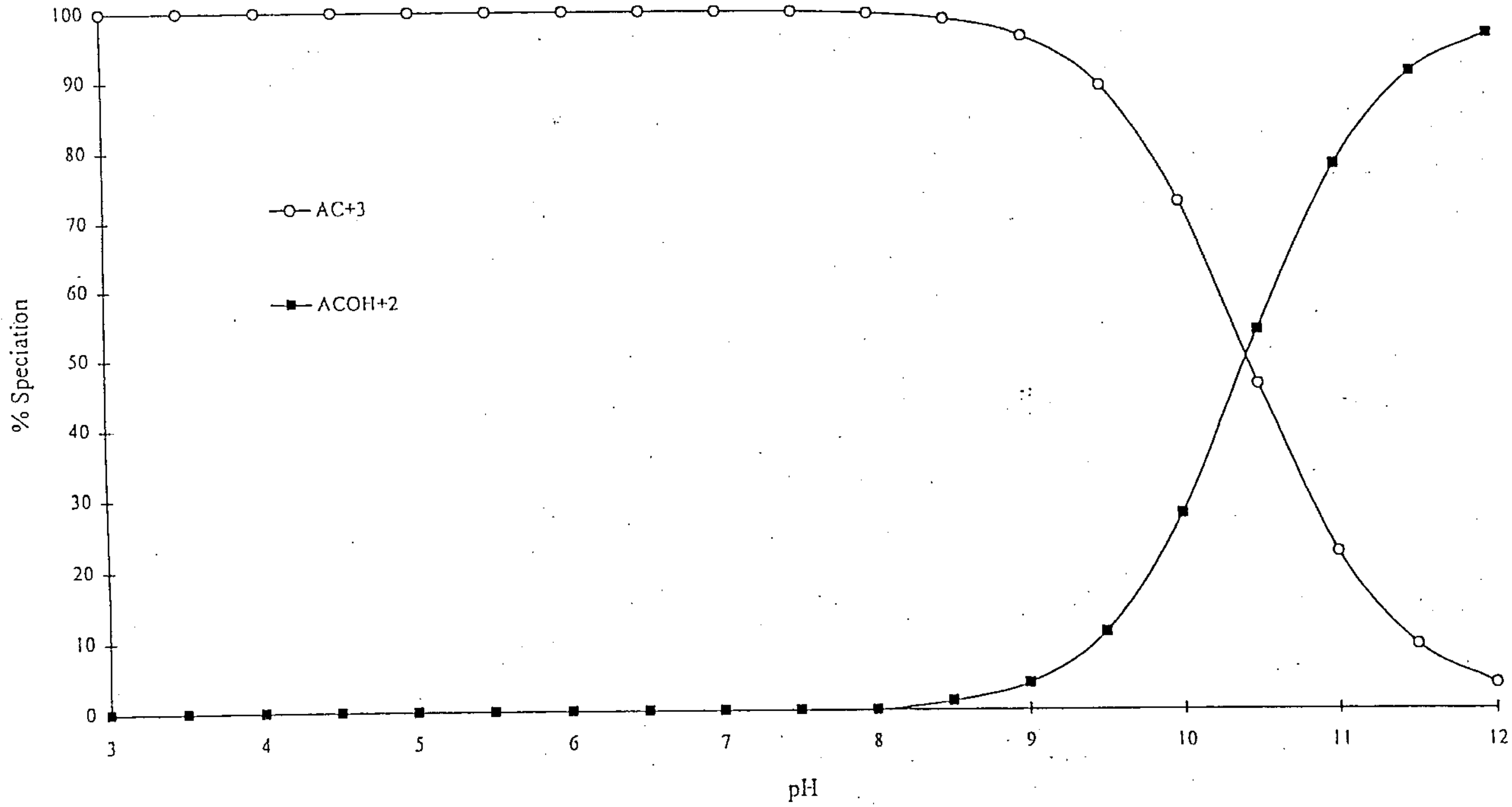

Figure 6
Predicted Speciation of Actinium in Pure Water at 25°C; [Ac] = 10^{-10} mol dm^{-3}

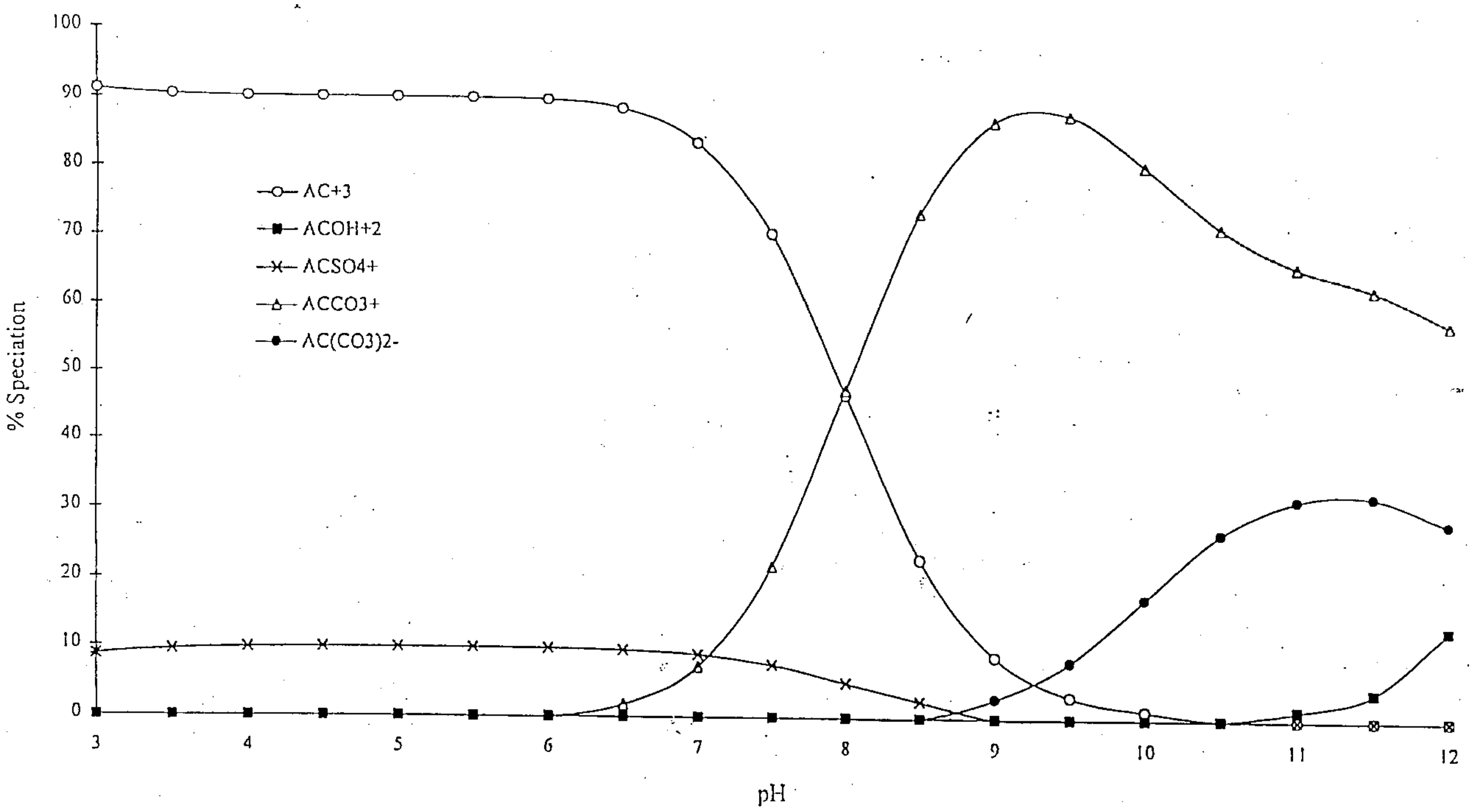

Figure 7
Predicted Speciation of Actinium in Bentonite-Equilibrated De-ionised Water at 25℃; [Ac] = 10^{-10} mol dm^{-3}

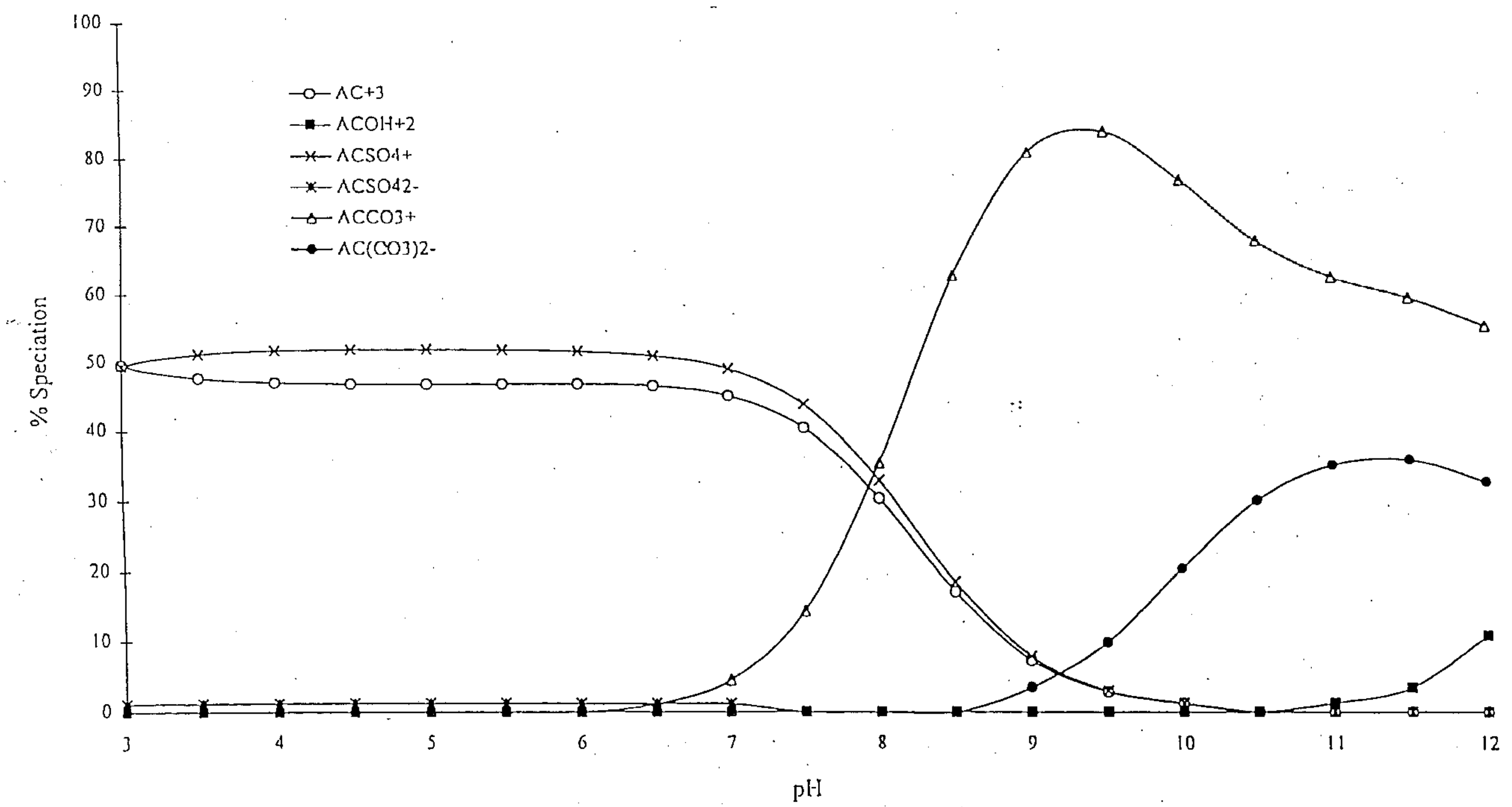

Figure 8
Predicted Speciation of Actinium in Tuff–Equilibrated De–ionised Water at 25°C; [Ac] = 10^{-10} mol dm^{-3}

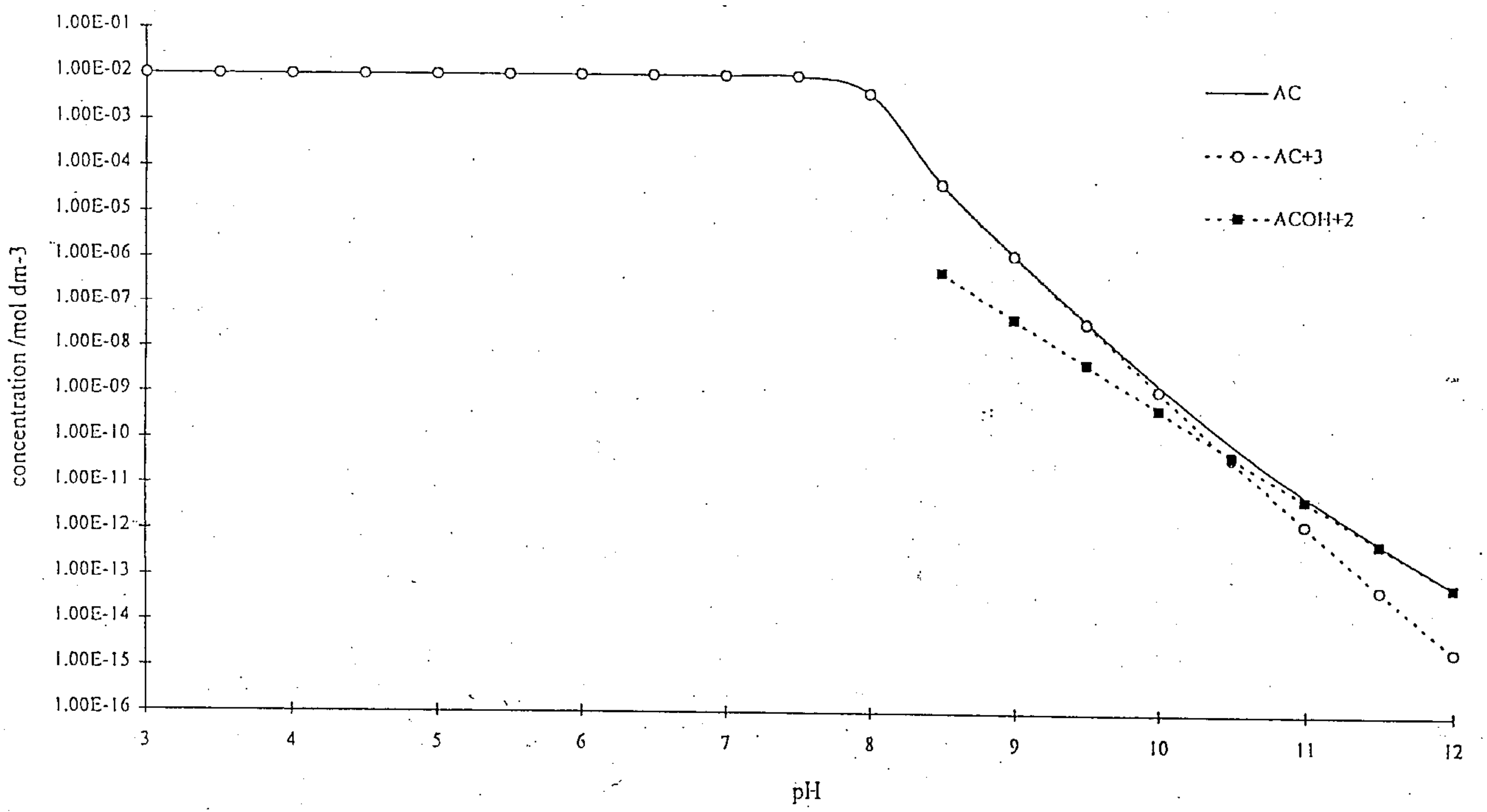

Figure 9
Solubility of $Ac(OH)_3(s)$ in Pure Water at 25℃

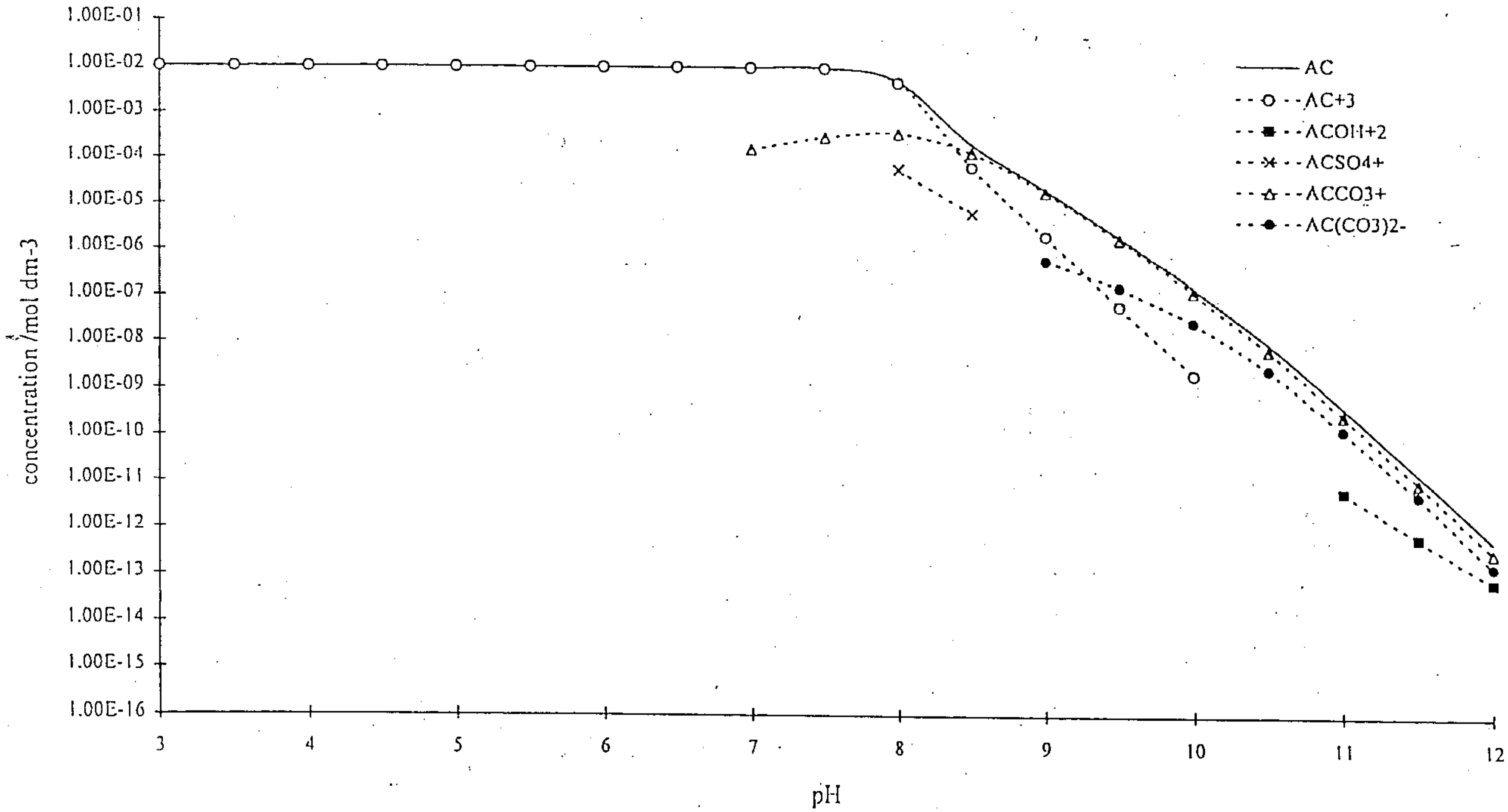

Figure 10
Solubility of $Ac(OH)_3(s)$ in Bentonite–Equilibrated De–ionised Water at 25℃

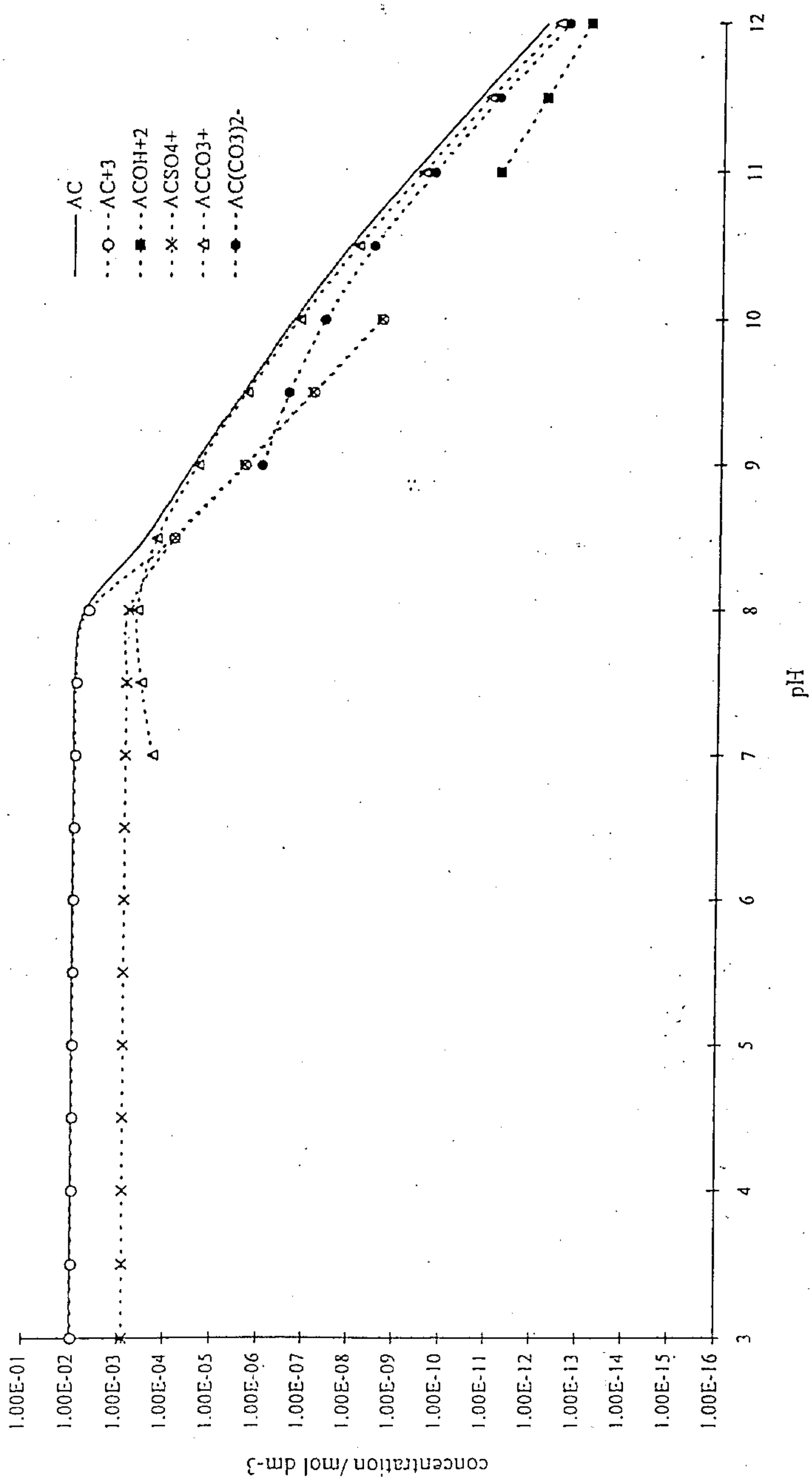

Figure 11

Solubility of $Ac(OH)_3(s)$ in Tuff-Equilibrated De-ionised Water at 25°C

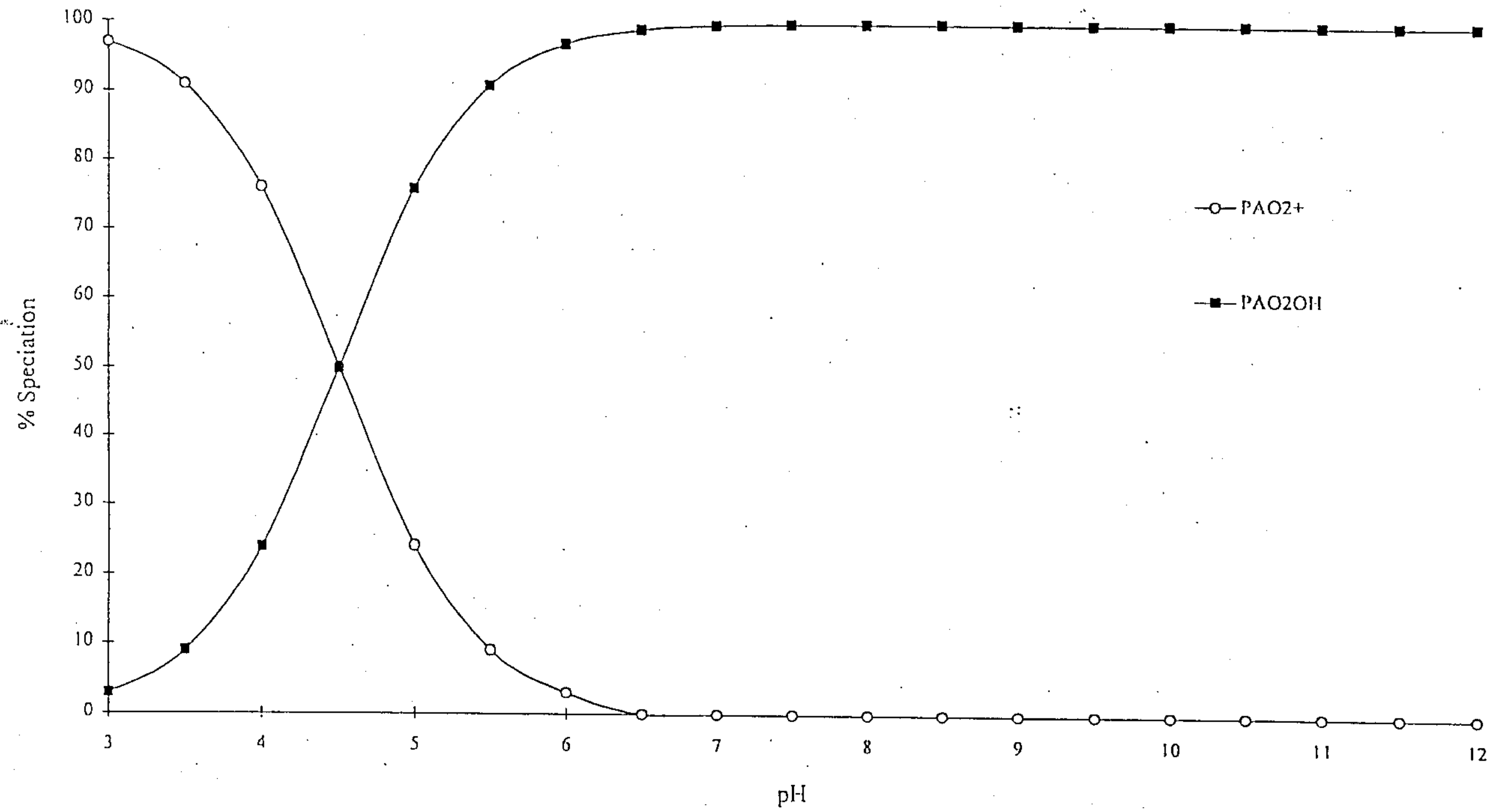

Figure 12
Predicted Speciation of Protactinium in Pure Water at 25°C; [Pa] = 10^{-10} mol dm^{-3}

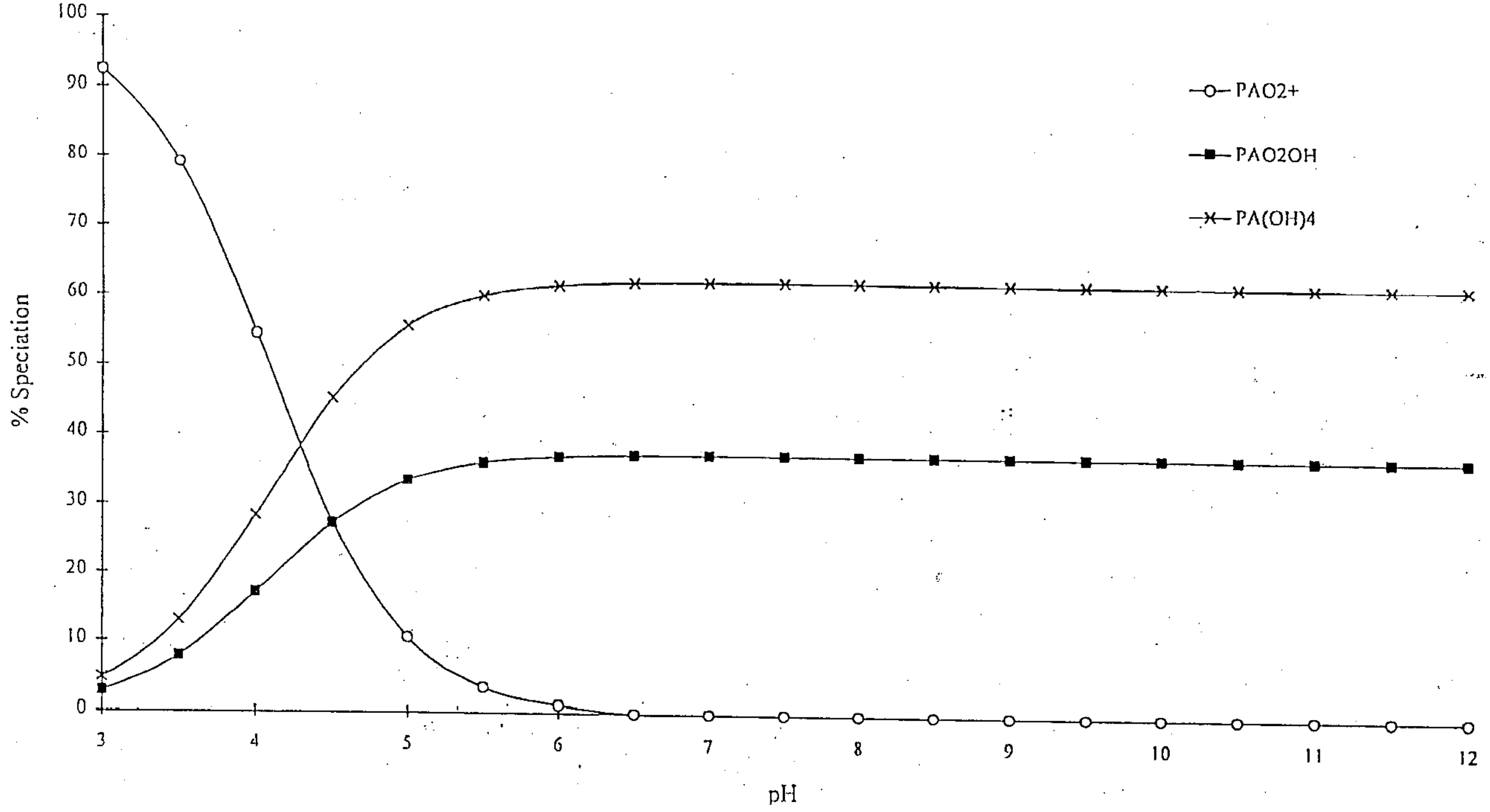

Figure 13

Predicted Speciation of Protactinium in Pure Water at the Lower Water Stability Boundary at 25°C; [Pa] = 10^{-10} mol dm^{-3}

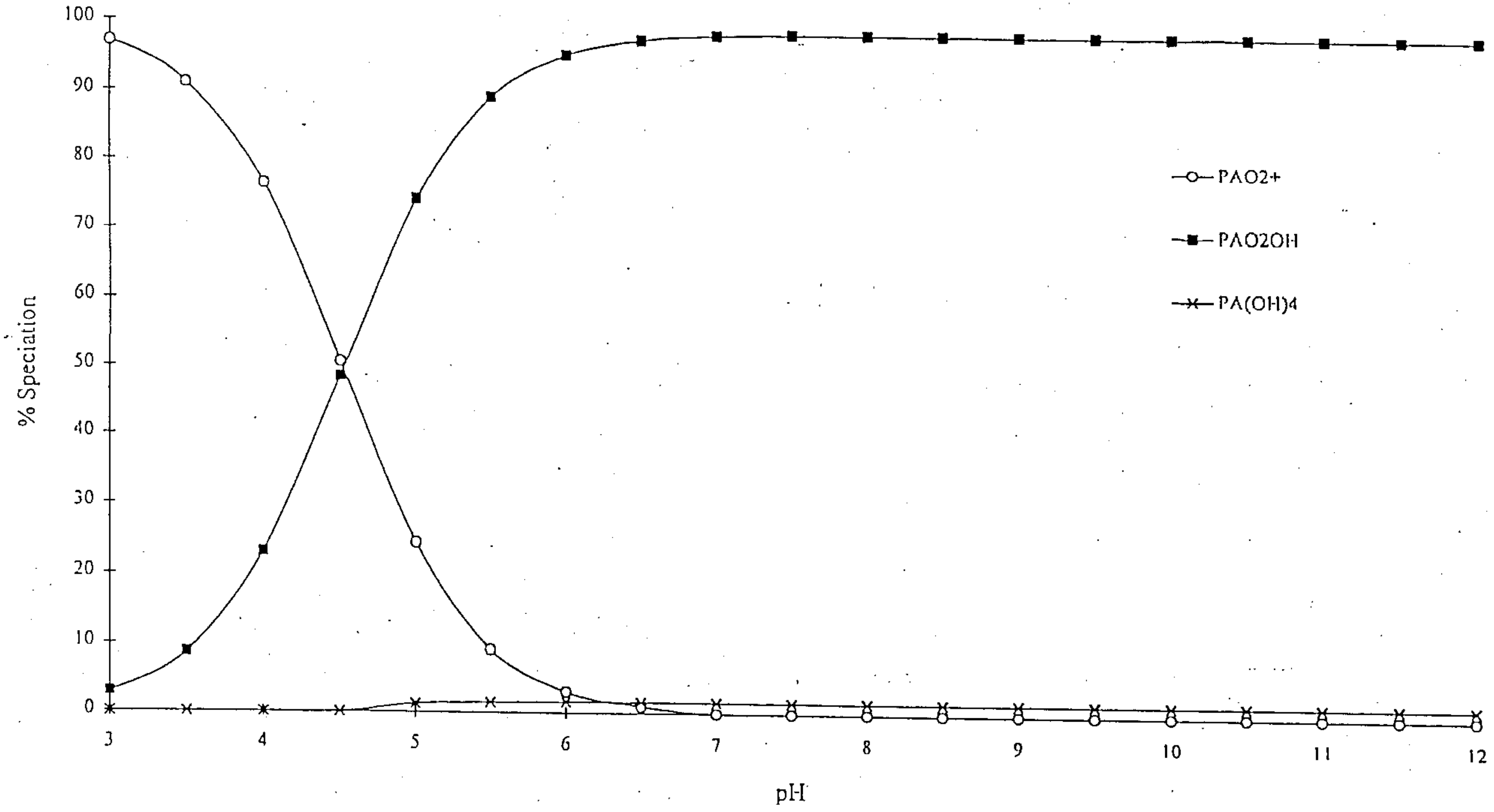

Figure 14

Predicted Speciation of Protactinium in Granodiorite-Equilibrated De-ionised Water at 25°C; [Pa] = 10^{-10} mol dm^{-3}

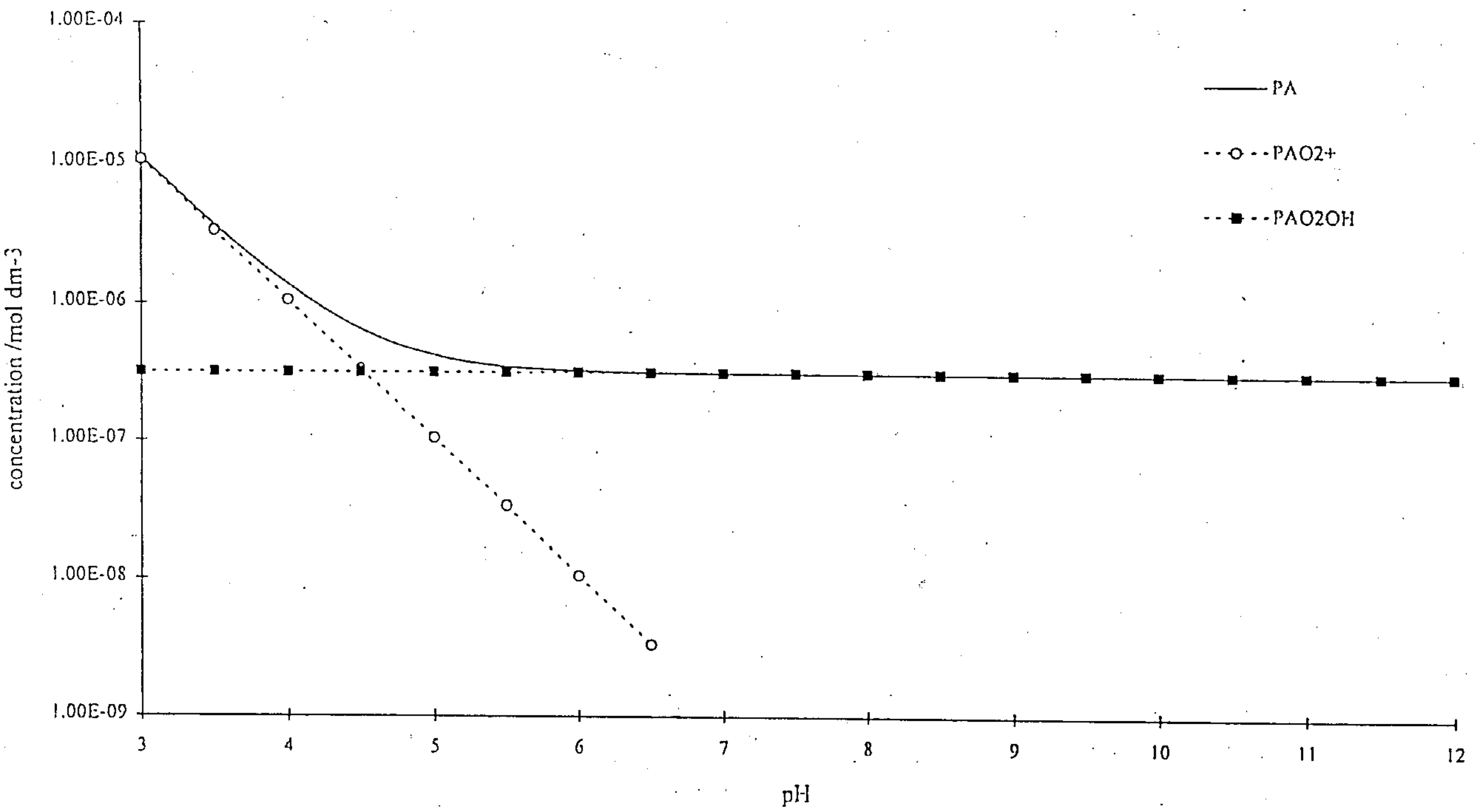

Figure 15
Solubility of Pa_2O_5(s) in Pure Water at 25℃

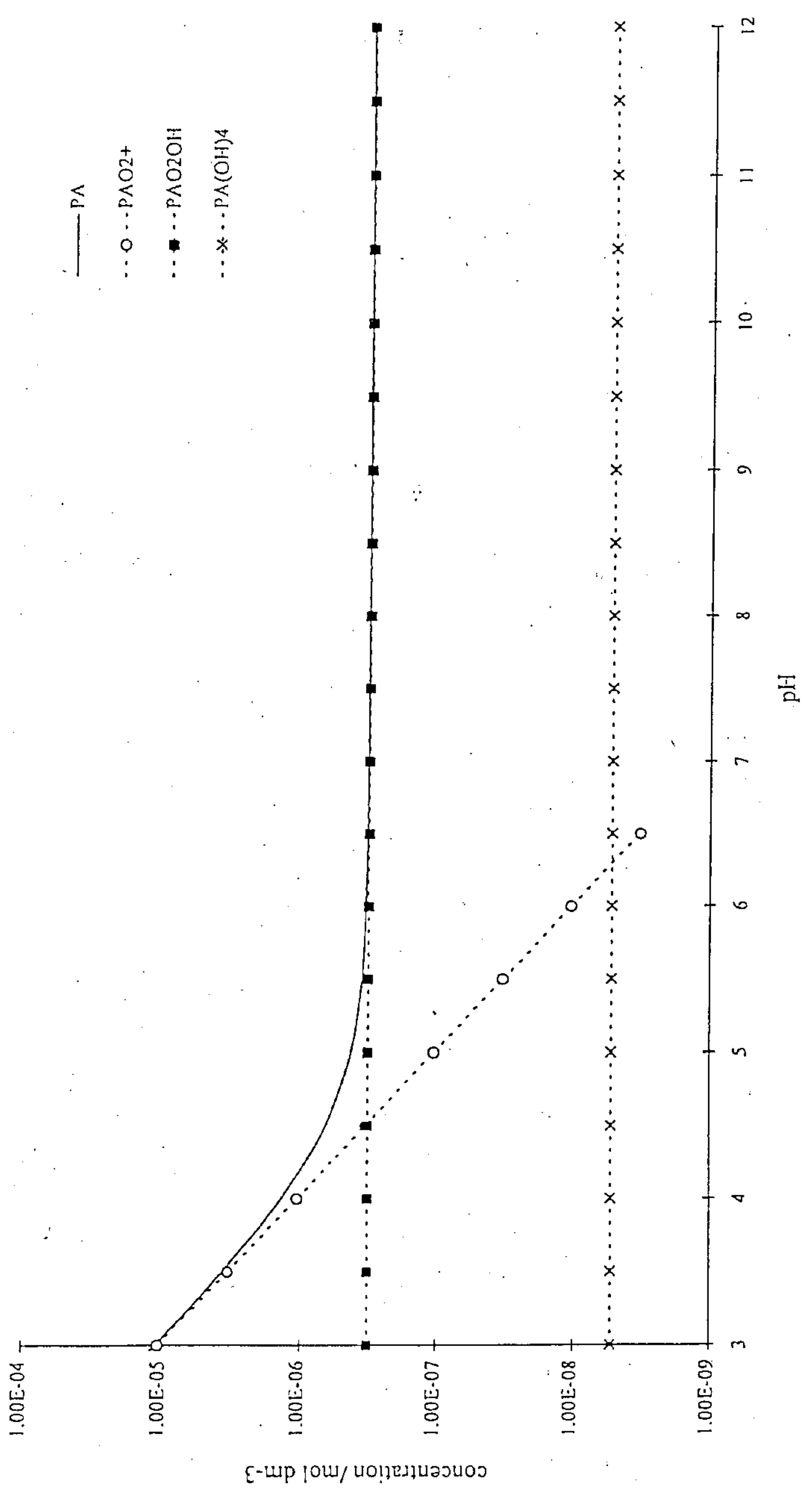

Figure 16

Solubility of Pa$_2$O$_5$ in Granodiorite-Equilibrated De-ionised Water at 25°C

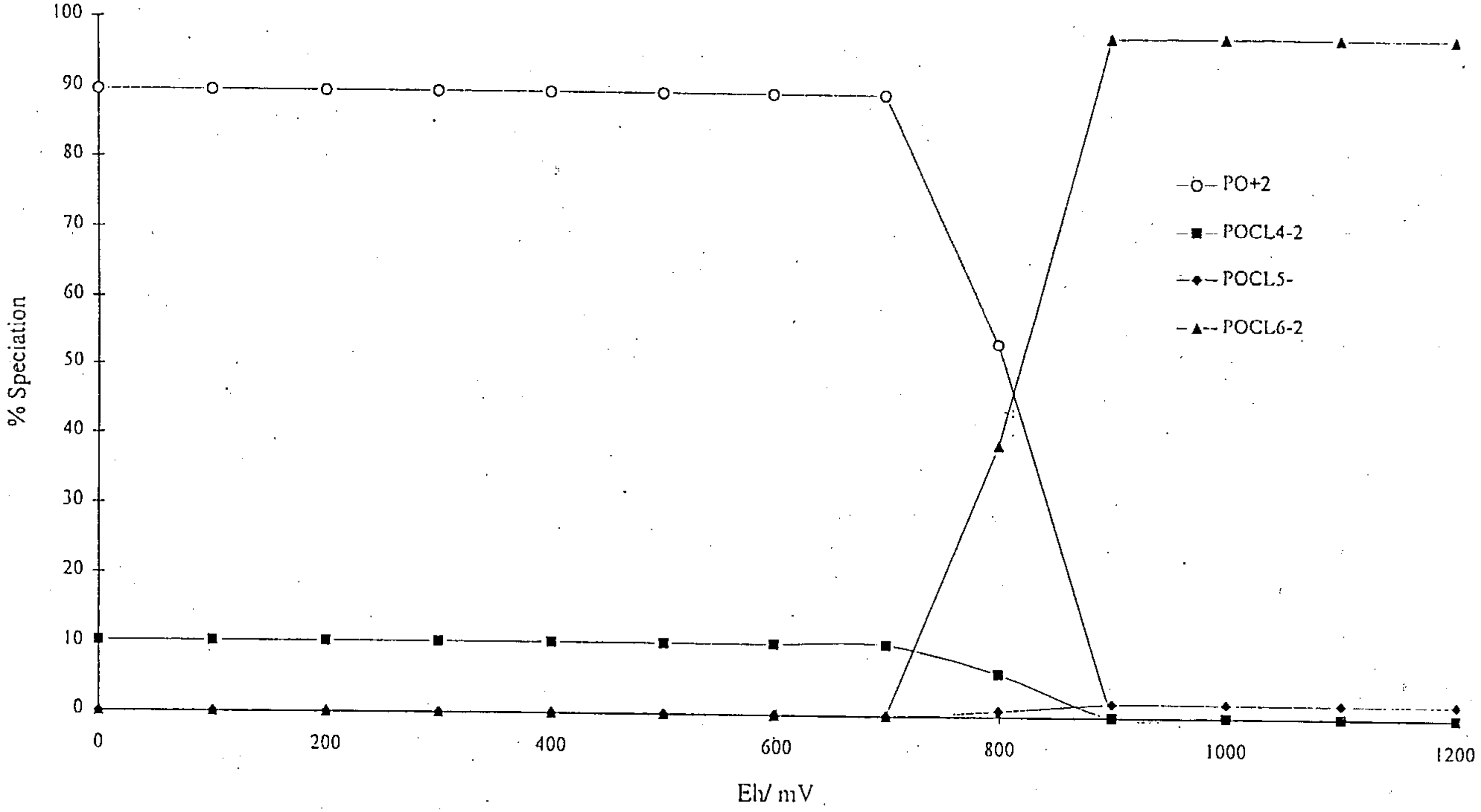

Figure 17
Predicted Speciation of Polonium in 1M HCl as a Function of Eh at 25°C; [Po] = 10^{-10} mol dm^{-3}

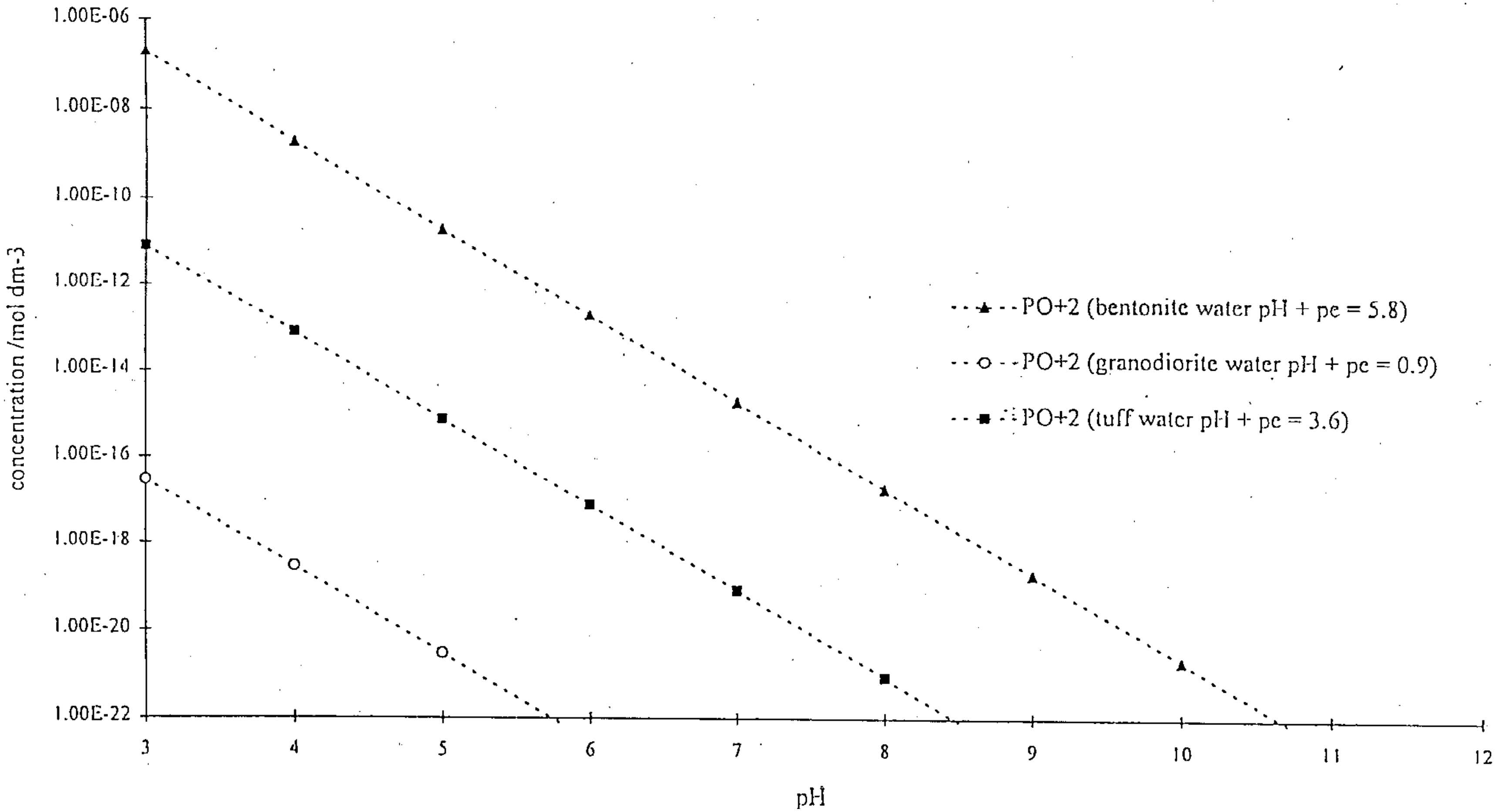

Figure 18
Predicted Concentration of Po^{2+} in Equilibrium with Po(s) for pH + pe Values Corresponding to the Po Batch Sorption Experiments

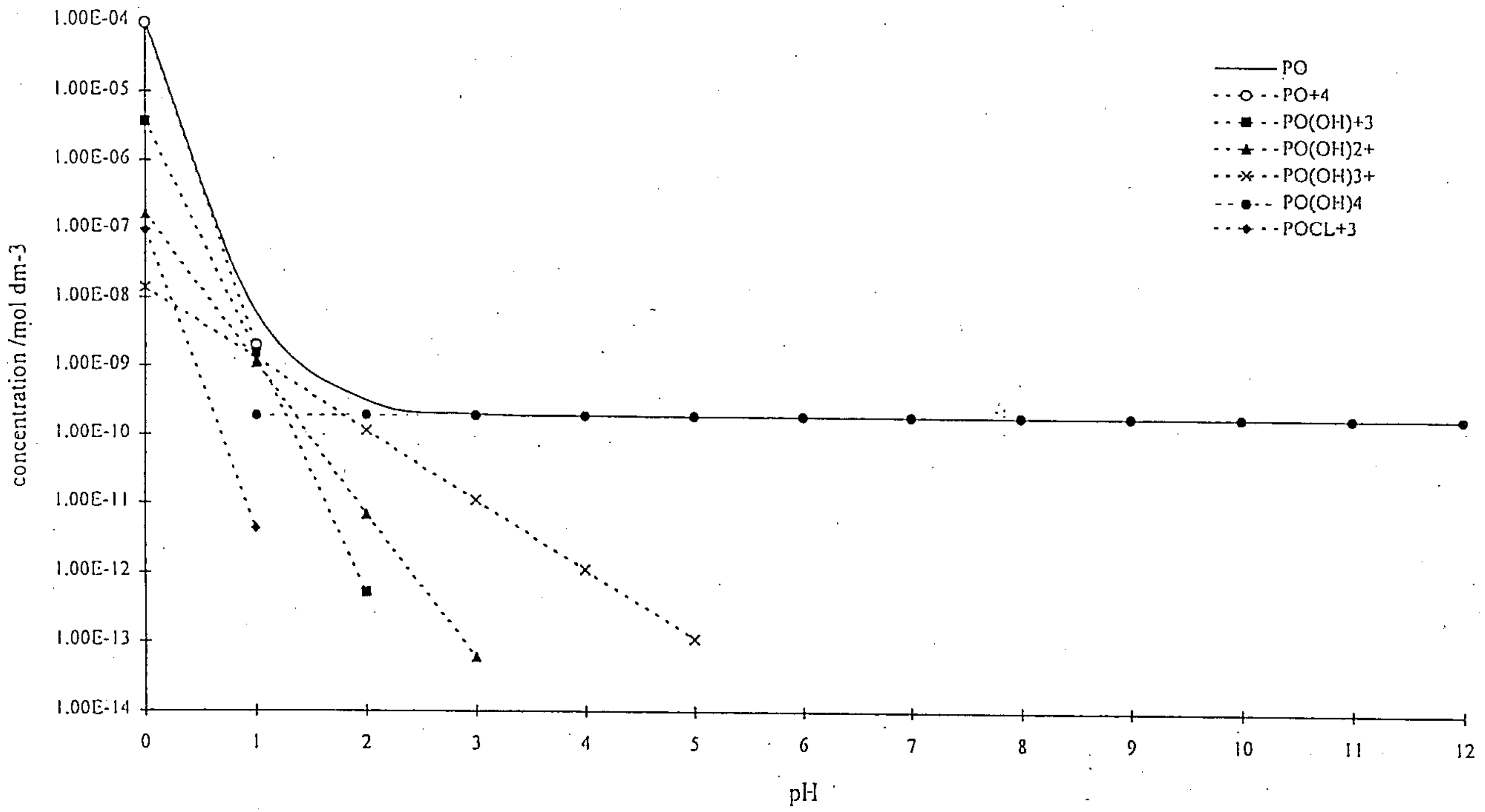

Figure 19
Predicted Solubility of PoO_2(b) at 25°C

Appendix 1：Choice of Approaches to Maintaining Strongly-Reducing Conditions in Sorption Experiments

Maintenance of a reducing environment in an aqueous solution could, in principle, be carried out by:

(a) the presence of hydrogen gas in the atmosphere;
(b) the use of solid reducing agents e.g. zinc powder or basalt;
(c) electrolytic methods;
(d) the use of soluble reducing agents such as hydrosulphite, hydrazine or hypophosphite;

All of these experimental methods will cause interactions that will not occur in the repository. Most were tried experimentally before deciding on the most suitable method for Eh control.

The use of an argon/4 % hydrogen mixture gave an Eh value of +177mV vs the SHE at pH 8. A subsequent literature search suggested that even in the presence of a palladium catalyst, an Eh of only −120mV could be obtained. Solid reducing agents such as metallic zinc or basalt have been used to produce low Eh values, but the solid added to the system is likely to sorb the species being studied. The use of electrolytic methods was considered too complex for sorption experiments where a large number of individual experiments need to be carried out, and in addition, chlorine may be evolved. When choosing a chemical reducing agent to act as a "holding" reductant to maintain for example uranium or technetium in the +4 oxidation state, the chosen compound should maintain the required strongly-reducing conditions for the duration of the experiment. Both the reductant and its oxidation product should be soluble, since solids could absorb the radioelement under study. In addition, it should not compete for sites on the surface of the geological material being examined nor should it form strong complexes with the radioelement in question. Soluble reducing agents were tried, with varying degrees of success. Table of standard oxidation potentials are of limited use in choosing a suitable redox couple to control Eh, since they are generally used under very different conditions to those under which E_0 was measured and many redox processes are very slow in reaching equilibrium. Hypophosphite, hydrazine, and hydrosulphite were selected for evaluation, and of these, only the last would maintain a sufficiently low value of Eh at the two pH value chosen, so this was selected for future use in the form of sodium hydrosulphite. Even this compound is not ideal, however, since:

(1) It hydrolyses slowly in alkaline solution to give sulphide and sulphite:

$$6OH^{-} + 3S_2O_4{}^{2-} \rightarrow S^{2-} + 5SO_3{}^{2-} + 3H_2O$$

Consequently, additions of alkali are required to maintain the pH

(2) The sulphide produced on hydrolysis could react with iron-containing minerals to form ferrous sulphide. Sorption onto this, if it is formed in significant quantities, could complement sorption onto the bulk mineral phases, giving rise to an enhanced R_D value.

(3) The sulphite produced on hydrolysis may precipitate $CaSO_3$ 1/2 H_2O (solubility 3.3 $\times 10^{-4}$M) on reaction with calcium in the solution. This, like ferrous sulphide, may sorb the radioelement.

It is not believed, however, that the use of sodium hydrosulphite presented any significant problems in the course of the present work.

Appendix 2 : An update of the sorption database (JNC-SDB) according to this report

The following corrections are carried out in JNC-SDB to be consistent with this report :

(1) One distribution coefficient (K_d: uranium sorption onto bentonite under strong-reducing conditions) is corrected based on Table18 of this report.

(2) Same Kd's error values are corrected (ex., uranium sorption onto bentonite under strong-reducing conditions based on Table 6 of this report).

国際単位系（SI）

表１．SI 基本単位

基本量	SI 基本単位	
	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd

表２．基本単位を用いて表されるSI組立単位の例

組立量	SI 基本単位	
	名称	記号
面積	平方メートル	m^{2}
体積	立法メートル	m^{3}
速さ，速度	メートル毎秒	m/s
加速度	メートル毎秒毎秒	m/s^{2}
波数	毎メートル	m-1
密度（質量密度）	キログラム毎立法メートル	kg/m^{3}
質量体積（比体積）	立法メートル毎キログラム	m^{3}/kg
電流密度	アンペア毎平方メートル	A/m^{2}
磁界の強さ	アンペア毎メートル	A/m
（物質量の）濃度	モル毎立方メートル	mol/m^{3}
輝度	カンデラ毎平方メートル	cd/m^{2}
屈折率	（数の）　1	1

表５．SI 接頭語

乗数	接頭語	記号	乗数	接頭語	記号
10^{24}	ヨタ	Y	10^{-1}	デシ	d
10^{21}	ゼタ	Z	10^{-2}	センチ	c
10^{18}	エクサ	E	10^{-3}	ミリ	m
10^{15}	ペタ	P	10^{-6}	マイクロ	µ
10^{12}	テラ	T	10^{-9}	ナノ	n
10^{9}	ギガ	G	10^{-12}	ピコ	p
10^{6}	メガ	M	10^{-15}	フェムト	f
10^{3}	キロ	k	10^{-18}	アト	a
10^{2}	ヘクト	h	10^{-21}	ゼプト	z
10^{1}	デカ	da	10^{-24}	ヨクト	y

表３．固有の名称とその独自の記号で表されるSI組立単位

組立量	SI 組立単位			
	名称	記号	他のSI単位による表し方	SI基本単位による表し方
平面角	ラジアン(a)	rad		m・m^{-1}=1(b)
立体角	ステラジアン(a)	sr(c)		m^{2}・m^{-2}=1(b)
周波数	ヘルツ	Hz		s^{-1}
力	ニュートン	N		m・kg・s^{-2}
圧力，応力	パスカル	Pa	N/m^{2}	m^{-1}・kg・s^{-2}
エネルギー，仕事，熱量	ジュール	J	N・m	m^{2}・kg・s^{-2}
工率，放射束	ワット	W	J/s	m^{2}・kg・s^{-3}
電荷，電気量	クーロン	C		s・A
電位差（電圧），起電力	ボルト	V	W/A	m^{2}・kg・s^{-3}・A^{-1}
静電容量	ファラド	F	C/V	m^{-2}・kg^{-1}・s^{4}・A^{2}
電気抵抗	オーム	Ω	V/A	m^{2}・kg・s^{-3}・A^{-2}
コンダクタンス	ジーメンス	S	A/V	m^{-2}・kg^{-1}・s^{3}・A^{2}
磁束	ウエーバ	Wb	V・s	m^{2}・kg・s^{-2}・A^{-1}
磁束密度	テスラ	T	Wb/m^{2}	kg・s^{-2}・A^{-1}
インダクタンス	ヘンリー	H	Wb/A	m^{2}・kg・s^{-2}・A^{-2}
セルシウス温度	セルシウス度(d)	℃		K
光束	ルーメン	lm	cd・sr(c)	m^{2}・m^{-2}・cd=cd
照度	ルクス	lx	lm/m^{2}	m^{2}・m^{-4}・cd=m^{-2}・cd
（放射性核種の）放射能	ベクレル	Bq		s^{-1}
吸収線量，質量エネルギー分与，カーマ	グレイ	Gy	J/kg	m^{2}・s^{-2}
線量当量，周辺線量当量，方向性線量当量，個人線量当量，組織線量当	シーベルト	Sv	J/kg	m^{2}・s^{-2}

(a) ラジアン及びステラジアンの使用は、同じ次元であっても異なった性質をもった量を区別するときの組立単位の表し方として利点がある。組立単位を形作るときのいくつかの用例は表４に示されている。

(b) 実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号“１”は明示されない。

(c) 測光学では、ステラジアンの名称と記号srを単位の表し方の中にそのまま維持している。

(d) この単位は、例としてミリセルシウス度m℃のようにSI接頭語を伴って用いても良い。

表４．単位の中に固有の名称とその独自の記号を含むSI組立単位の例

組立量	SI 組立単位		
	名称	記号	SI 基本単位による表し方
粘度	パスカル秒	Pa・s	m^{-1}・kg・s^{-1}
力のモーメント	ニュートンメートル	N・m	m^{2}・kg・s^{-2}
表面張力	ニュートン毎メートル	N/m	kg・s^{-2}
角速度	ラジアン毎秒	rad/s	m・m^{-1}・s^{-1}=s^{-1}
角加速度	ラジアン毎平方秒	rad/s^{2}	m・m^{-1}・s^{-2}=s^{-2}
熱流密度，放射照度	ワット毎平方メートル	W/m^{2}	kg・s^{-3}
熱容量，エントロピー	ジュール毎ケルビン	J/K	m^{2}・kg・s^{-2}・K^{-1}
質量熱容量（比熱容量），質量エントロピー	ジュール毎キログラム毎ケルビン	J/(kg・K)	m^{2}・s^{-2}・K^{-1}
質量エネルギー（比エネルギー）	ジュール毎キログラム	J/kg	m^{2}・s^{-2}・K^{-1}
熱伝導率	ワット毎メートル毎ケルビン	W/(m・K)	m・kg・s^{-3}・K^{-1}
体積エネルギー	ジュール毎立方メートル	J/m^{3}	m^{-1}・kg・s^{-2}
電界の強さ	ボルト毎メートル	V/m	m・kg・s^{-3}・A^{-1}
体積電荷	クーロン毎立方メートル	C/m^{3}	m^{-3}・s・A
電気変位	クーロン毎平方メートル	C/m^{2}	m^{-2}・s・A
誘電率	ファラド毎メートル	F/m	m^{-3}・kg^{-1}・s^{4}・A^{2}
透磁率	ヘンリー毎メートル	H/m	m・kg・s^{-2}・A^{-2}
モルエネルギー	ジュール毎モル	J/mol	m^{2}・kg・s^{-2}・mol^{-1}
モルエントロピー，モル熱容量	ジュール毎モル毎ケルビン	J/(mol・K)	m^{2}・kg・s^{-2}・K^{-1}・mol^{-1}
照射線量（X線及びγ線）	クーロン毎キログラム	C/kg	kg^{-1}・s・A
吸収線量率	グレイ毎秒	Gy/s	m^{2}・s^{-3}
放射強度	ワット毎ステラジアン	W/sr	m^{4}・m^{-2}・kg・s^{-3}=m^{2}・kg・s^{-3}
放射輝度	ワット毎平方メートル毎ステラジアン	W/(m^{2}・sr)	m^{2}・m^{-2}・kg・s^{-3}=kg・s^{-3}

表６．国際単位系と併用されるが国際単位系に属さない単位

名称	記号	SI 単位による値
分	min	1 min=60s
時	h	1h =60 min=3600 s
日	d	1 d=24 h=86400 s
度	°	1° =(π/180) rad
分	’	1’ =(1/60)° =(π/10800) rad
秒	”	1” =(1/60)’ =(π/648000) rad
リットル	l、L	1l=1 dm^{3}=10^{-3}m^{3}
トン	t	1t=10^{3} kg
ネーパ	Np	1Np=1
ベル	B	1B=(1/2)ln10(Np)

表７．国際単位系と併用されこれに属さない単位で
SI単位で表される数値が実験的に得られるもの

名称	記号	SI 単位であらわされる数値
電子ボルト	eV	1eV=1.60217733(49)×10^{-19}J
統一原子質量単位	u	1u=1.6605402(10)×10^{-27}kg
天文単位	ua	1ua=1.49597870691(30)×10^{11}m

表８．国際単位系に属さないが国際単位系と
併用されるその他の単位

名称	記号	SI 単位であらわされる数値
海里		１海里=1852m
ノット		１ノット=１海里毎時=(1852/3600)m/s
アール	a	1 a=1 dam^{2}=10^{2}m^{2}
ヘクタール	ha	1 ha=1 hm^{2}=10^{4}m^{2}
バール	bar	1 bar=0.1MPa=100kPa=1000hPa=10^{5}Pa
オングストローム	Å	1 Å=0.1nm=10^{-10}m
バーン	b	1 b=100fm^{2}=10^{-28}m^{2}

表９．固有の名称を含むCGS組立単位

名称	記号	SI 単位であらわされる数値
エルグ	erg	1 erg=10^{-7} J
ダイン	dyn	1 dyn=10^{-5}N
ポアズ	P	1 P=1 dyn・s/cm^{2}=0.1Pa・s
ストークス	St	1 St =1cm^{2}/s=10^{-4}m^{2}/s
ガウス	G	1 G ˆ10^{-4}T
エルステッド	Oe	1 Oe ˆ(1000/4π)A/m
マクスウェル	Mx	1 Mx ˆ10^{-8}Wb
スチルブ	sb	1 sb =1cd/cm^{2}=10^{4}cd/m^{2}
ホト	ph	1 ph=10^{4}lx
ガル	Gal	1 Gal =1cm/s^{2}=10^{-2}m/s^{2}

表10．国際単位に属さないその他の単位の例

名称	記号	SI 単位であらわされる数値
キュリー	Ci	1 Ci=3.7×10^{10}Bq
レントゲン	R	1 R = 2.58×10^{-4}C/kg
ラド	rad	1 rad=1cGy=10^{-2}Gy
レム	rem	1 rem=1 cSv=10^{-2}Sv
X線単位		1X unit=1.002×10^{-4}nm
ガンマ	γ	1γ=1 nT=10^{-9}T
ジャンスキー	Jy	1 Jy=10^{-26}W・m^{-2}・Hz^{-1}
フェルミ		1 fermi=1 fm=10^{-15}m
メートル系カラット		1 metric carat = 200 mg = 2×10^{-4}kg
トル	Torr	1 Torr = (101 325/760) Pa
標準大気圧	atm	1 atm = 101 325 Pa
カロリー	cal	
ミクロン	µ	1 µ =1µm=10^{-6}m

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