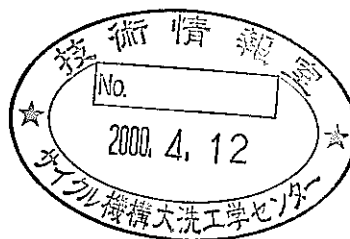


SORPTION STUDIES OF PLUTONIUM ON
GEOLOGICAL MATERIALS - YEAR2

February, 2000



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2000 年 2 月

酸化状態の異なるプルトニウムの収着現象に関する研究

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要 旨

本報告書では、以下の2つの事項について報告する。

異なる酸化条件下における、玄武岩及び砂岩へのプルトニウムの収着挙動を明らかにするために実験的研究を行った。溶液中の酸化還元電位は、還元剤2種類及び酸化剤1種類を使用し、制御を行った。

熱力学モデルを使用し、試験結果の解析を行った。今回、酸化鉄をベースとした収着モデルを使用した。砂岩については、プルトニウムの収着データを再現することができたが、玄武岩については、収着データを低めに予測する傾向が見られた。

本報告書はサミットAEA株式会社が核燃料サイクル開発機構との契約により実施した業務成果に関するものである。

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SORPTION STUDIES OF PLUTONIUM ON GEOLOGICAL MATERIALS – YEAR 2

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ABSTRACT

Batch sorption experiments have been carried out to investigate the sorption behaviour of plutonium onto basalt and sandstone from the appropriate rock-equilibrated waters under different redox conditions. Redox potentials in solution were controlled by the addition of two reducing agents and one oxidising agent.

Thermodynamic chemical modelling was undertaken to interpret the results. The sorption models were based on iron oxide. They adequately reproduced the data for sorption of plutonium onto sandstone, but tended to underpredict sorption onto basalt.

This work was performed by Summit AEA Corporation under contract with Japan Nuclear Cycle Development Institute.

JNC Liaison: Waste Management and Fuel Cycle Research Center, Waste Isolation Research Division, Barrier Performance Group

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EXECUTIVE SUMMARY

The aim of the study was to investigate the sorption of plutonium onto basalt and sandstone as a function of redox conditions. Preliminary thermodynamic chemical modelling was used to provide guidance as to the region of Pu(IV) stability and to investigate the speciation of plutonium under strongly reducing and strongly oxidising conditions. The solubility of plutonium at near-neutral pH is too low to allow the direct measurement of oxidation state.

Plutonium was added to the sorption experiments as acidic solutions of Pu(III), Pu(IV) and Pu(VI). Solutions containing plutonium-239 in hydrochloric acid were treated with hydroxy ammonium chloride or sodium chlorate to provide solutions containing Pu(III), Pu(IV) or Pu(VI), and the UV/visible spectra of each solution obtained in order to confirm the respective oxidation states. A similar methodology was used for the preparation of plutonium-238 'spike' solutions used in the batch sorption experiments, thus giving confidence that the plutonium-238 was added to the synthetic rock-equilibrated waters as acidic solutions of Pu(III), Pu(IV) and Pu(VI).

The preliminary modelling predicted that for both rock-equilibrated solutions at pH 8, the chemical conditions expected by using sodium dithionite (Eh \sim -500 mV) would provide predominantly Pu(III) in solution; Pu(IV) would dominate the solution in the range between -100mV and +150mV (where hydroxy ammonium chloride would be suitable), and that strongly oxidising conditions close to the water stability boundary, such as those expected from potassium periodate, would provide conditions in the Pu(V) / Pu(VI) stability field. However, when the initial plutonium solutions were prepared, it was observed that the plutonium concentration was low following filtration when periodate was present. This was believed to be due to the formation of a precipitate of calcium periodate. Hence, an alternative oxidising agent had to be chosen. A wide range of different available oxidants was considered. Although it would not give as high an Eh value as periodate, hydrogen peroxide was selected as the oxidising agent that would give the highest practicable redox potential whilst avoiding any precipitation or other difficulties. The use of an air atmosphere was not considered because of the difficulties that would be introduced in controlling the solution carbonate levels.

Samples of basalt and sandstone were equilibrated for three months with the appropriate rock equilibrated water 'spiked' with plutonium-238 (as Pu(III), Pu(IV) or Pu(VI)) and pre-filtered to ensure the concentrations were below the solubility limits. For each rock, experiments were carried out in duplicate, and with the addition of sodium dithionite, hydroxy ammonium chloride, or hydrogen peroxide to provide the appropriate redox environments.

In the presence of sodium dithionite (final Eh values of -500 to -480 mV vs. S.H.E.), R_D values are very similar for both rock types, values being $\sim 1 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$ following centrifugation, and $\sim 2 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ after either 0.45 μm or 10000MWCO filtration.

In the presence of hydroxy ammonium chloride (final Eh values of \sim +40 mV in the case of basalt, and -40 mV in the case of sandstone), R_D values are also very similar for both rock types. Following centrifugation, the values were $\sim 4 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$, slightly lower than in the presence of sodium dithionite. After 0.45 μm filtration, values were similar to those obtained in the presence of sodium dithionite, being in the range 6.7×10^3 to $5.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$. After

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10000MWCO filtration, R_D values were a little higher than in the presence of dithionite, being in the range 2.9×10^4 to $3.6 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$.

In the experiments where hydrogen peroxide was present (final Eh values of +350mV in the case of basalt, and +370 mV in the case of sandstone), R_D values following centrifugation were $1.2 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for basalt, and $\sim 8 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for sandstone. After 0.45 μm filtration, R_D values were lower than in the cases of hydroxy ammonium chloride and sodium dithionite ($\sim 9 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for basalt and $\sim 5 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$ for sandstone). After 10000MWCO filtration, R_D values in the case of basalt were in the same range ($\sim 7 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$) as those obtained for both rocks in the presence of either sodium dithionite or hydroxy ammonium chloride. For sandstone, they were an order of magnitude lower ($\sim 5 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$). The differences in the R_D value for basalt following the two types of filtration indicate a tendency towards colloid formation, which is not evident in the case of sandstone.

Geochemical modelling to predict the aqueous speciation of plutonium over the range of experimental redox conditions showed the following:

- strongly reducing: Pu(III) species dominate.
- intermediate: Pu(IV) species dominate.
- oxidising: likely to be Pu(IV)/Pu(V) but some uncertainty in thermodynamic data.

Sorption models have been applied to assist in the interpretation of the JNC experimental data. These models are based on sorption onto iron oxide type surfaces within the rocks. A plutonium(III) sorption model was derived in last year's programme of work. This year's programme of work included parameterisation of a Pu(IV) and Pu(V) sorption model. These models have been used to predict the sorption of plutonium onto basalt and sandstone under the strongly reducing, intermediate and oxidising redox conditions.

The main points arising from the modelling were:

- The iron oxide models developed were able to reproduce adequately the data for sorption of plutonium onto sandstone, but tended to underpredict sorption onto basalt. Although not possible to evaluate rigorously in the current work, it is believed that alternative minerals (e.g. biotite, pyroxene) could contribute to sorption in the case of basalt.
- The species predicted to dominate sorption were plutonium (III) under strongly reducing conditions, and various combinations of plutonium(III) and plutonium(IV) under intermediate and oxidising conditions. Plutonium(V) species were not predicted to play an important role.

A paper based on the previous year's study for JNC, entitled 'Effect of Carbonate Concentration on the Sorption of Plutonium onto Geological Materials' by G M N Baston, J A Berry, M Brownsword, D J Ilett, C M Linklater, C J Tweed and M Yui, was presented at the Materials Research Society Fall Meeting, Boston, USA, December 1999 and has been accepted for publication in 'Scientific Basis for Nuclear Waste Management XXIII'. The paper is attached to this report as Appendix 1.

For JNC's convenience, earlier unpublished work by AEA Technology for JNC on the sorption of plutonium onto bentonite, tuff and granodiorite at 60°C is summarised at the end of this report as Appendix 2.

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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 the sorption behaviour of radionuclides on geological media are, therefore, needed in order to predict nuclide migration. This information is very important for the radiological assessment of potential repository sites.

The first years of the research programme undertaken by AEA Technology for JNC included investigating major chemical parameters that govern the migration behaviour of the radioelements important to JNC's assessments; uranium, technetium, curium, neptunium, actinium, protactinium, polonium, plutonium and americium, under the predicted conditions in and around the potential JNC repository [1-8]. As in these earlier studies, the philosophy underlying the present 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 Nirex 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 [9].

The aim of the present study was to investigate the sorption behaviour of plutonium onto basalt and sandstone as a function of the oxidation state of plutonium. The redox potential in solution was varied using two reducing agents and an oxidising agent in order to give as wide a range of redox potentials as possible.

The present study extends work carried out previously on the sorption of plutonium as a function of carbonate concentration [8,10]. (The paper that has been published on this earlier work [10] is attached as Appendix 1).

For JNC's convenience, earlier work by AEA Technology for JNC on the sorption of plutonium onto bentonite, tuff and granodiorite at 60°C is summarised at the end of this report as Appendix 2.

2 SPECTROSCOPIC STUDY

The addition of plutonium in known single oxidation states was required in the batch sorption experiments. Therefore, spectroscopic studies were carried out to investigate the reducing / oxidising agents required to ensure that single oxidation states of plutonium could be generated in the stock solutions.

In order to confirm methods of providing individual solutions of plutonium containing Pu(III), Pu(IV) and Pu(VI), solutions of plutonium-239 in 1 mol dm⁻³ hydrochloric acid (plutonium concentration approximately 10⁻³ mol dm⁻³) were treated with various reagents (see Figure 1), and the UV/Visible spectra of the solutions obtained in order to confirm the respective oxidation states [11]; see Figures 2, 3 and 4.

To prepare a solution containing Pu(III), a measured aliquot was taken from a solution of PuCl₄ containing plutonium (107 g dm⁻³) and diluted with 3 mol dm⁻³ hydrochloric acid to

give a stock solution containing plutonium at 1 g dm^{-3} . This solution was treated with hydroxy ammonium chloride to reduce the plutonium to Pu(III). On reduction, the typical blue colour of Pu(III) was observed. A 1 cm^3 aliquot of this solution was diluted with 2 cm^3 water to produce a solution containing 0.3 g dm^{-3} plutonium in 1 mol dm^{-3} hydrochloric acid. The spectrum obtained is typical of Pu(III) (Figure 2).

Some of the Pu(III) solution as prepared above was treated with $0.1 \text{ mol dm}^{-3} \text{ NaClO}_3$ solution in a molar ratio of $1 \text{ ClO}_3^- : 6 \text{ Pu}$ and left overnight for oxidation to Pu(IV) to occur. When oxidation was complete, 1 cm^3 of the Pu(IV) solution was diluted with 2 cm^3 water to produce a solution containing 0.3 g dm^{-3} plutonium in 1 mol dm^{-3} hydrochloric acid. The spectrum obtained is typical of Pu(IV) (Figure 3).

Some of the Pu(IV) solution was treated with an excess of $0.1 \text{ mol dm}^{-3} \text{ NaClO}_3$ and the solution left for several hours for oxidation to Pu(VI) to occur. Again, a dilution was performed to give a solution containing 0.3 g dm^{-3} plutonium in 1 mol dm^{-3} hydrochloric acid. The spectrum obtained is typical of Pu(VI) (Figure 4).

3 BATCH SORPTION EXPERIMENTS

All experiments were performed in a nitrogen-atmosphere glovebox with an oxygen level of less than 1 ppm. Solutions were de-oxygenated by bubbling nitrogen through them. The experimental procedures are outlined in the flowsheet in Figure 5, and were similar to those used previously [8].

3.1 Preparation of Rocks and Pre-equilibration

Samples of basalt and sandstone used in the Year 1 plutonium sorption study (Projects 2 and 3) [8] were crushed and sieved so that the whole sample passed through a $250 \mu\text{m}$ sieve. Synthetic solutions based on basalt- and sandstone-equilibrated waters were prepared, and were the same as those used in the Year 1 plutonium sorption study [8], except that the pH was adjusted to ~ 8 (Table 1). The pH value selected in this work was lower than the natural equilibrium pH for the two rock equilibrated deionised waters as determined in the Year 1 study [8]. This lower pH value was selected as modelling work carried out in the previous year's programme suggested that it would be difficult to prepare a solution of predominantly Pu(III) at natural pH values with a practicable reducing agent.

As in the Year 1 study, a four week pre-equilibration of the synthetic rock-equilibrated deionised waters with the rocks was performed at a water-to-rock ratio of 5:1. The equilibration and sorption experiments were performed on a 100 cm^3 scale in order to improve the limit of detection at the end of the sorption experiments. At the end of the pre-equilibration period, 75 cm^3 rock-equilibrated water were removed and discarded. This volume was replaced with an equivalent volume of the appropriate rock-equilibrated water containing either reducing agent or oxidising agent, and which had previously been 'spiked' with plutonium-238 (as Pu(III), Pu(IV) and Pu(VI)), the pH value adjusted to ~ 8 , and then filtered ($0.45 \mu\text{m}$). This filtration was to ensure that the initial plutonium concentration was below the solubility limit. The plutonium-238 solutions were prepared using a similar methodology to that described in Section 2, but with very small masses of plutonium (Pu-238 rather than Pu-239) to avoid the solubility limits of plutonium in near-neutral solutions from being exceeded. The plutonium was thus added as acidic Pu(III), Pu(IV) and Pu(VI) spikes, but direct measurements of

oxidation states were not possible at these very low concentrations. Initial concentrations of plutonium were in the range $6.9 \times 10^{-11} \text{ mol dm}^{-3}$ to $1.1 \times 10^{-10} \text{ mol dm}^{-3}$.

3.2 Oxidising and Reducing Agents Used

Because of the very low solubility of plutonium at near-neutral pH values in several oxidation states, it is not possible to measure directly the oxidation state of plutonium in the experiments [12]. Preliminary thermodynamic chemical modelling was therefore used as an aid, to guide the choice of experimental conditions. This initial modelling was 'point' modelling where individual HARPHERQ calculations were performed for the specific conditions anticipated in the experiments. Predictions indicated that for both solutions at pH 8, the chemical conditions expected by using sodium dithionite ($E_h \sim -500\text{mV}$) would provide predominantly Pu(III) in solution; Pu(IV) would dominate in solution in the range between -100mV and $+150\text{mV}$ (regardless of the plutonium dataset used; see later discussions) and that strongly oxidising conditions close to the water stability boundary, such as those expected from potassium periodate, would provide conditions in the Pu(V) / Pu(VI) stability field. It was predicted that it would not be possible to prepare a solution at near neutral pH containing 100% Pu(VI), as even at the upper limit of the stability of water at pH 8, there would still be significant Pu(V) present.

The redox reagents chosen were:

- (i) for strongly-reducing conditions; sodium dithionite,
- (ii) for intermediate conditions; hydroxy ammonium chloride,
- (iii) for oxidising conditions, potassium periodate.

The concentration of redox reagent chosen for each region was $\sim 10^{-3} \text{ mol dm}^{-3}$.

However, when initial plutonium solutions were prepared, it was observed that the plutonium concentration was low following $0.45\mu\text{m}$ filtration when periodate was present. This was believed to be due to the formation of a precipitate of calcium periodate and sorption / co-precipitation of plutonium. The possibility of modifying the groundwater composition to reduce the calcium concentration was considered. However, as the experiments involved equilibration with rock samples, this approach would not have been helpful as a significant level of calcium would still leach from the rocks into solution and the precipitation would recur. Hence, an alternative oxidising agent had to be chosen. A wide range of different available oxidants was considered. Anions such as chlorate are likely to form similarly sparingly soluble calcium salts and would have presented the same difficulties as periodate. Oxidising cations could not be used because they would tend to sorb on the rocks rather than maintaining a high E_h in solution. The use of an air atmosphere was not considered because of the difficulties that would be introduced in controlling the solution carbonate levels within the range of interest to JNC. Although it was known not to give as high an E_h value as periodate, hydrogen peroxide was selected as the oxidising agent that would give the highest practicable redox potential whilst avoiding any precipitation or other difficulties. The experiments were thus set up as planned but with hydrogen peroxide instead of periodate.

After three weeks, the E_h values for each type of rock were approximately:

-450 mV vs. SHE for the experiments with sodium dithionite
-150 mV vs. SHE for the experiments with hydroxy ammonium chloride
+400 mV vs. SHE for the experiments with hydrogen peroxide.

3.3 Execution of Batch Sorption Experiments

The sorption experiments were performed in duplicate. The polythene bottles were gently agitated on a shaker table. The experiments ran for 3 months. The Eh and pH values were checked every 2 weeks, and were adjusted on two occasions. Three liquid/solid phase separation techniques were employed:

- centrifugation at 1100g for 15 minutes, with aliquots being removed from near the surface of the supernatant liquid;
- centrifugation followed by filtration through a 0.45 μ m filter;
- centrifugation followed by filtration through a 0.45 μ m filter, then through a 10000MWCO filter.

All filters were pre-conditioned before use [13]. Solutions were filtered into dilute acid prior to the preparation of counting trays for analysis for plutonium by alpha-spectrometry. Pu-239 was used as a yield tracer.

4 EXPERIMENTAL RESULTS

Table 2 shows the final Eh and pH values measured after 3 months equilibration, and also the R_D values after successive phase separations.

4.1 Experiments Conducted in the Presence of Sodium Dithionite

In the presence of sodium dithionite, (final Eh values of -500 to -480 mV vs. S.H.E.) R_D values for the corresponding phase separations are very similar for both rock types. Values are in the range 7.9×10^2 to $1.2 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$ following centrifugation, 1.1×10^4 to $2.2 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ after 0.45 μ m filtration, and 1.2×10^4 to $2.9 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ after 10000MWCO filtration. The similarity of values following the two types of filtration indicates no tendency towards colloid formation for either type of rock.

4.2 Experiments Conducted in the Presence of Hydroxy Ammonium Chloride

In the presence of hydroxy ammonium chloride, (final Eh values of +40 and +50mV vs. S.H.E. in the case of basalt, and -40 mV vs. S.H.E. in the case of sandstone), R_D values for the corresponding phase separations are also very similar for both rock types. Following centrifugation, the values are in the range 2.5×10^2 to $5.2 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$, slightly lower than in the presence of sodium dithionite. After 0.45 μ m filtration, values are similar to those obtained in the presence of sodium dithionite, being in the range 6.7×10^3 to $5.3 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$. After 10000MWCO filtration, R_D values are in the range 2.9×10^4 to $3.6 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$. In this case the R_D values following the two types of filtration indicate some tendency towards colloid formation in the basalt experiments.

4.3 Experiments Conducted in the Presence of Hydrogen Peroxide

Final Eh values of +350mV vs. S.H.E. in the case of basalt, and +370 mV vs. S.H.E. in the case of sandstone were slightly lower than had been expected, following measurements of +400mV after the experiments had been equilibrating for three weeks (despite further additions of hydrogen peroxide).

R_D values following centrifugation are $1.2 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for basalt, and 7.6×10^2 to $8.8 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for sandstone. After $0.45 \mu\text{m}$ filtration, R_D values are lower than in the cases of hydroxy ammonium chloride and sodium dithionite (8.2×10^2 and $9.4 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$ for basalt and 4.8×10^3 and $5.8 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$ for sandstone). After 10000MWCO filtration, R_D values in the case of basalt are in the same range as those obtained for both rocks in the presence of either sodium dithionite or hydroxy ammonium chloride (4.4×10^4 and $1.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$). For sandstone, they are an order of magnitude lower (5.4×10^3 and $5.5 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$). Again, the differences in R_D values for basalt following the two types of filtration indicate a tendency towards colloid formation, which is not evident in the case of sandstone.

4.4 Vessel Wall Sorption

Table 3 shows the percentage of plutonium sorbed onto the walls of the polythene bottles after the equilibration had finished. Since the maximum value was only 0.38%, it was not necessary to make corrections to the R_D values to allow for this.

5 GEOCHEMICAL MODELLING OF SORPTION RESULTS

Geochemical modelling was used to interpret the results of the batch-sorption experiments. The detailed modelling comprised two main activities:

1. Prediction of the aqueous speciation of plutonium over the full range of experimental redox conditions;
2. Parameterisation and application of a sorption model to the experimental data.

All modelling was carried out using the HARPHRQ geochemical modelling code [14]. The HATCHES thermodynamic database [15], version NEA11.0, was used as the basis for all calculations. Where indicated, the JNC plutonium dataset was used instead of the NEA11.0 plutonium dataset. The results of the studies are discussed fully in the following sections.

5.1 Plutonium Aqueous Speciation

The aqueous speciation of plutonium is complex with a strong dependence on the redox potential and pH. In addition, there is also a strong tendency to form complexes with other solution species, especially carbonate, which can markedly alter the stability of the various species.

The HATCHES NEA database, version NEA11.0, contains thermodynamic data for a wide range of plutonium species. The data are compiled from several sources including:

- Allard [16], Pu(III) carbonate and hydrolysis data
- Kim et al. [17], Pu(IV) carbonate data

- Lierse and Kim [18], Pu(IV) and Pu(VI) hydrolysis and Pu(V) carbonate data
- Fuger and Oetting [19], Pu(V) and Pu(VI) data
- Phillips [20], Pu(V) hydroxide data
- Robouch and Vitorge [21], Pu(VI) carbonate data

However, as reported previously [8] plutonium has been the focus of recent research activity, and it is now believed that certain aspects of the existing datasets require revision. In particular, it appears that the Kim et al. [17] dataset overestimates the stability of plutonium(IV) carbonate species. Under reducing conditions, this can result in overprediction of the stability of plutonium(IV) relative to plutonium(III). A recent study by Rai et al. [22] has addressed this issue and a revised plutonium(IV) dataset is available. The Rai et al. work was funded by JNC and has been incorporated into the JNC plutonium database. The JNC database also contains significantly revised datasets for plutonium(III) hydrolysis and carbonate species, plutonium(V) carbonate species, and plutonium(VI) hydrolysis and carbonate species. The JNC database was made available to AEA Technology and was used in the previous year's programme of work to investigate the sorption of plutonium under strongly-reducing conditions at three concentrations of carbonate [8].

In view of the uncertainties in the plutonium datasets available, two predictions of plutonium speciation were made for the basalt- and sandstone-equilibrated waters adjusted to pH~8.. The plutonium speciation as a function of redox potential predicted by the HATCHES NEA12_R2 data is shown in Figures 6 and 7 and by the JNC data in Figures 8 and 9.

Some differences are evident between the predictions from the two datasets. Firstly, the HATCHES database predicts that $\text{Pu}(\text{CO}_3)_3^{-2}(\text{aq})$ will dominate the Pu(IV) stability region whereas $\text{Pu}(\text{OH})_4(\text{aq})$ is the main species predicted by the JNC data for this region. (Note that although the experiments for this work were carried out in a nitrogen-atmosphere glovebox, low concentrations of carbonate arising from the rock samples are present in the sandstone-equilibrated water. This is also possibly the case for the basalt-equilibrated water since the basalt sample showed signs of weathering). This leads to an extension of the Pu(IV) stability region to lower Eh values for the HATCHES data as discussed earlier; more so for the sandstone-equilibrated water as this has a higher carbonate concentration.

Secondly, Pu(V) carbonate is predicted to dominate under higher redox conditions using the HATCHES data, whilst $\text{PuO}_2^+(\text{aq})$ is the dominant species using the JNC dataset. This leads to a reduction in the extent of the Pu(IV) stability region under higher redox conditions for predictions using the HATCHES data. The differences here arise mainly from the differences in log K for the $\text{PuO}_2\text{CO}_3^-(\text{aq})$ species which comes from Lierse and Kim [18] for HATCHES and is referenced to "[SHIB98C]" in the JNC data.

The presence of significant quantities of Pu(VI) in the basalt- and sandstone-equilibrated deionised waters adjusted to pH 8.1 is only predicted by the JNC dataset under high redox conditions close to the upper water stability boundary: Pu(V) species are predicted by both datasets to dominate at pH 8.1 under the higher redox conditions considered.

From consideration of thermodynamics alone, the final redox potentials measured in the experiments (Table 2) suggest the presence of predominantly Pu(III) and Pu(IV) respectively for the strong and mild reducing conditions considered. Under the oxidising conditions, there is more uncertainty; predictions using HATCHES suggest a mix of Pu(IV)/Pu(V) whilst use

of the JNC data suggests only Pu(IV) is present. It should be noted that in the latter case the plutonium was added as Pu(VI) and that there is some uncertainty as to the oxidation-reduction kinetics of plutonium ions (see e.g. [12]) especially in non-acidic solutions. In particular, disproportionation of Pu(V) to Pu(IV) and Pu(VI) is known to occur and it is also common for several oxidation states of plutonium to co-exist in solution. However, from thermodynamic considerations, the presence of significant quantities of Pu(VI) appears unlikely.

5.2 Assessment of Trends Shown by the Experimental Data

The experiments were designed to examine plutonium sorption under different redox conditions. The experimental data (given in Table 2 and described in detail in Section 4) are illustrated in Figure 10. The following comments can be made:

Basalt

- Plutonium sorption onto this rock type is strong over a wide range of redox conditions. R_D values (10,000MWCO) were in excess of $10^4 \text{ cm}^3 \text{ g}^{-1}$ under all condition studied.
- Sorption was strongest under intermediate redox conditions. At $\sim 40\text{-}50\text{mV}$, R_D values (10,000MWCO) of 7×10^4 to $4 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$ were measured.

Sandstone

- Plutonium sorption onto this rock type was strong over the Eh range -500mV to -40mV (R_D values, 10,000MWCO, were in excess of $10^4 \text{ cm}^3 \text{ g}^{-1}$).
- Under oxidising conditions (Eh $+370\text{mV}$), there was a slight reduction in sorption (R_D values, 10,000MWCO, were $\sim 5 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$).

5.2.1 Comparison with Last Year's JNC Experiments

The measurements made under strongly reducing conditions in this work can be compared to values obtained from similar experiments carried out as part of last year's programme of work for JNC (described in Table 8 of [8]). The earlier experiments were also carried out under strongly reducing conditions, but at a slightly higher pH, pH 10-10.8 (compared to pH ~ 8 for this years' work). The previous work gave R_D values of 7×10^4 to $1 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$ for basalt, and $\sim 4 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ for sandstone. These R_D values are slightly higher than those obtained this year, possibly due to a pH-dependent effect on sorption.

5.2.2 Comparison with Published Data for Plutonium Sorption

Direct comparison with published data for plutonium sorption is difficult as important aspects of experimental design often vary, especially the reducing agents used and the methods adopted to control the atmosphere above the experiment. In many published plutonium sorption studies, information concerning the plutonium oxidation state is incomplete or ambiguous. This is because direct measurement of plutonium oxidation state is often impracticable (due to plutonium being present in very low concentrations). Indirect methods can be used, e.g. the use of geochemical modelling techniques to predict the most thermodynamically stable oxidation state. However, many studies do not include such approaches.

There follows a list of published R_D values considered representative of plutonium sorption (onto sandstone and basalt) in different oxidation states. In compiling the list, expert judgement was used to assess which oxidation state was most likely to be present (e.g. based

on the state in which plutonium was added at the start of the experiments, and the experimental conditions used). It should be noted that there is a degree of uncertainty associated with expert judgements.

Plutonium(III)

Plutonium(III) would be expected to dominate speciation under very strongly reducing conditions. Published data relevant to Pu(III) sorption is extremely limited. No data were found that were considered suitable for direct comparison with the JNC measurements.

Plutonium(IV)

Under 'anaerobic' and/or 'reducing' conditions, plutonium(IV) is generally believed to be the stable oxidation state. Some published R_D values that are believed representative of plutonium(IV) sorption, and involve basalt and sandstone, are as follows:

- 400 to 3000 cm^3g^{-1} – measured for a sandstone sample at Rockwell International Laboratories [23]. Various experiments were carried out using different solution compositions, with hydrazine as the reducing agent. Precipitation of an insoluble Pu-Ca complex may be implicated in some of the experiments.
- 2800 to 10^4 cm^3g^{-1} – measured for a sandstone sample by AEA Technology as part of Nirex investigations [24].
- 2×10^4 to 3×10^4 cm^3g^{-1} – measured for a basalt sample at the Lawrence Livermore Laboratory under anaerobic conditions [23].

Plutonium(V/VI)

Under atmospheric conditions, plutonium(V) is generally believed to be the stable oxidation state. If conditions are very oxidising plutonium(VI) may also be present. Some published R_D values that are believed representative of plutonium(V/VI) sorption, and involve basalt and sandstone, are as follows:

- 80 to 500 cm^3g^{-1} - measured for a sandstone sample at Rockwell International Laboratories [23].
- 600 to 1300 cm^3g^{-1} – measured for a basalt sample at Lawrence Livermore Laboratory under aerobic conditions [23].

Comparison with data obtained during the present JNC study

As mentioned previously, there are no data with which to compare the results obtained under strongly reducing conditions (under these conditions, plutonium(III) is predicted to dominate plutonium speciation, Section 5.1).

For the JNC experiments carried out under intermediate and oxidising conditions, it is predicted that plutonium(IV) or (IV)/(V) will dominate speciation (see earlier). The strong sorption measured in most of the JNC experiments (in excess of 10^4 cm^3g^{-1} in most cases) is consistent with the sorption of plutonium as plutonium(IV). Even under oxidising conditions the JNC R_D values are somewhat higher than might be expected for plutonium(V)/(VI), particularly in the case of basalt.

5.3 Parameterisation of Sorption Models

Rocks are a complex mixture of different mineral phases, making representation of the rock surface in a sorption model difficult. Thus, when applying a modelling approach to investigate sorption onto rocks it is common practice to select a mineral that is considered to dominate the sorptive properties of the rock in question and parameterise the model according

to that mineral. To parameterise such a single mineral model, the following methodology is used:

- compilation of available data describing the surface reactions of the mineral of interest. (Data of interest include measurements of surface area, site density, point of zero charge, experimental studies of the sorption of relevant elements and, where practicable, spectroscopic studies designed to investigate speciation of the sorbed element.)
- selection of sorption reactions that are consistent with the compiled data regarding the nature of the sorbed complex.
- modelling or 'fitting' to the available experimental data for the single mineral so that equilibrium constants can be derived for the selected sorption reactions.

Once the model has been parameterised, it may be used in the investigation and interpretation of experimental results for the natural rock samples.

Last year's studies for JNC [8] included parameterisation of a sorption model appropriate for use under strongly reducing conditions. The model was based upon sorption of plutonium(III) species onto a haematite-type surface within the rocks concerned. (Selection of an appropriate sorbing phase is described in last year's final report [8]). No data were found describing plutonium(III) sorption onto iron oxide. Thus, it was necessary to derive a plutonium(III) sorption dataset by fitting to the experimental data obtained for the rocks themselves. The best fit to the data was achieved using a dataset involving sorption of two plutonium(III) carbonates, $\text{Pu}(\text{CO}_3)^+$ and $\text{Pu}(\text{CO}_3)_2^-$, and two plutonium(III) hydrolysis products, $\text{Pu}(\text{OH})^{+2}$ and $\text{Pu}(\text{OH})_2^+$. A full description of the model is given in Reference [8].

This year's work included parameterisation of sorption models appropriate for use under intermediate and oxidising conditions. Data for plutonium(IV) and plutonium(V) sorption onto iron oxides (haematite and goethite) were found, and have been used to derive plutonium(IV) and plutonium(V) sorption datasets. No data were found suitable for parameterisation of a plutonium(VI) model. However, the detailed speciation modelling suggests that it is unlikely that this oxidation state plays an important role in the JNC experiments.

Table 4 summarises the supporting data used when carrying out the haematite and goethite modelling during this year's investigations (surface properties and sorption reactions involving groundwater ions). The dataset derived for plutonium(III) sorption during last year's studies is shown in Table 5.

In Section 5.4, application of the plutonium(III), (IV) and (V) datasets to the data obtained for basalt and sandstone is described.

All sorption modelling has been carried out using the HATCHES database in conjunction with the revised JNC plutonium thermodynamic dataset.

5.3.1 Parameterisation of Iron Oxide Based Models for Plutonium(IV) Sorption

Experimental sorption data are available for plutonium(IV) sorption onto goethite [25] and haematite (unpublished AEA Technology data). These data include a range of experimental conditions (e.g. a range of pH values, and concentrations of carbonate) and are suitable for

use to parameterise sorption models. For robust models, it is preferable to parameterise against data obtained over as wide a range of appropriate conditions as possible. The above studies included modelling, and plutonium(IV) sorption modelling datasets were available [25, unpublished AEA Technology data]. However, these datasets involved the sorption of aqueous plutonium carbonate species that are not present in the revised JNC thermodynamic dataset, e.g. $\text{Pu}(\text{CO}_3)_2^0$ and $\text{Pu}(\text{CO}_3)_3^{2-}$. A new set of plutonium reactions more appropriate for use with the JNC thermodynamic dataset were adopted as part of the current study. A comparison of the sorbing species in the original plutonium(IV) sorption dataset and those in the revised dataset is given below:

<u>Original sorbing species</u>	<u>Sorbing species in revised dataset</u>
$\text{Pu}(\text{OH})_4^0$	$\text{Pu}(\text{OH})_4^0$
$\text{Pu}(\text{OH})_3^+$	
$\text{Pu}(\text{CO}_3)_2^0$	$\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$
$\text{Pu}(\text{CO}_3)_3^{2-}$	

Equilibrium constants for the new sorption reactions were obtained by fitting to the literature experimental datapoints. The final plutonium(IV) datasets are summarised in Table 6. Comparisons of the experimental and modelled data for haematite are shown in Table 7 and for goethite in Figure 11.

Model sensitivity to carbonate conditions

To investigate the potential sensitivity of the model to carbonate conditions, a suite of calculations were carried out to predict plutonium(IV) sorption behaviour (onto haematite) as a function of the partial pressure of CO_2 and at different pH values. The sorption reactions given in Table 6 were used. The model predictions are illustrated in Figure 12. Interestingly, the model predicts that at neutral pH, plutonium sorption remains relatively constant over a wide range of CO_2 partial pressure. At pH 8, however, sorption is reduced significantly at high CO_2 partial pressures. In the model, this effect can be explained by the fact that at high CO_2 partial pressures (>1 atmosphere, $\log p\text{CO}_2 -3.5$), sorption is controlled by the combined sorption of $\text{Pu}(\text{OH})_4^0$ and $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$. The $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ species would be expected to sorb more strongly at more acidic pH values and so maintain sorption in the presence of carbonate at a high level when the water is neutral or slightly acidic. However, when the pH increases, sorption of the charged species decreases sharply and the net effect is a reduction in sorption in the presence of carbonate.

The model presented above suggests that the effect of pH and the effect of carbonate on plutonium(IV) sorption behaviour are intimately inter-related. To represent the system adequately in the laboratory a potentially large matrix of experiments would be necessary, covering a range of pH values and range of carbonate conditions. Such a large matrix of experiments is out of the scope of most investigations. Laboratory studies to date have generally involved a subset of the range of conditions possible and available datasets appear to give conflicting information about the sensitivity of plutonium(IV) sorption to the presence of carbonate (see discussion in last year's final report [8]). For example, the Sanchez et al. data (describing plutonium(IV) sorption onto goethite) showed that sorption was significantly reduced at high concentrations of carbonate [25], whereas unpublished AEA Technology data for haematite (the data used to parameterise the model in the current study) gave uniformly strong sorption at all carbonate conditions studied. These apparently conflicting trends can be explained by the model in the following ways:

- The Sanchez et al. data were obtained at a constant pH value of 8.6. At this pH, the model suggests that plutonium(IV) sorption will be very sensitive to carbonate conditions.
- The AEA Technology data at high CO₂ partial pressures were obtained at pH ~7, i.e. a pH value where sorption remains high even in the presence of high carbonate concentrations.

The modelling carried out in the current study has resulted in an interpretation of plutonium(IV) sorption behaviour which is consistent with all the available experimental data (despite the initial appearance that opposing experimental trends are observed). The ability of the model to reproduce the experimental trends gives confidence in the model parameters used.

5.3.2 Parameterisation of Iron Oxide Based Models for Plutonium(V) Sorption

Laboratory sorption data are available for plutonium(V) sorption onto goethite over a range of experimental conditions [25]. Data for plutonium(V) sorption onto haematite are more limited and comprise single datapoints [26, 27].

The best fit to the goethite experimental data was achieved using equilibrium constants of -20.75 and 4.0 for sorption of PuO_2^+ and $\text{PuO}_2\text{CO}_3^-$, respectively. The modelled and experimental data are illustrated in Figure 13. The model has been fitted to the data obtained after an equilibration time of 1 hour, rather than to data obtained after longer experimental timescales. This is because over time, there is evidence that plutonium(V) is reduced to plutonium(IV) on the goethite surface. By selecting the data obtained after 1 hour there is a greater likelihood that the data represents sorption of plutonium(V). However, if in the experimental system, significant plutonium(IV) is present on the goethite surface even at short times, then the modelling approach adopted may not be appropriate.

To extrapolate the goethite constants for use with a haematite model a 'two-component' equilibrium approach was used. To use this approach it is assumed that a typical sorption reaction can be considered to comprise:

- an initial protonation/deprotonation step, K1;
- a subsequent interaction step (K2) between the aqueous species and the charged sorbing site.

The approach is based on the principle that, although the equilibrium constants (the intrinsic acidity constants) for the K1 component of the reaction vary from mineral to mineral, the constants for the K2 component remain the same. Thus, stability constants can be calculated for sorption onto the mineral of interest based on data for another mineral.

Using the two-component equilibrium approach, equilibrium constants of -19.98 and 3.63 were calculated for sorption of PuO_2^+ and $\text{PuO}_2\text{CO}_3^-$ onto goethite, respectively. The details of the calculations were:

Sorption of PuO_2^+

	K1	K2	K _{total}
Goethite	-9.52	-11.23	-20.75
Haematite	-8.75	-11.23	-19.98

Sorption of $\text{PuO}_2\text{CO}_3^-$

	K1	K2	K _{total}
Goethite	5.57	-1.57	4
Haematite	5.20	-1.57	3.63

These calculated plutonium(V) sorption constants were used, along with the haematite dataset given in Table 4, to model sorption onto haematite under the experimental conditions of the literature datapoints given in References [26] and [27]. Using this dataset, sorption was significantly overestimated relative to the measured data. To correct this, the equilibrium constants were reduced pro rata (i.e. keeping their relative magnitudes constant), until good agreement with the datapoints was achieved. Table 8 summarises the calculations carried out to derive the plutonium(V) haematite model. A good fit to both experimental datapoints was achieved using equilibrium constants of -22 and -1 for the sorption of PuO_2^+ and $\text{PuO}_2\text{CO}_3^-$, respectively. The experiments were carried out under different carbonate conditions. The ability of the model to reproduce the observed data in both cases gives some confidence in the model parameters used. However, it should be emphasised that a more ideal approach would include validation of the model against data for haematite obtained over a wider range of conditions.

The final plutonium(V) sorption dataset for haematite and goethite are given in Table 6.

5.4 Application of Iron Oxide Based Models to the JNC Experimental Data

During this year's study, models based on both haematite and goethite were applied to the data. Haematite was used in the first instance as it is believed to be the most appropriate iron oxide (see last year's report [8] for further discussion of this topic). The haematite model was found to underestimate sorption in many cases. To investigate whether a less crystalline iron oxide could give results closer to the measured values, further calculation were carried out using a goethite model.

5.4.1 Haematite-based Model

As mentioned previously, last year's studies used a model based upon sorption onto a haematite-type surface within the rocks concerned. The justification for selection of haematite as an appropriate sorbing phase was discussed in last year's final report [8]. A set of sorption reactions are now available for plutonium(III), (IV) and (V) sorption onto haematite (shown in Tables 5 and 6). In the following calculations, all of these sorption reactions were included in each input file.

To apply this model to the JNC experimental data for basalt and sandstone it is necessary to quantify the amount of rock surface occupied by haematite. As discussed in last year's report [8], this quantity is very difficult to measure directly. The approach adopted last year was to assume, as a first approximation, that 1wt% haematite was present in all the rock types studied. An alternative approach is to assume that all of the rock surface is covered with a thin layer of haematite. Thus, the surface area of haematite present in the sample is assumed to be equivalent to the measured total surface area of the sample. The latter approach is likely to overestimate the surface area of haematite (and consequently sorption), whereas the former approach is likely to underestimate the available haematite surface area. The two approaches can thus be considered to define an envelope, within which the true value could lie.

The results of modelling calculations using the two approaches are given in Tables 9 and 10. The model predictions are potentially sensitive to carbonate concentration, as discussed previously in Section 5.3.1. This is important in the case of the basalt calculations, because there is uncertainty in the carbonate concentration in the solution (being below the limit of detection, approximately $8 \times 10^{-5} \text{ mol dm}^{-3}$). Sensitivity calculations showed that predictions of sorption under strongly reducing conditions were extremely sensitive to this parameter; predicted R_D values were reduced by orders of magnitude if very low carbonate concentrations are assumed, e.g. around $10^{-7} \text{ mol dm}^{-3}$. Predictions carried out under intermediate and oxidising conditions were not significantly affected. The results of the sensitivity calculations have been added to Tables 9 and 10.

The sensitivity of the model under strongly reducing conditions, i.e. plutonium(III), to carbonate conditions is worthy of further discussion. The model was developed during last year's studies and was parameterised to fit experimental data that showed a slight trend toward increased sorption at higher carbonate concentrations. This explains the predicted trend. However, the degree of sensitivity exhibited in the current calculations is unexpected. It would appear that the model is affected strongly by pH, and that the predicted degree of sensitivity to carbonate is stronger at pH 8 (the pH value for this year's work) than at pH 10 to 11 (the pH value of last year's work with rock-equilibrated de-ionised water, and also the pH at which the model was fitted). As this year's experiments were carried out at only one carbonate concentration, there are not sufficient experimental data with which to test the predicted behaviour at pH 8. It must be remembered, therefore, that the model has not been tested under the range of conditions to which it is now being applied.

The model predictions are illustrated in Figures 14 and 15 and compared to the experimentally measured R_D values. The following comments can be made.

Under strongly reducing conditions

- Plutonium(III) species are predicted to sorb.
- The model has a tendency to overestimate sorption (for both basalt and sandstone).

The plutonium(III) model is very sensitive to carbonate conditions. In the case of the basalt experiments, there is some uncertainty as to the exact carbonate concentration in the experimental solutions (the concentration was below detection limits). Measurable carbonate was present in the sandstone solutions, but associated with a $\pm 10\%$ error. If lower carbonate concentrations are assumed then predicted R_D values would be significantly reduced, more in line with the measured values (e.g. see basalt calculations).

Under intermediate and oxidising conditions

Basalt

- Sorption onto basalt is significantly underpredicted (even when assuming that the entire rock surface is covered with haematite).
- Sorption is dominated by the plutonium(IV) species, $\text{Pu}(\text{OH})_4^0$.
- No significant plutonium(V) sorption is predicted.

Sandstone

- The model tends to slightly underpredict sorption. The model does however reproduce the slight drop in sorption as the conditions become more oxidising. In the model this drop can be explained by changes in the predicted sorbed species as the conditions become more oxidising.
- Under intermediate conditions, sorbed species are predicted to be a combination of plutonium(III) carbonates and $\text{Pu}(\text{OH})_4^0$.
- Under the oxidising conditions of the experiments, only $\text{Pu}(\text{OH})_4^0$ sorbs. No significant plutonium(V) sorption is predicted.

The plutonium(IV) component of the system is predicted to play an important role. The plutonium(IV) model has been tested against independent data obtained over a range of experimental conditions (see Section 5.3.1). There is therefore some confidence in the model parameters used. The 'closeness of fit', or the ability of the model to reproduce the JNC experimental data, can be interpreted as an indicator of whether or not haematite gives a good representation of the main sorbing surface in the rock (one of the underlying assumptions for the modelling approach adopted in the current work). In the case of the sandstone calculations, the model reproduces the experimental data quite well, although tending to underestimate sorption slightly. This could suggest that haematite gives a good representation of the main sorbing surface in the sandstone. In the case of the basalt calculations, the model significantly underestimates sorption. This could suggest that a haematite surface alone does not give the best representation of the sorbing surface in the basalt, and that an approach based on an alternative mineral could reproduce more accurately the experimental data.

5.4.2 Goethite-based Model

The haematite-based model tended to underestimate sorption under intermediate and oxidising conditions (Section 5.4.1). It is possible that an approach based on a less crystalline iron oxide could reproduce the experimental data more accurately. As part of the current study, a set of sorption reactions were derived for plutonium(IV) and plutonium(V) sorption onto goethite (Sections 5.3.1 and 5.3.2). Calculations have been carried out to apply a goethite-based model to the JNC data. As with the haematite-based modelling, two methods were used to estimate the amount of goethite surface present in the samples:

- assuming 1wt% goethite was present in the samples, and;
- assuming that the entire rock surface was covered by goethite.

The results of calculations using this model are given in Tables 11 and 12. Using the goethite-based model, higher R_D values are predicted than using the haematite-based model. However, sorption onto the basalt is still significantly underestimated. Interestingly, using the goethite-based model, there are changes to the types of species predicted to sorb:

- the plutonium(IV) carbonate species, $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$, plays a more important role;
- significant sorption of the plutonium(V) carbonate species, $\text{PuO}_2\text{CO}_3^-$, is predicted under oxidising conditions.

Using the goethite-based model, there is a slight increase in the sensitivity of the model to carbonate conditions (probably due to the increased importance of sorbed plutonium(IV) and plutonium(V) carbonate species).

Using the goethite-based model, there is a slight increase in the sensitivity of the model to carbonate conditions (probably due to the increased importance of sorbed plutonium(IV) and plutonium(V) carbonate species).

5.5 Potential Role of Alternative Sorbing Phases

The modelling described in the current study has suggested that models based on iron oxide phases gives a good representation of the dominant sorbing surface in the sandstone. However, these iron oxide-based models were found to underestimate sorption onto the basalt (under intermediate and oxidising conditions).

It is possible that, in the case of the basalt sample, an alternative mineral or combination of minerals controls sorption. As mentioned in the Year 8 final report [8], it would be useful to evaluate the role of chlorite and biotite. Both minerals are present as primary phases within the basalt, and have been identified as highly sorptive with respect to plutonium (chlorite was also identified within the sandstone sample). Other primary minerals present in the basalt that might contribute to sorption are the ferromagnesian minerals, pyroxene and olivine. Although, no data are available to assess the sorptive capacity of these minerals, the composition of their surfaces include Fe-O sites that could potentially interact with plutonium.

It has not been possible to carry out a more rigorous evaluation of any of these alternative minerals in the current work, largely because data suitable for parameterisation of a sorption model involving these phases are unavailable.

6 DISCUSSION AND CONCLUSIONS

Batch sorption experiments have shown that sorption of plutonium onto basalt and sandstone at pH 8 is strong under both strongly-reducing and intermediate conditions. R_D values after 3 months' equilibration are generally of the order of $10^4 \text{ cm}^3 \text{ g}^{-1}$ following $0.45 \mu\text{m}$ and 10000MWCO filtration. For plutonium under oxidising conditions, sorption is slightly less strong, R_D values following $0.45 \mu\text{m}$ filtration being one to two orders of magnitude less than for plutonium(IV) in the case of basalt, and about one order of magnitude less in the case of sandstone. After 10000MWCO filtration, R_D values for basalt are similar to those for plutonium(III) and plutonium(IV), but about an order of magnitude less in the case of sandstone. In the case of basalt, there is evidence for colloid formation in the size range 10000MWCO to $0.45 \mu\text{m}$ for both oxidising and intermediate conditions.

Thermodynamic chemical modelling was undertaken to aid the planning of the experiments, and to interpret the results. Geochemical modelling to predict the aqueous speciation of plutonium over the range of experimental redox conditions predicted the following:

- strongly reducing: Pu(III) species dominate.
- intermediate: Pu(IV) species dominate.
- oxidising: likely to be Pu(IV)/Pu(V) but some uncertainty in thermodynamic data.

Sorption models have been applied to assist in the interpretation of the JNC experimental data. These models are based on sorption onto iron oxide type surfaces within the rocks. A plutonium(III) sorption model was derived in last year's programme of work. This year's

programme of work included parameterisation of a Pu(IV) and Pu(V) sorption model. These models have been used to predict the sorption of plutonium onto basalt and sandstone under the under the strongly reducing, intermediate and oxidising conditions.

The main points arising from the modelling were:

- The iron oxide models developed were able to adequately reproduce the data for sorption of plutonium onto sandstone, but tended to underpredict sorption onto basalt. Although not possible to evaluate rigorously in the current work, it is believed that alternative minerals (e.g. biotite, pyroxene) could contribute to sorption in the case of basalt.
- The species predicted to dominate sorption were plutonium (III) under strongly reducing conditions, and various combinations of plutonium(III) and plutonium(IV) under intermediate and oxidising conditions. Plutonium(V) species were not predicted to play an important role.

7 ACKNOWLEDGEMENT

This work is funded by JNC, as part of the Safety Assessment Programme for a potential Japanese HLW Repository.

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TABLE 1 ANALYSIS OF DE-IONISED WATER AFTER EQUILIBRATION FOR FOUR WEEKS WITH BASALT AND SANDSTONE AT ROOM TEMPERATURE

Species	After Equilibration with Basalt / $\mu\text{g cm}^{-3}$	After Equilibration with Sandstone/ $\mu\text{g cm}^{-3}$
Al	0.89	1.1
B	0.11	0.18
Ca	15	4.8
Fe	0.043	0.08*
K	10*	10*
Mg	3.3	1*
Na	44	≤ 4
Si	24	5.4
Sr	0.05	0.14
F ⁻	0.36	0.04
Cl ⁻	8.3	1.9
Br ⁻	≤ 0.06	≤ 0.06
SO ₄ ²⁻	5.5	6.1
CO ₃ ²⁻	≤ 5	18
†Final pH	†10.8	†10.0

Samples were filtered through a 10000 MWCO filter prior to analysis.

* represents results within an order of magnitude of the detection limit. These have a higher uncertainty than the $\pm 10\%$ of the other values.

† pH adjusted to ~8 using hydrochloric acid

TABLE 2 SORPTION OF PLUTONIUM ONTO BASALT AND SANDSTONE UNDER VARIOUS REDOX CONDITIONS

Rock	Redox Agent	Final pH	Final Eh mV vs. S.H.E.	R_D $\text{cm}^3 \text{g}^{-1}$		
				Centrifuged	0.45 μm	10000MWCO
Basalt	$\text{Na}_2\text{S}_2\text{O}_4$	8.0	-480	$8.9 \times 10^2 \pm 0.9 \times 10^2$	$1.6 \times 10^4 \pm 0.1 \times 10^4$	$1.7 \times 10^4 \pm 0.2 \times 10^4$
		8.1	-490	$7.9 \times 10^2 \pm 0.7 \times 10^2$	$1.1 \times 10^4 \pm 0.1 \times 10^4$	$1.2 \times 10^4 \pm 0.1 \times 10^4$
	$\text{NH}_2\text{OH.HCl}$	8.1	+50	$5.2 \times 10^2 \pm 0.5 \times 10^2$	$3.7 \times 10^4 \pm 0.3 \times 10^4$	$3.6 \times 10^5 \pm 0.6 \times 10^5$
		8.1	+40	$2.5 \times 10^2 \pm 0.2 \times 10^2$	$6.7 \times 10^3 \pm 0.6 \times 10^3$	$6.6 \times 10^4 \pm 0.7 \times 10^4$
	H_2O_2	8.1	+350	$1.2 \times 10^2 \pm 0.1 \times 10^2$	$8.2 \times 10^2 \pm 0.7 \times 10^2$	$4.4 \times 10^4 \pm 0.4 \times 10^4$
		8.2	+350	$1.2 \times 10^2 \pm 0.1 \times 10^2$	$9.4 \times 10^2 \pm 0.8 \times 10^2$	$1.7 \times 10^4 \pm 0.2 \times 10^4$
Sandstone	$\text{Na}_2\text{S}_2\text{O}_4$	8.0	-490	$1.1 \times 10^3 \pm 0.1 \times 10^3$	$1.5 \times 10^4 \pm 0.2 \times 10^4$	$1.8 \times 10^4 \pm 0.2 \times 10^4$
		8.1	-500	$1.2 \times 10^3 \pm 0.1 \times 10^3$	$2.2 \times 10^4 \pm 0.2 \times 10^4$	$2.9 \times 10^4 \pm 0.3 \times 10^4$
	$\text{NH}_2\text{OH.HCl}$	8.1	-40	$5.2 \times 10^2 \pm 0.5 \times 10^2$	$5.3 \times 10^4 \pm 0.5 \times 10^4$	$4.8 \times 10^4 \pm 0.5 \times 10^4$
		8.0	-40	$3.8 \times 10^2 \pm 0.3 \times 10^2$	$2.3 \times 10^4 \pm 0.2 \times 10^4$	$2.9 \times 10^4 \pm 0.3 \times 10^4$
	H_2O_2	8.1	+370	$8.8 \times 10^2 \pm 0.8 \times 10^2$	$4.8 \times 10^3 \pm 0.4 \times 10^3$	$5.4 \times 10^3 \pm 0.5 \times 10^3$
		8.0	+370	$7.6 \times 10^2 \pm 0.7 \times 10^2$	$5.8 \times 10^3 \pm 0.5 \times 10^3$	$5.5 \times 10^3 \pm 0.4 \times 10^3$

Errors shown are 2σ and are based on counting statistics alone. Initial plutonium-238 concentrations $6.9 \times 10^{-11} \text{ mol dm}^{-3}$ to $1.1 \times 10^{-10} \text{ mol dm}^{-3}$

TABLE 3 SORPTION OF PLUTONIUM ONTO THE VESSEL WALLS

Rock	Redox Agent Present	Plutonium on Vessel Walls (%)
Basalt	Sodium dithionite	0.09
	Hydroxy ammonium chloride	0.13
	Hydrogen peroxide	0.38
Sandstone	Sodium dithionite	0.11
	Hydroxy ammonium chloride	0.05
	Hydrogen peroxide	0.07

TABLE 4 SURFACE PROPERTIES OF HAEMATITE AND EQUILIBRIUM CONSTANTS FOR INTERACTIONS BETWEEN THE SURFACE AND SOLUTION IONS

Surface properties		
	Haematite	Goethite
Surface area / m ² g ⁻¹	1.8	51.8
Site density / mol m ⁻²	1.67 10 ⁻⁵	4.25 10 ⁻⁶
Inner capacitance / F m ⁻²	0.9	1.4
Outer capacitance / F m ⁻²	0.2	0.2
Point of zero charge	pH 7.0	pH 7.1
Surface reactions with equilibrium constants		
	Log K values	
	Haematite	Goethite
SOH = SO ⁻ + H ⁺	-8.75	-9.52
SOH + H ⁺ = SOH ₂ ⁺	+5.2	+5.57
SOH + Na ⁺ = [SO ⁻ -Na ⁺] ⁰ + H ⁺	-7.95	-8.4
SOH + K ⁺ = [SO ⁻ -K ⁺] ⁰ + H ⁺	-7.95	-8.4
SOH + H ⁺ + Cl ⁻ = [SOH ₂ ⁺ -Cl ⁻] ⁰	+6.0	+7.0
SOH + H ⁺ + NO ₃ ⁻ = [SOH ₂ ⁺ -NO ₃ ⁻] ⁰	+6.0	+7.0
SOH + Mg ²⁺ = [SO ⁻ -Mg ²⁺] ⁺ + H ⁺	-4.68	-5.45
SOH + Mg ²⁺ + H ₂ O = [SO ⁻ -MgOH ⁺] ⁰ + 2H ⁺	-14.48	-15.25
SOH + Ca ²⁺ = [SO ⁻ -Ca ²⁺] ⁺ + H ⁺	-4.23	-5.0
SOH + Ca ²⁺ + H ₂ O = [SO ⁻ -CaOH ⁺] ⁰ + 2H ⁺	-14.73	-15.5
SOH + H ⁺ + SO ₄ ²⁻ = [SOH ₂ ⁺ -SO ₄ ²⁻] ⁻	+8.73	+9.1
SOH + 2H ⁺ + SO ₄ ²⁻ = [SOH ₂ ⁺ -HSO ₄ ⁺] ⁰	+14.03	+14.4
SOH + H ⁺ + CO ₃ ²⁻ = [SOH ₂ ⁺ -CO ₃ ²⁻] ⁻ (inner-sphere reaction)	+10.22	+10.59
SOH + 2H ⁺ + CO ₃ ²⁻ = [SOH ₂ ⁺ -HCO ₃ ⁺] ⁰	+19.27	+19.64

Unless otherwise indicated, formation of an outer-sphere adsorbed complex is represented by the sorption reactions

TABLE 5 PLUTONIUM(III) SORPTION DATASET (DERIVED BY FITTING TO THE EXPERIMENTAL DATA OBTAINED DURING LAST YEAR'S STUDY)

Reaction	Equilibrium constant (log K)
SOH + Pu ⁴⁺ + e ⁻ + H ₂ O - 2H ⁺ = [SO ⁻ -Pu(OH) ²⁺] ⁺	+7.35
SOH + Pu ⁴⁺ + e ⁻ + 2H ₂ O - 3H ⁺ = [SO ⁻ -Pu(OH) ₂ ⁺] ⁰	+1.14
SOH + Pu ⁴⁺ + e ⁻ + CO ₃ ²⁻ - H ⁺ = [SO ⁻ -PuCO ₃ ⁺] ⁰	+25.25
SOH + Pu ⁴⁺ + e ⁻ + 2CO ₃ ²⁻ + H ⁺ = [SOH ₂ ⁺ -Pu(CO ₃) ₂] ⁰	+47.09

All reactions involve formation of an inner-sphere adsorbed complex. Equilibrium constants derived by fitting to JNC rock data during Year 8 JNC studies (appropriate for use with haematite supporting data).

TABLE 6 PLUTONIUM(IV) and PLUTONIUM(V) SORPTION DATASETS (DERIVED BY FITTING TO THE APPROPRIATE SINGLE MINERAL DATA DURING THIS YEAR'S STUDY)

Reaction	Equilibrium constant (log K)	
	Haematite	Goethite
Plutonium(IV)		
$\text{SOH} + \text{Pu}^{4+} + 4\text{H}_2\text{O} - 4\text{H}^+ = [\text{SOH-Pu}(\text{OH})_4]^0$	-4.5	-3.5
$\text{SOH} + \text{Pu}^{4+} + 2\text{H}_2\text{O} + 2\text{CO}_3^{2-} - \text{H}^+ = [\text{SOH}_2^+ \text{-Pu}(\text{OH})_2(\text{CO}_3)_2]^{2-}$	+29.1	+33.0
Plutonium(V)		
$\text{SOH} + \text{Pu}^{4+} + 2\text{H}_2\text{O} - 5\text{H}^+ - \text{e}^- = [\text{SO}^- \text{-PuO}_2^+]^0 5\text{H}^+ + \text{e}^-$	-22.0	-20.75
$\text{SOH} + \text{Pu}^{4+} + 2\text{H}_2\text{O} + \text{CO}_3^{2-} - 3\text{H}^+ - \text{e}^- = [\text{SOH}_2^+ \text{-PuO}_2\text{CO}_3]^{0-}$	-1.0	+4.0

All reactions involve formation of an inner-sphere adsorbed complex.

TABLE 7 COMPARISON OF EXPERIMENTAL AND MODELLED DATA FOR PLUTONIUM(IV) SORPTION ONTO HAEMATITE

Experimental conditions			$R_D, \text{cm}^3 \text{g}^{-1}$	
pH	Atmosphere	$\log_{10} p\text{CO}_2$	Experimental	Modelled
8.3	N ₂ glove box	-7	1500	1300
7.9	N ₂ glove box	-7	780	1300
7.4	Atmospheric	-3.5	1400	1300
7.5	Atmospheric	-3.5	2000	1300
7.0	Mixed CO ₂ /N ₂ glovebox	-2.1	1800	1700
7.1	Mixed CO ₂ /N ₂ glovebox	-2.1	1100	1300

TABLE 8 SUMMARY OF THE CALCULATIONS CARRIED OUT TO DERIVE A MODEL OF PLUTONIUM(V) SORPTION ONTO HAEMATITE

	Ticknor et al study [26]	Triay et al study [27]
Summary of experiments	Study of plutonium sorption onto ten different minerals under different O ₂ conditions, and using solutions of varying salinity	Study of plutonium sorption onto tuffs and single mineral separates
Summary of experimental conditions for the selected haematite datapoint	Atmospheric O ₂ conditions Low salinity solution ('140TDS') Initial pH = 7.5 (final pH = 8-8.5) Initial conc. Pu 1.49 x 10 ⁻¹⁰ M Speciation Pu 67% Pu(V):33% Pu(IV) (analysed using a liquid:liquid extraction technique)	CO ₂ overpressure (value not given) Low salinity solution (J-13 water) pH 7 Initial conc. Pu 1.38 x 10 ⁻⁹ M Speciation Pu believed dominated by Pu(V)
Measured R _D value / cm ³ g ⁻¹	>2200	3000, 4000
Modelled values using equilibrium constants derived from goethite model using the two-component equilibrium approach:		
Modelled R _D values / cm ³ g ⁻¹	9 x 10 ⁶	10 ⁸
Modelled values following reduction of equilibrium constants (final values shown in Table 6)		
Modelled R _D values / cm ³ g ⁻¹	3230	4004
Predicted sorbed species	80% PuO ₂ ⁺ :20% PuO ₂ CO ₃ ⁻	90% PuO ₂ CO ₃ ⁻ : 10% PuO ₂ ⁺

TABLE 9 APPLICATION OF THE HAEMATITE MODEL TO THE JNC EXPERIMENTAL DATA: ASSUMING 1 WT% HAEMATITE PRESENT

			Model predictions		Measured
Eh	pH	Carbonate, mol dm ⁻³	R _D , cm ³ g ⁻¹	Sorbed species	R _D , cm ³ g ⁻¹
Basalt					
-480	8.0	*8.33 x 10 ⁻⁵	1.3 x 10 ⁴ (330, for lower carbonate, see footnote)	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻	1.7 x 10 ⁴
+50	8.1	*8.33 x 10 ⁻⁵	13	^{IV} Pu(OH) ₄ ⁰	3.6 x 10 ⁵
+350	8.1	*8.33 x 10 ⁻⁵	12	^{IV} Pu(OH) ₄ ⁰	4.4 x 10 ⁴
Sandstone					
-490	8.0	3 x 10 ⁻⁴	5.4 x 10 ⁴	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻	1.8 x 10 ⁴
-40	8.1	3 x 10 ⁻⁴	59	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻ ^{IV} Pu(OH) ₄ ⁰	4.8 x 10 ⁴
+370	8.1	3 x 10 ⁻⁴	12	^{IV} Pu(OH) ₄ ⁰	5400

*carbonate concentrations in the basalt-equilibrated water were below the limit of detection (8 x 10⁻⁵ mol dm⁻³). Initial model calculations were based on the detection limit itself. Sensitivity calculations were performed to test how predictions were affected if lower carbonate concentrations were used. For the conditions studied, only the calculations for strongly reducing conditions were sensitive to this parameter; predicted R_D values at -480mV were significantly decreased if lower carbonate concentrations are used, e.g. 330 cm³ g⁻¹ for a carbonate concentration of ~10⁻⁷ mol dm⁻³ (sorbed species now dominated by ^{III}Pu(OH)₂⁺)

TABLE 10 APPLICATION OF THE HAEMATITE MODEL TO THE JNC EXPERIMENTAL DATA: ASSUMING ENTIRE ROCK SURFACE COVERED BY HAEMATITE

			Model predictions		Measured
Eh	pH	Carbonate, mol dm ⁻³	R _D , cm ³ g ⁻¹	Sorbed species	R _D , cm ³ g ⁻¹
Basalt					
-480	8.0	*	1.4 x 10 ⁶ (8.2 10 ⁴ , for lower carbonate, see footnote)	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻	1.7 x 10 ⁴
+50	8.1	*	3099	^{IV} Pu(OH) ₄ ⁰	3.6 x 10 ⁵
+350	8.1	*	3071	^{IV} Pu(OH) ₄ ⁰	4.4 x 10 ⁴
Sandstone					
-490	8.0	3 x 10 ⁻⁴	1.9 x 10 ⁷	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻	1.8 x 10 ⁴
-40	8.1	3 x 10 ⁻⁴	2.2 x 10 ⁴	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻ ^{IV} Pu(OH) ₄ ⁰	4.8 x 10 ⁴
+370	8.1	3 x 10 ⁻⁴	5970	^{IV} Pu(OH) ₄ ⁰	5400

*carbonate concentrations in the basalt-equilibrated water were below the limit of detection (~8 x 10⁻⁵ mol dm⁻³). Initial model calculations were based on the detection limit itself. Sensitivity calculations were performed to test how predictions were affected if lower carbonate concentrations were used. For the conditions studied, only the calculations for strongly reducing conditions were significantly sensitive to this parameter; predicted R_D values at -480mV were significantly decreased if lower carbonate concentrations are used, e.g. 8.2 x 10⁴ cm³ g⁻¹ for a carbonate concentration of ~10⁻⁷ mol dm⁻³ (sorbed species now dominated by ^{III}Pu(OH)₂⁺)

TABLE 11 APPLICATION OF THE GOETHITE MODEL TO THE JNC EXPERIMENTAL DATA: ASSUMING 1 WT% GOETHITE PRESENT

			Model predictions		Measured
Eh	pH	Carbonate, mol dm ⁻³	R _D , cm ³ g ⁻¹	Sorbed species	R _D , cm ³ g ⁻¹
Basalt					
+50	8.1	*	1249 (912, for lower carbonate, see footnote)	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻	3.6 x 10 ⁵
+350	8.1	*	1333 (913)	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻	4.4 x 10 ⁴
Sandstone					
-40	8.1	3 x 10 ⁻⁴	4995	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻	4.8 x 10 ⁴
+370	8.1	3 x 10 ⁻⁴	5348	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻ , ^V PuO ₂ CO ₃ ⁻	5400

*carbonate concentrations in the basalt-equilibrated water were below the limit of detection ($\sim 8 \times 10^{-5}$ mol dm⁻³). Initial model calculations were based on the detection limit itself. Sensitivity calculations were performed to test how predictions were affected if a lower carbonate concentration were used ($\sim 10^{-7}$ mol dm⁻³). The predicted R_D values are shown in parenthesis. In each case, the sorbed speciation changes from a mixture of hydrolysis products and carbonate species, to solely hydrolysis products.

TABLE 12 APPLICATION OF THE GOETHITE MODEL TO THE JNC EXPERIMENTAL DATA: ASSUMING ENTIRE ROCK SURFACE COVERED BY GOETHITE

			Model predictions		Measured
Eh	pH	Carbonate, mol dm ⁻³	R _D , cm ³ g ⁻¹	Sorbed species	R _D , cm ³ g ⁻¹
Basalt					
+50	8.1	*	9805 (7650, for lower carbonate, see footnote)	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻	3.6 x 10 ⁵
+350	8.1	*	10 ⁴ (7654)	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻ ^V PuO ₂ CO ₃ ⁻	4.4 x 10 ⁴
Sandstone					
-40	8.1	3 x 10 ⁻⁴	5.1 x 10 ⁴	^{III} PuCO ₃ ⁺ , ^{III} Pu(CO ₃) ₂ ⁻ ^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻	4.8 x 10 ⁴
+370	8.1	3 x 10 ⁻⁴	5.7 x 10 ⁴	^{IV} Pu(OH) ₄ ⁰ , ^{IV} Pu(OH) ₂ (CO ₃) ₂ ²⁻ ^V PuO ₂ CO ₃ ⁻	5400

*carbonate concentrations in the basalt-equilibrated water were below the limit of detection ($\sim 8 \times 10^{-5}$ mol dm⁻³). Initial model calculations were based on the detection limit itself. Sensitivity calculations were performed to test how predictions were affected if a lower carbonate concentration were used ($\sim 10^{-7}$ mol dm⁻³). The predicted R_D values are shown in parenthesis. In each case, the sorbed speciation changes from a mixture of hydrolysis products and carbonate species, to solely hydrolysis products.

FIGURE 1

**PREPARATION OF PLUTONIUM 'SPIKE' SOLUTIONS IN VARIOUS
OXIDATION STATES**

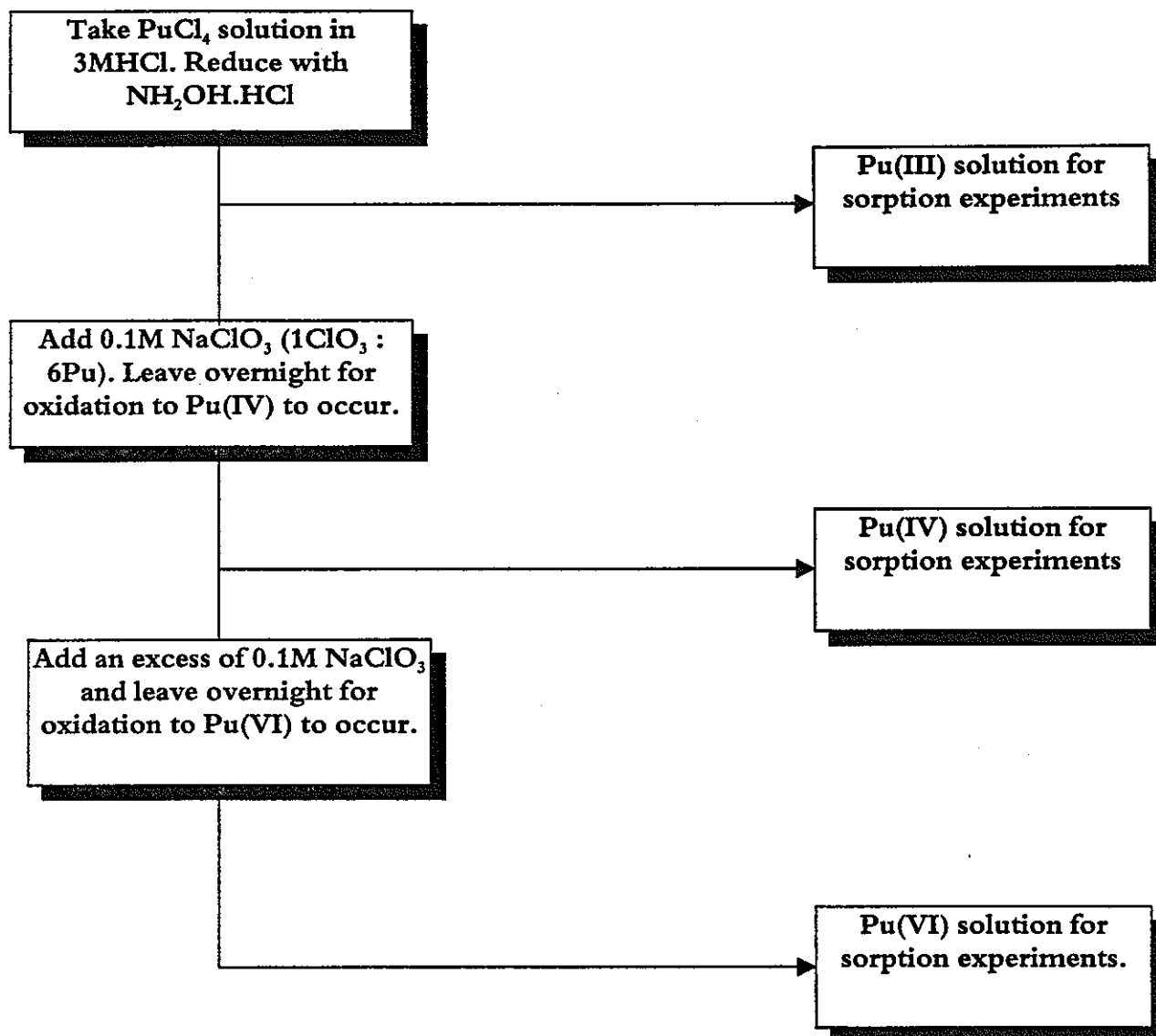


FIGURE 2
Pu(III) SPECTRUM IN 1M HCl (~0.3g/l Pu)

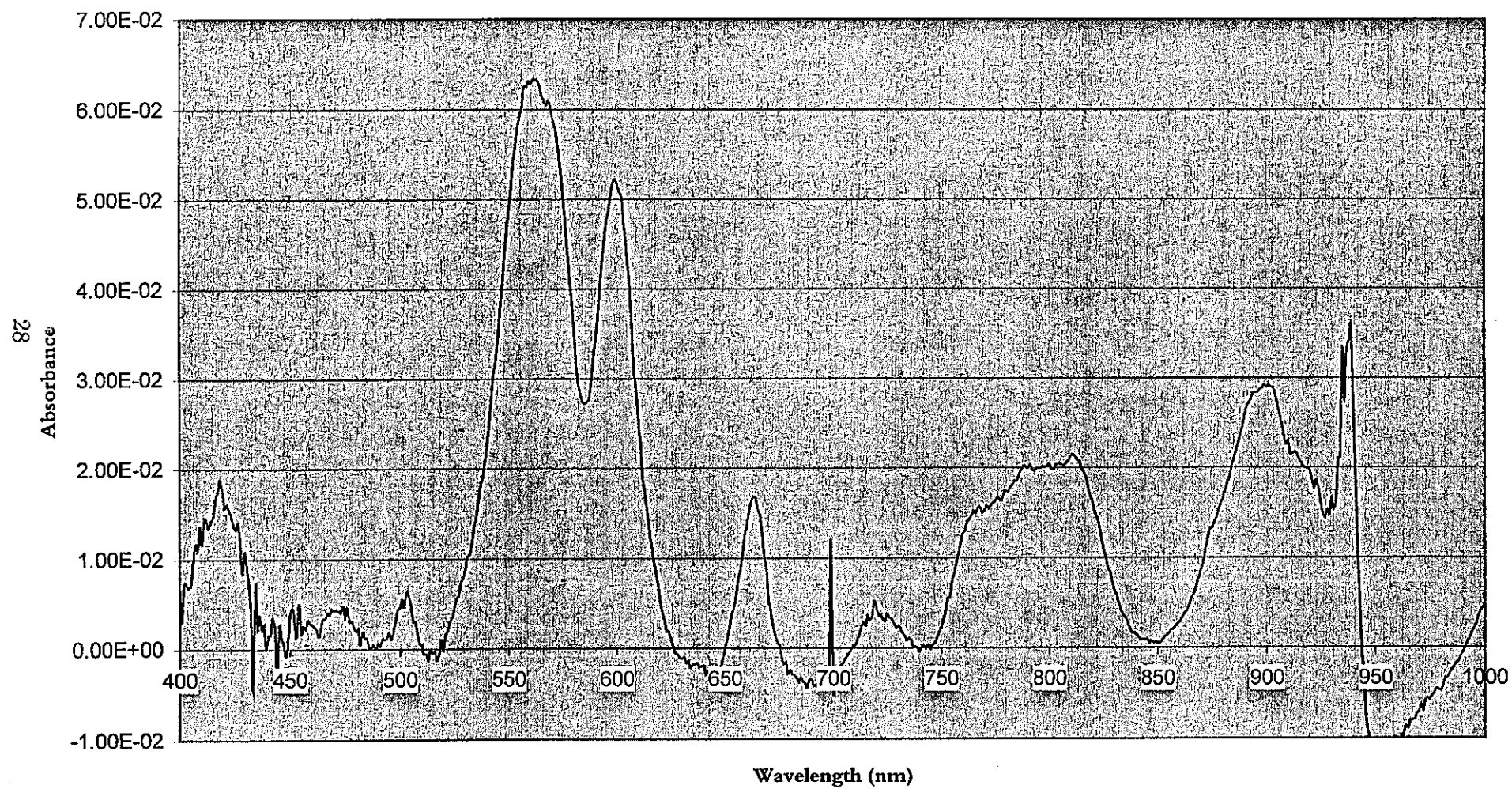


FIGURE 3
Pu(IV) SPECTRUM IN 1M HCl (~0.3g/l Pu)

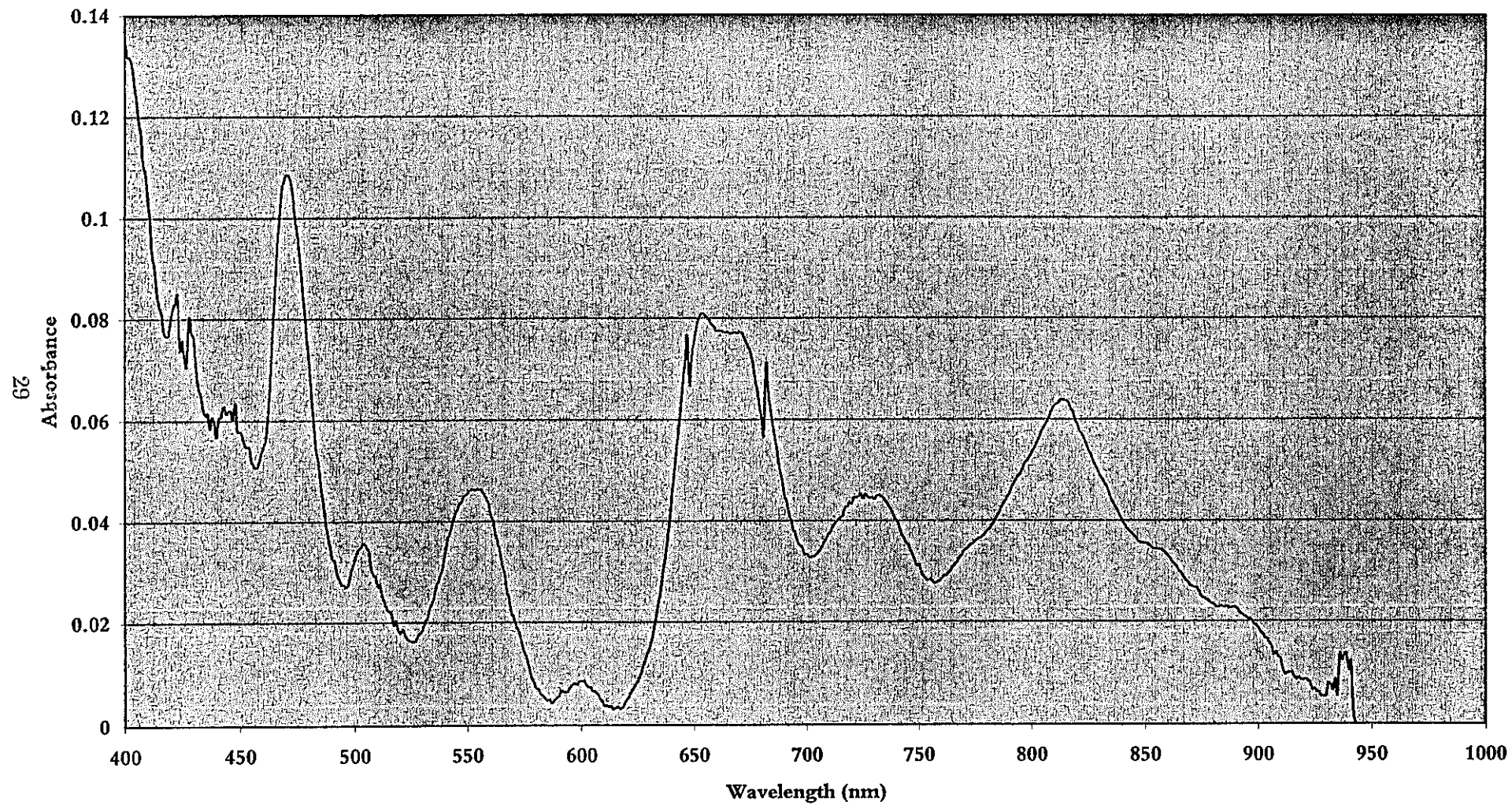


FIGURE 4
Pu(VI) SPECTRUM IN 1M HCl (~0.3g/l Pu)

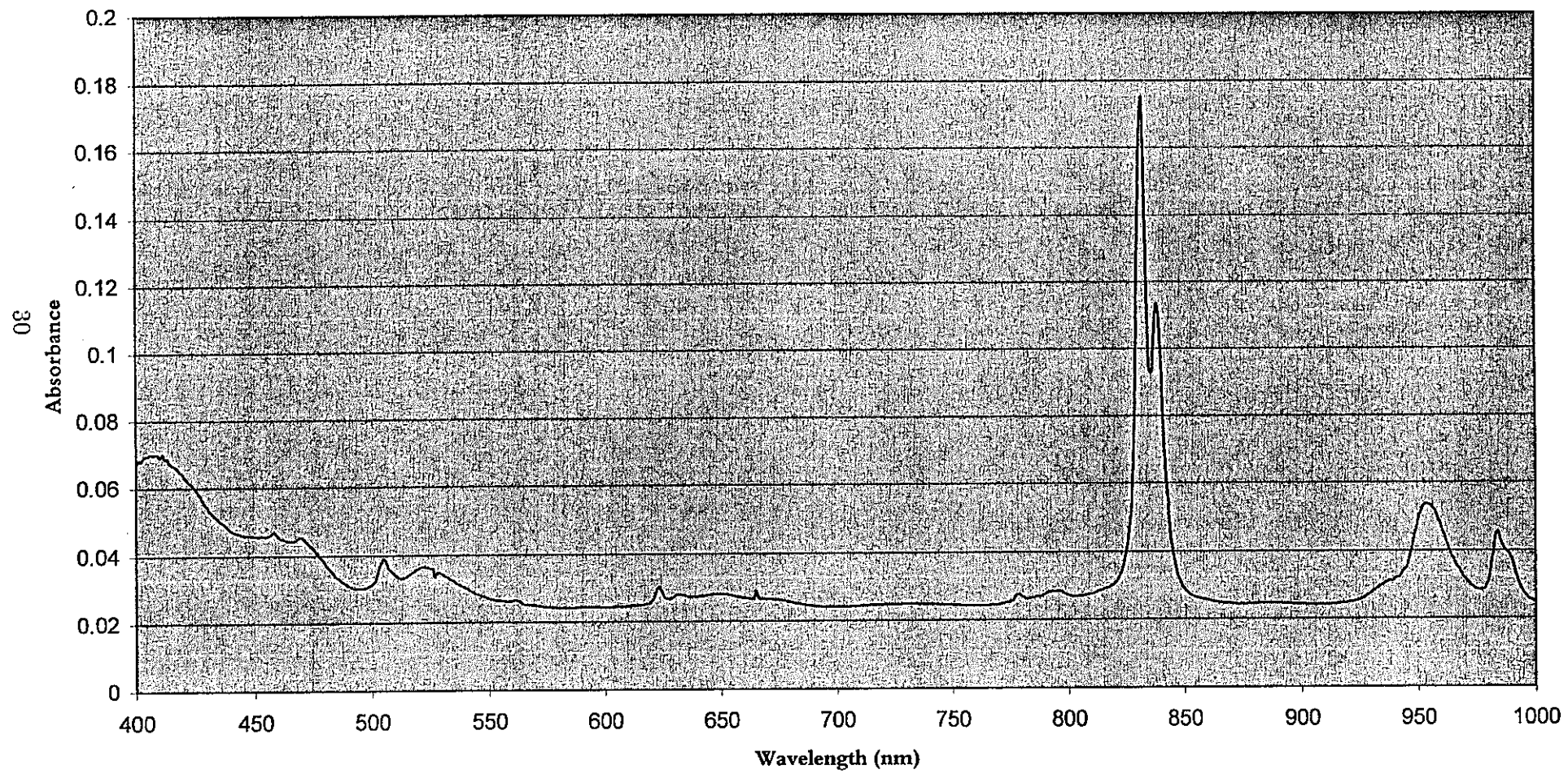


FIGURE 5
FLWSHEET FOR PLUTONIUM BATCH SORPTION EXPERIMENTS

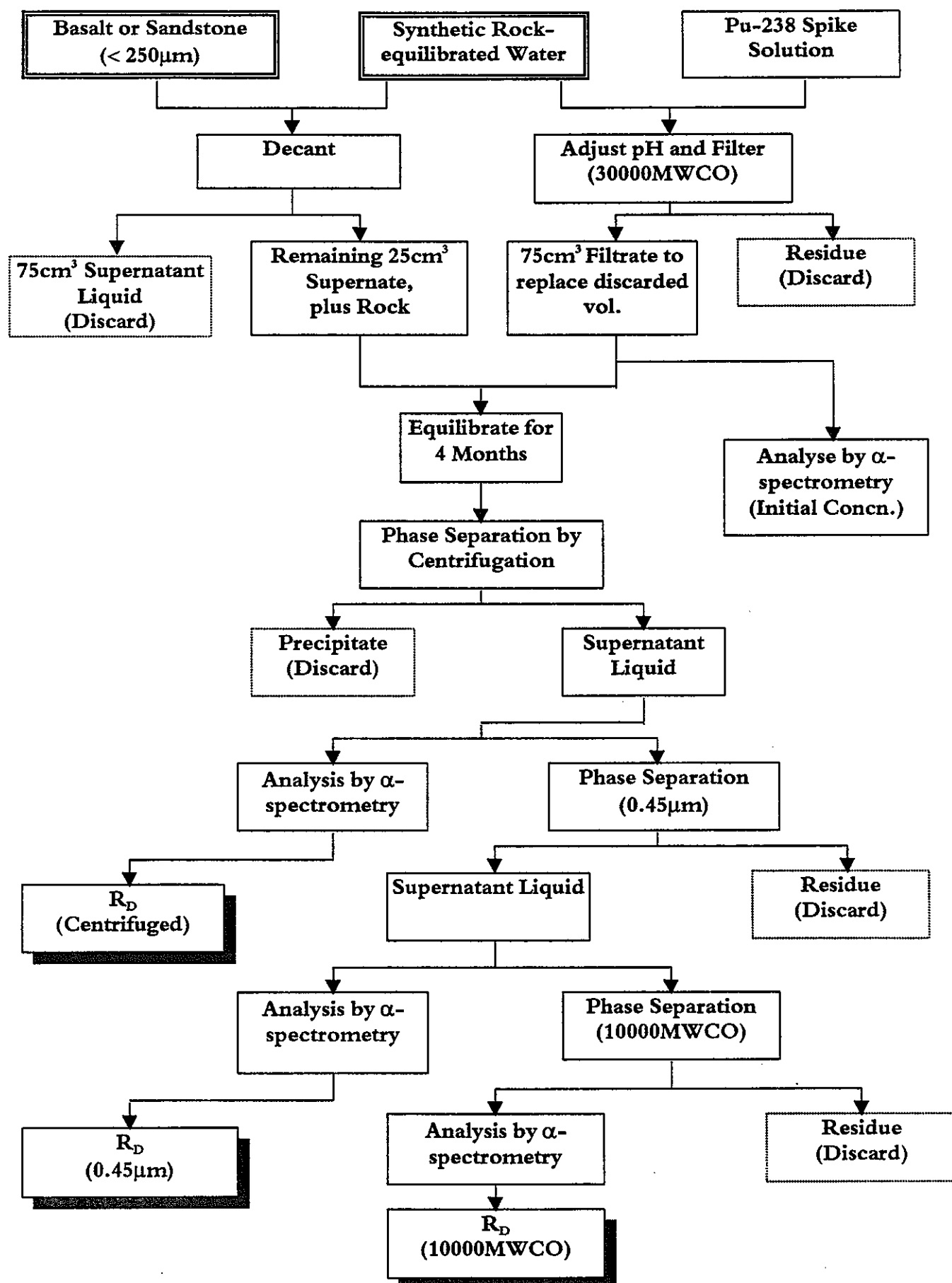


FIGURE 6: Pu Speciation in Basalt-equilibrated De-ionised water at pH8.1
(HATCHES NEA12_R2 data)

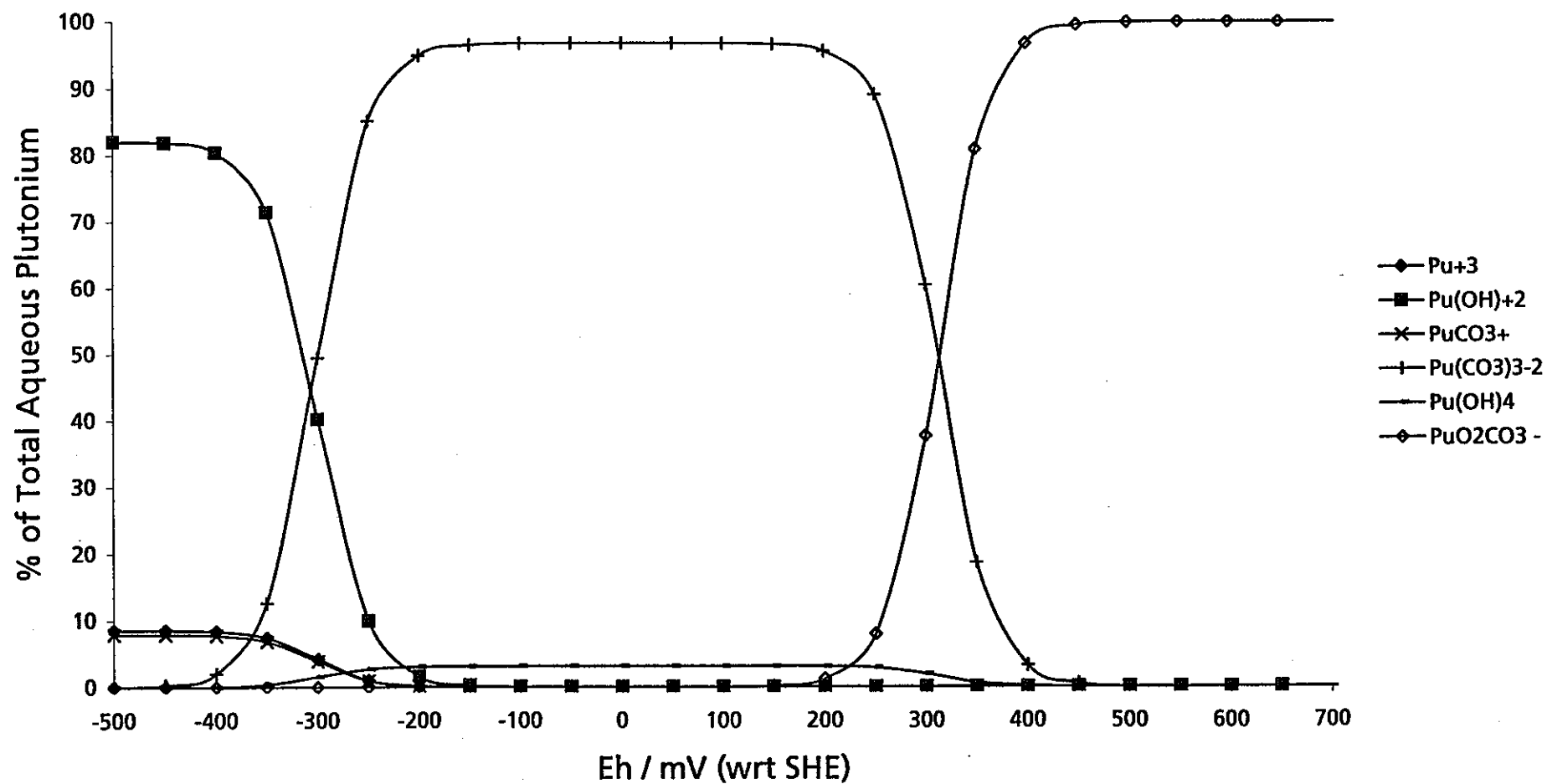


FIGURE 7: Pu Speciation in Sandstone-equilibrated De-ionised water at pH8.1
(HATCHES NEA12_R2 data)

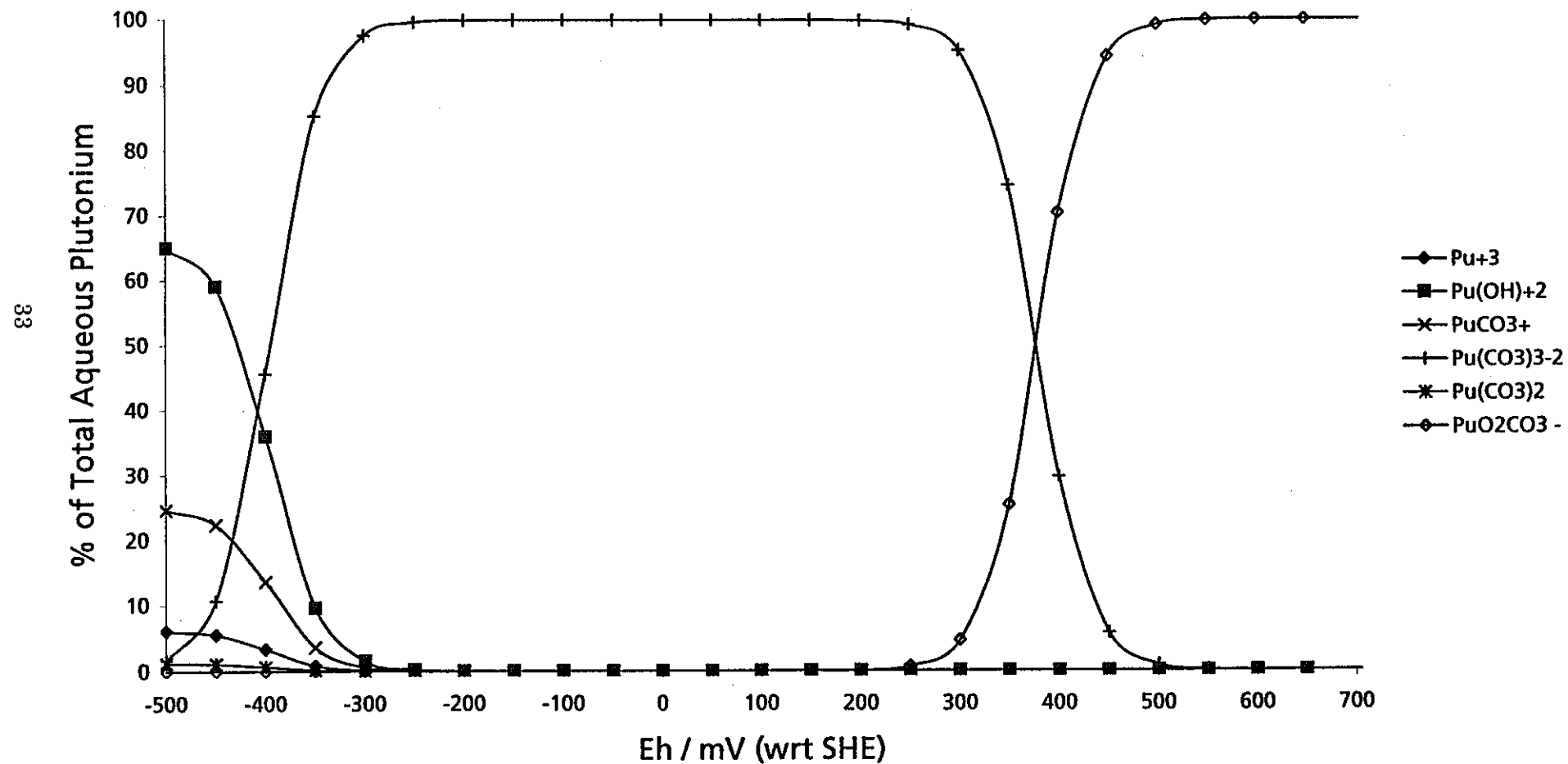


FIGURE 8: Pu Speciation in Basalt-equilibrated De-ionised water at pH8.1
(JNC data)

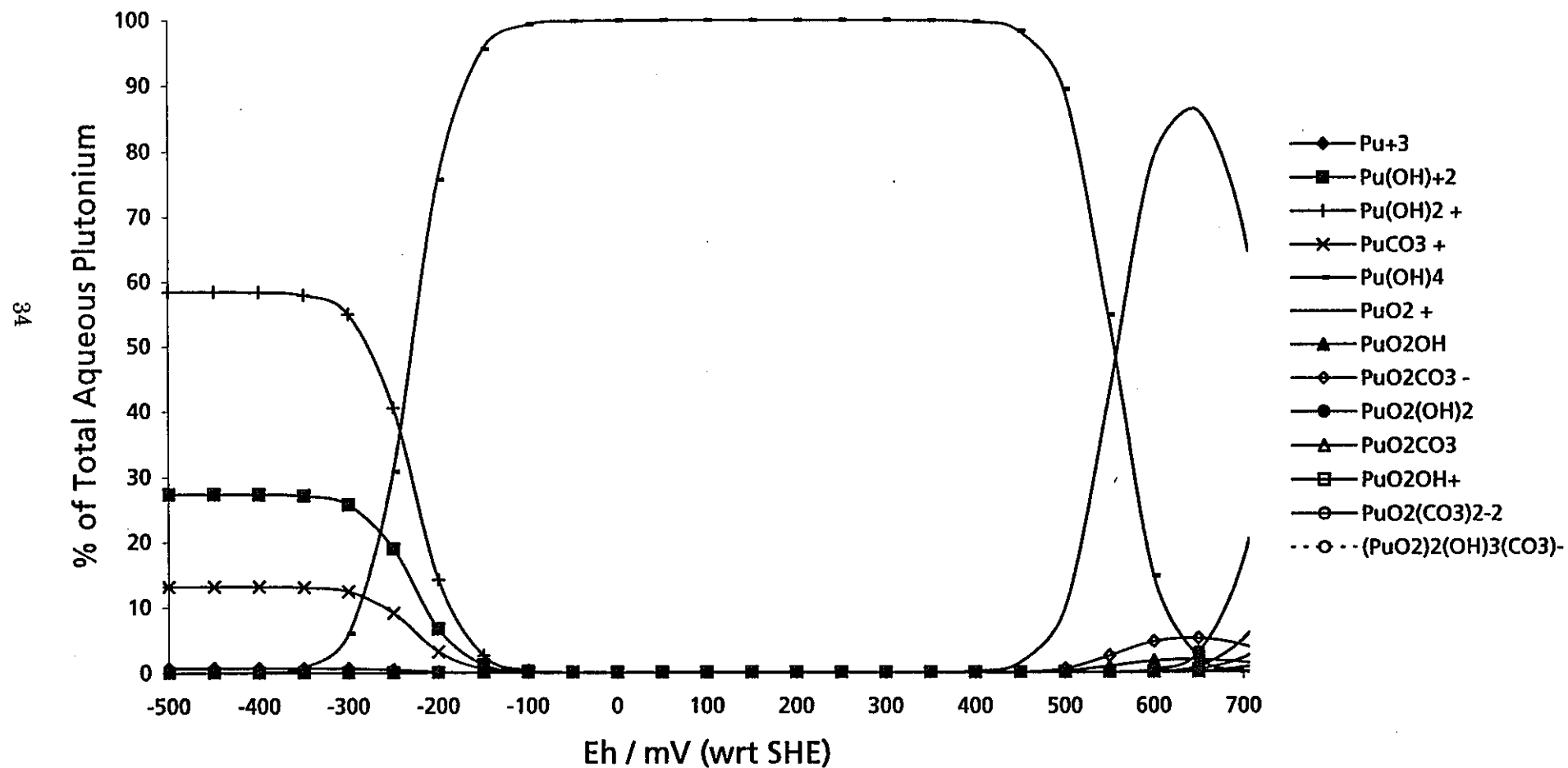
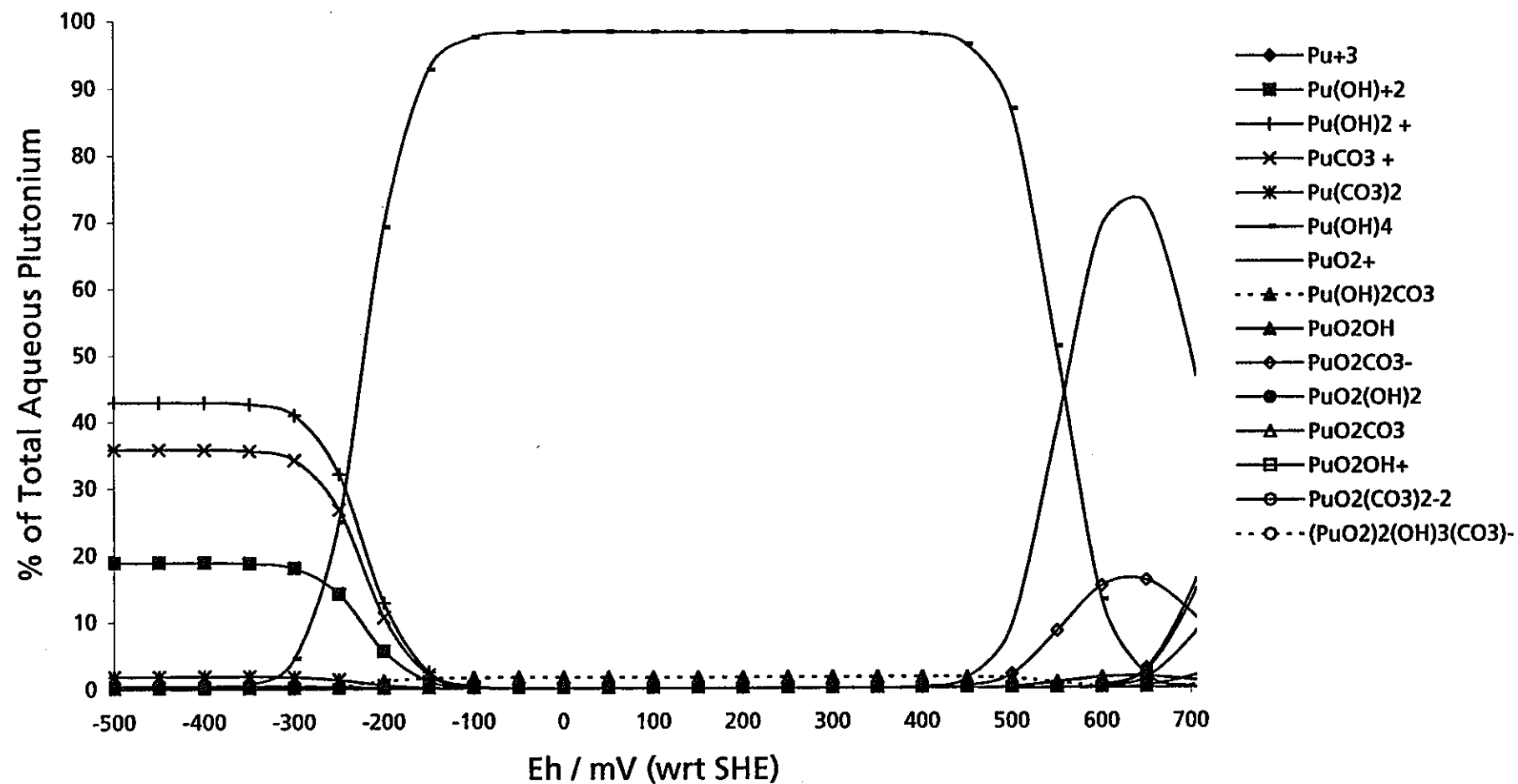


FIGURE 9: Pu Speciation in Sandstone-equilibrated De-ionised water at pH8.1
(JNC data)

35



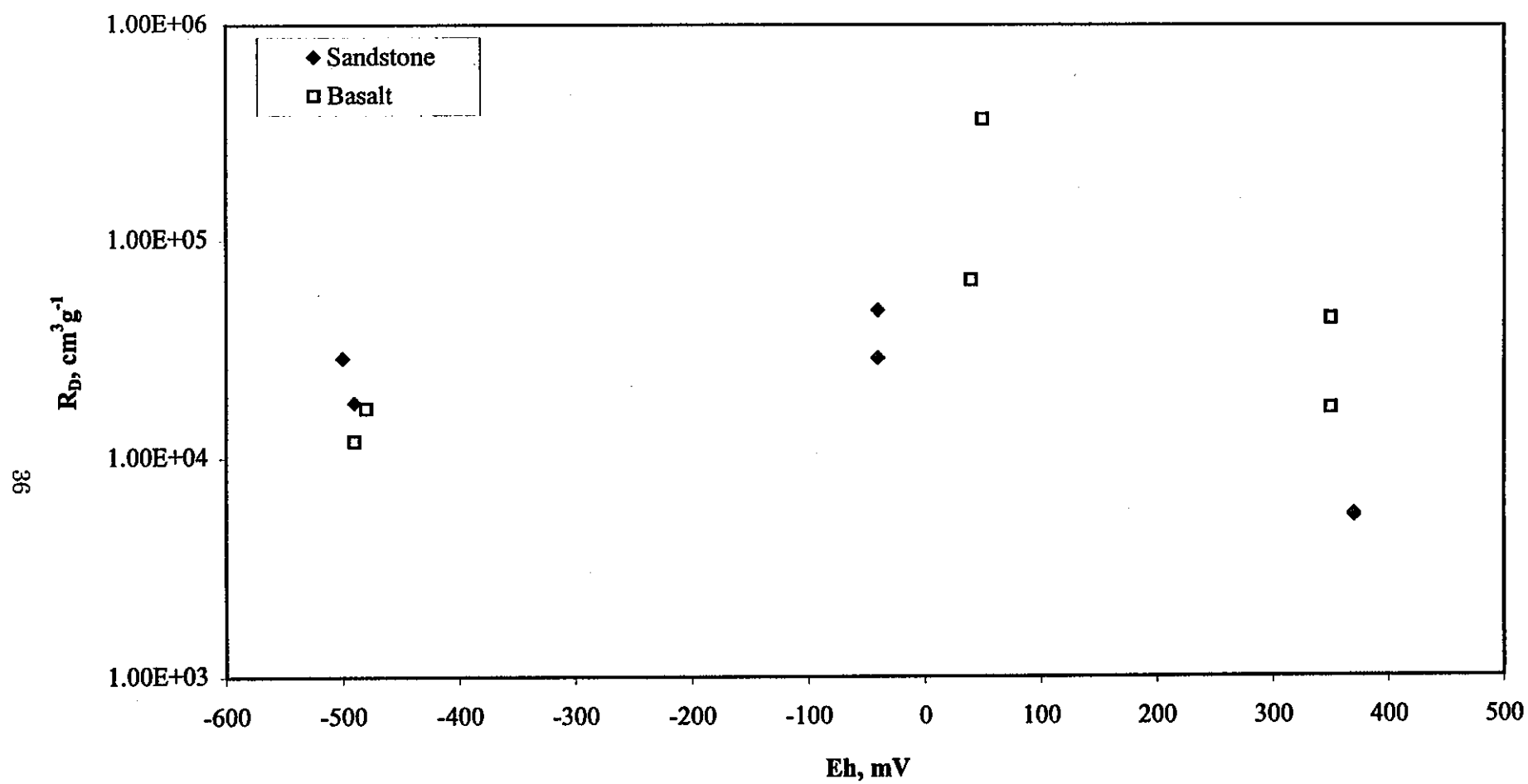


Figure 10. The measured R_D values plotted as a function of the final Eh.

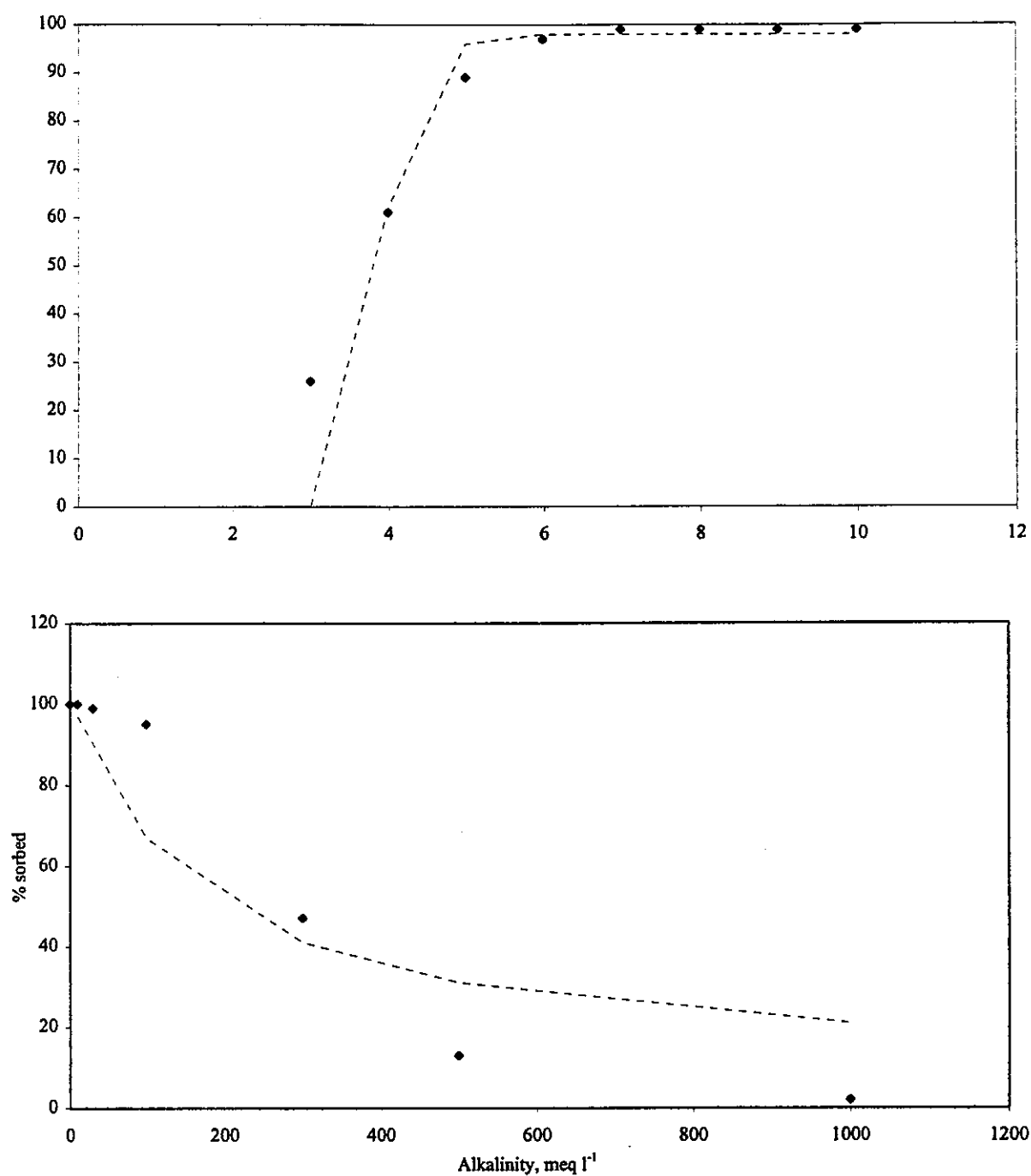


Figure 11. Experimental and modelled data for plutonium(IV) sorption onto goethite. Experimental data taken from Sanchez et al [25]. Plutonium sorption reactions used in the model are given in Table 6.

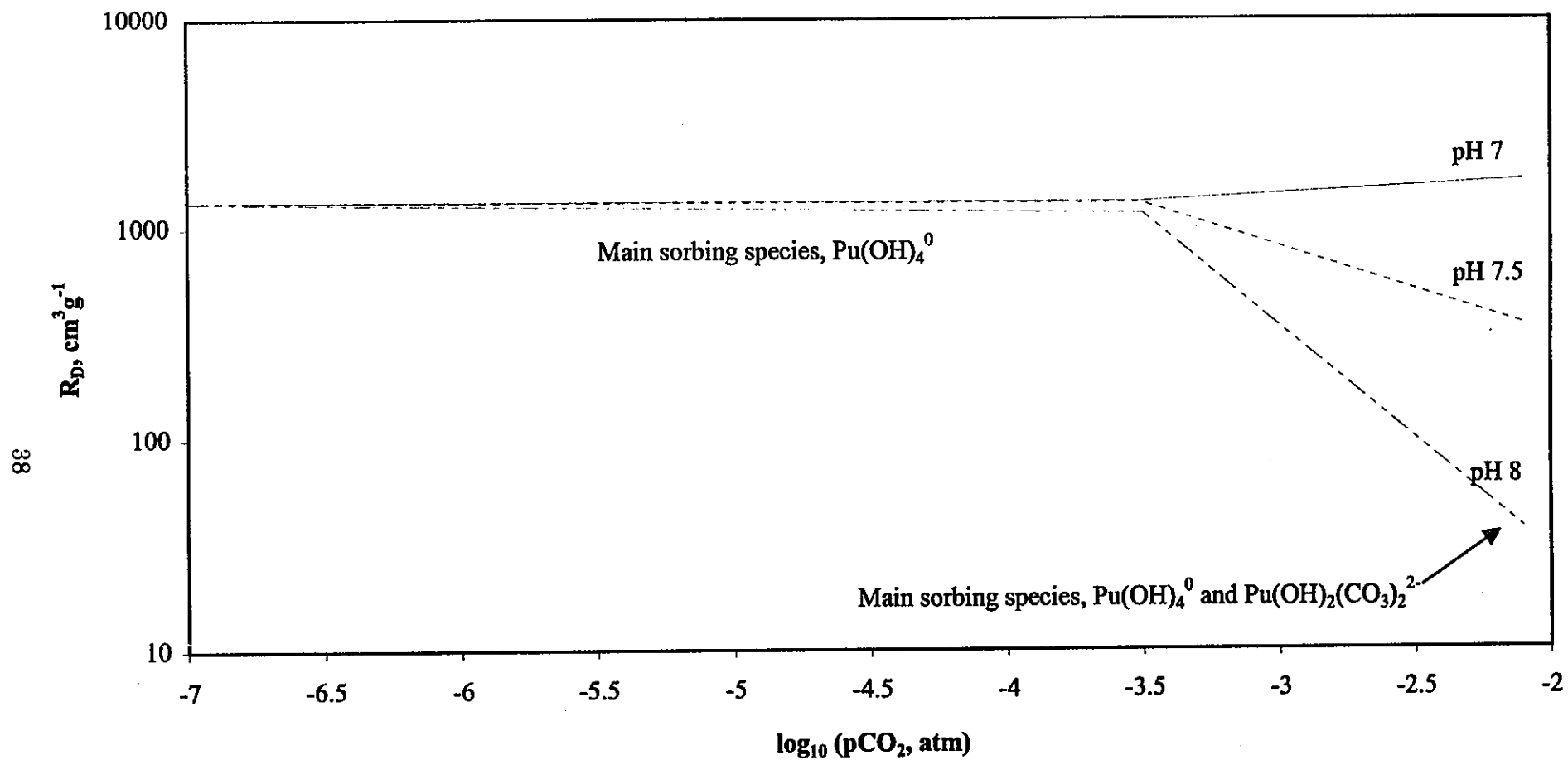


Figure 12. Predicted plutonium(IV) sorption behaviour as a function of the partial pressure of CO_2 . Model based on sorption onto haematite (using the sorption dataset shown in Table 4 and the plutonium(IV) sorption reactions given in Table 6).

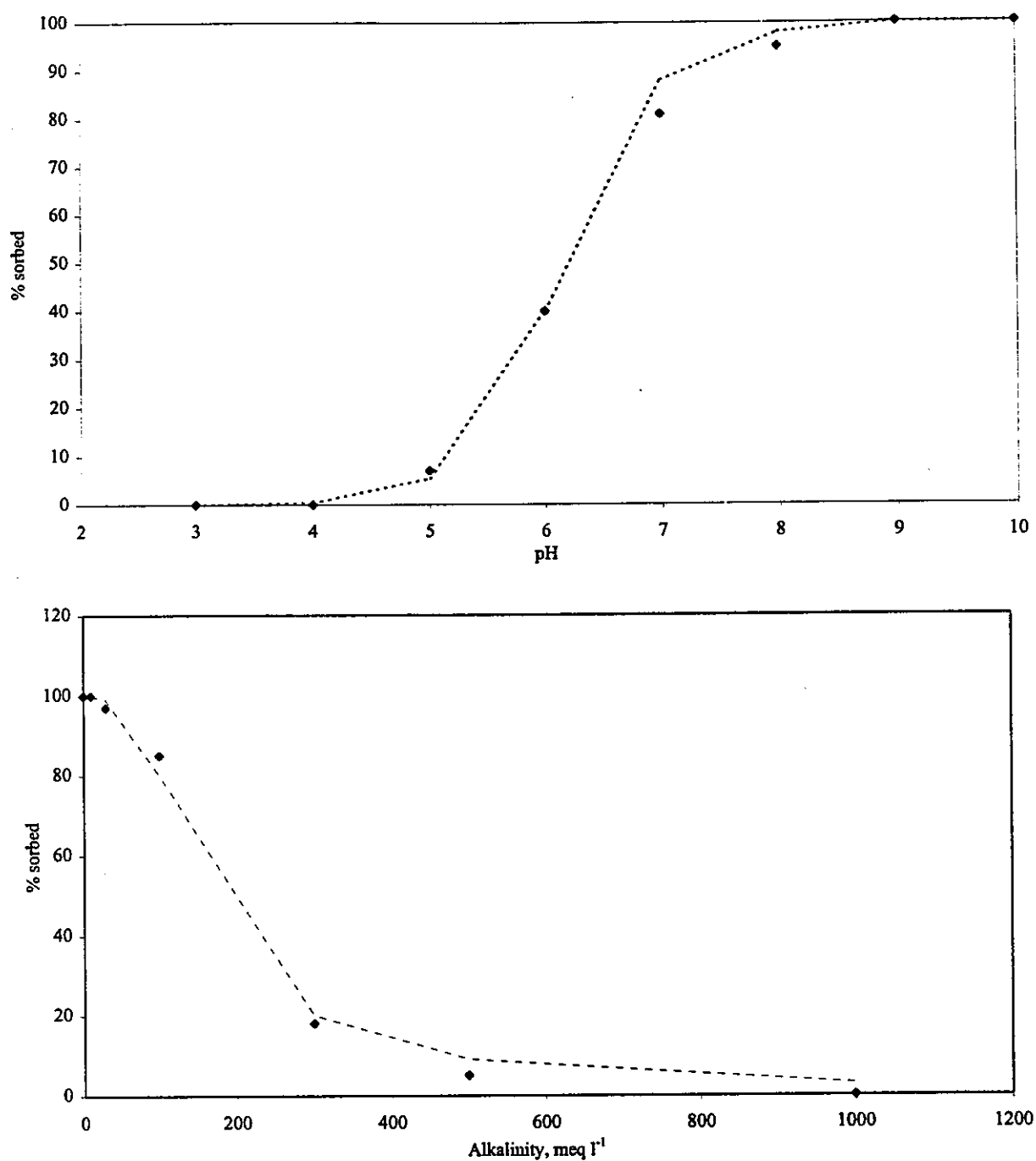


Figure 13. Experimental and modelled data for plutonium(V) sorption onto goethite. Experimental data taken from Sanchez et al [25]. Plutonium sorption reactions used in the model are given in Table 6.

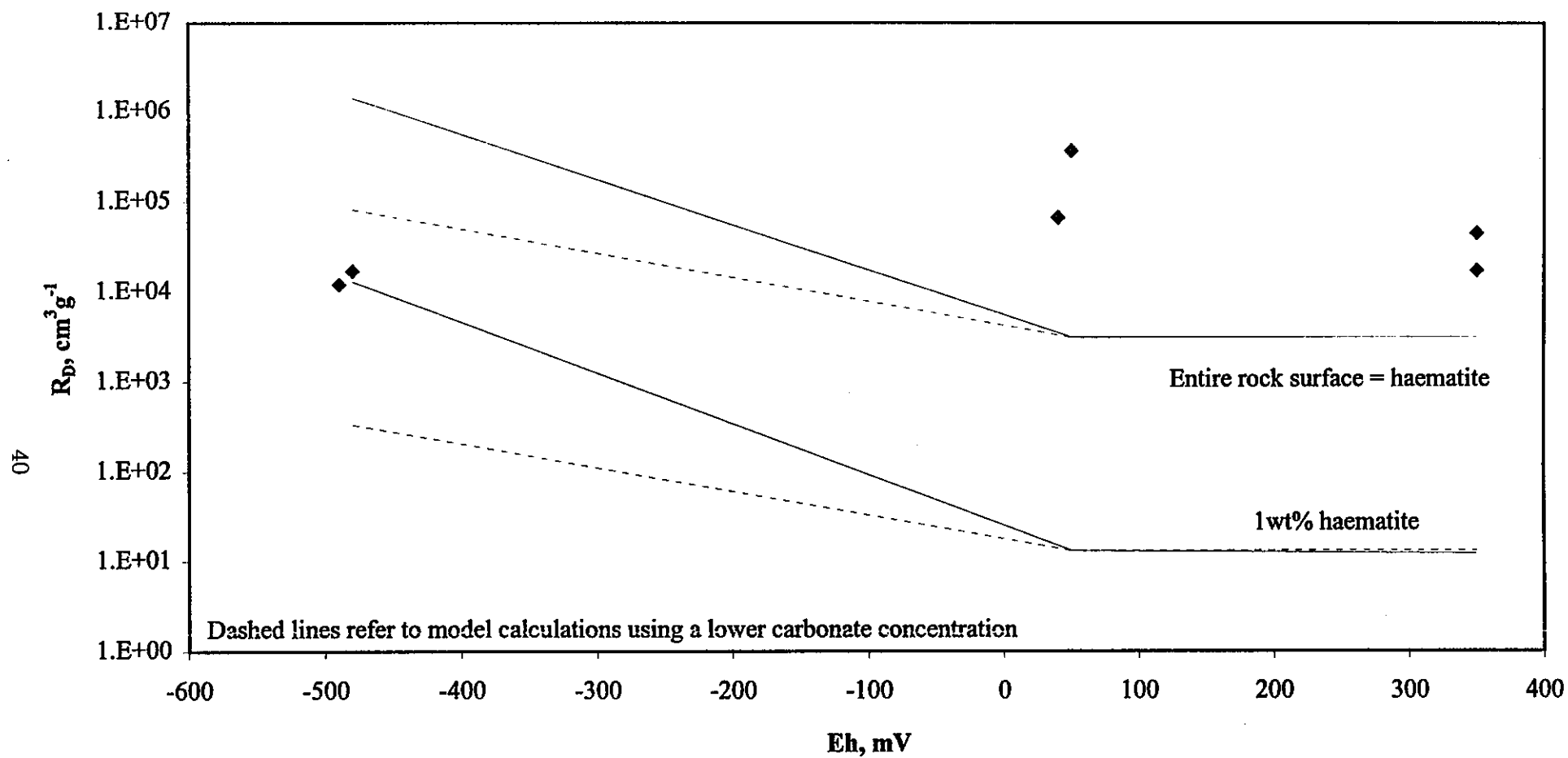


Figure 14. A comparison of experimental and modelled data for plutonium sorption onto basalt as a function of Eh. Experimental data are shown as points, modelled data as lines. Modelling was based on sorption onto haematite using the datasets given in Tables 4, 5 and 6. See text for a full explanation of the modelled data.

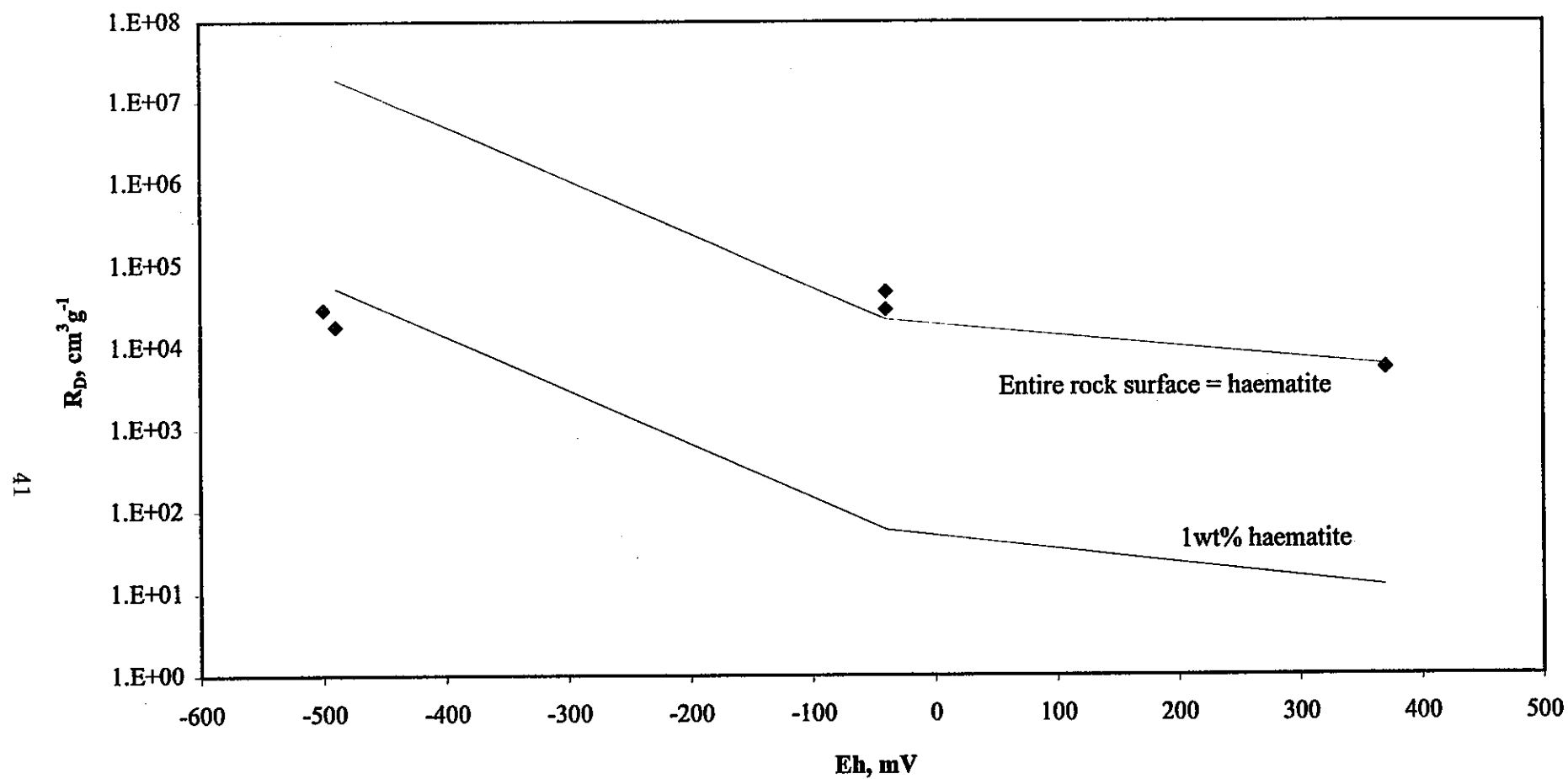


Figure 15. A comparison of experimental and modelled data for plutonium sorption onto sandstone as a function of Eh. Experimental data are shown as points, modelled data as lines. Modelling was based on sorption onto haematite using the datasets given in Tables 4, 5 and 6. See text for a full explanation of the modelled data.

APPENDIX 1

PUBLICATION

Effect of Carbonate Concentration on the Sorption of Plutonium onto Geological Materials.
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Presented at the Materials Research Society Fall Meeting, Boston, USA, December 1999, and
accepted for publication in 'Scientific Basis for Nuclear Waste Management XXIII'.

EFFECT OF CARBONATE CONCENTRATION ON THE SORPTION OF PLUTONIUM ONTO GEOLOGICAL MATERIALS

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ABSTRACT

This paper describes the most recent work in a programme of generic experimental and modelling sorption studies undertaken to increase confidence in the performance assessment for a potential high-level radioactive waste repository in Japan. The sorption of plutonium onto three rock samples was studied as a function of carbonate concentration under reducing conditions. Geochemical modelling was used to assist with experimental design and interpretation of results.

INTRODUCTION

The work described here forms part of the Japan Nuclear Cycle Development Institute (JNC) programme of generic studies undertaken to increase confidence in the performance assessment for a potential Japanese high-level radioactive waste (HLW) repository. In a continuation of work reported previously [1-3], batch sorption experiments have been carried out to study the sorption of plutonium at different carbonate solution concentrations onto samples of basalt, mudstone and sandstone (representing generic rock types from Japan).

One of the aims of the JNC programme is to generate data suitable for use in repository performance assessment calculations. Experimental conditions were therefore chosen in order to simulate, as closely as possible, those anticipated in the vicinity of a potential HLW repository in Japan. Thermodynamic chemical modelling was carried out to help to plan the experiments and to aid interpretation of the results.

EXPERIMENTAL

Batch sorption experiments were carried out in duplicate at room temperature ($21 \pm 3^\circ\text{C}$). Sorption was studied from synthetic rock-equilibrated de-ionised water under a nitrogen atmosphere and also under nitrogen atmospheres containing 0.4% and 2.0% carbon dioxide. In addition, sorption from synthetic rock-equilibrated seawater was studied under a nitrogen atmosphere and with a nitrogen / 2.0% carbon dioxide atmosphere. Reducing conditions, to simulate those expected *in-situ*, were obtained by adding sodium dithionite.

Samples of the geological materials and mineralogical descriptions were supplied by JNC [4]. The composition of the basalt was mainly plagioclase, feldspar and quartz. The mineralogy of the mudstone was dominated by quartz, muscovite, calcite and carbonaceous material, while that of the sandstone was predominantly quartz, plagioclase and chlorite. The methodology for the preparation of rock samples, and synthetic rock-equilibrated de-ionised water and seawater has been described previously [1-3]. The liquid : solid ratio was 5:1 (100 cm^3 : 20g). The de-ionised water solutions were of low ionic strength, with carbonate concentrations of $\sim 3 \times 10^{-4}\text{ M}$ in sandstone- and mudstone-equilibrated water and below detection limit for basalt-equilibrated water ($< 1 \times 10^{-4}\text{ M}$). The seawater solutions were similar to the initial composition of the

TABLE I: PREDICTED CARBONATE CONCENTRATIONS UNDER MIXED NITROGEN / CARBON DIOXIDE ATMOSPHERES

Solution	% CO ₂ in atmosphere	Predicted Carbonate Concentration / M
Rock-equilibrated de-ionised water	0.4	$8.07 \times 10^{-4} - 1.29 \times 10^{-3}$
Rock-equilibrated de-ionised water	2.0	$1.35 \times 10^{-3} - 1.85 \times 10^{-3}$
Rock-equilibrated seawater	2.0	$1.65 \times 10^{-2} - 1.68 \times 10^{-2}$

synthetic seawater (carbonate concentration $\sim 5 \times 10^{-4}$ M). Thermodynamic chemical modelling was used to predict the changes to the solution carbonate concentration and pH values for solutions in equilibrium with the 0.4% and 2.0% carbon dioxide atmospheres. The experimental solutions were adjusted to the predicted higher carbonate concentrations and lower pH values. These values for the three rocks were in the ranges shown in Table I. pH values subsequently remained stable throughout the course of the experiments, indicating constant carbonate concentrations. A predicted risk of precipitation of carbonates in the seawater experiments led to the use of lower calcium concentrations and the omission of magnesium in these cases.

At the end of a three-month equilibration period for each experiment, three phase-separation techniques were employed (centrifugation, and filtration through 0.45 μ m and 10000MWCO filters as described previously [1-3]). The radionuclides used were plutonium-238 for the sorption experiments, and plutonium-239 as a yield tracer in the preparation of α -spectrometry counting trays. Initial plutonium concentrations were in the range 5×10^{-11} M to 3×10^{-10} M.

TABLE II: PLUTONIUM SORPTION ONTO BASALT, MUDSTONE AND SANDSTONE FROM SYNTHETIC ROCK-EQUILIBRATED DE-IONISED WATER

Rock	% CO ₂ in atmosphere	Final pH	Final Eh / mV vs S.H.E.	R _D / m ³ kg ⁻¹		
				Centrifuged	0.45 μ m filtered	10000 MWCO filtered
Basalt	0.0	10.8	-550	0.39 ± 0.04	21 ± 2	120 ± 20
	0.0	10.8	-550	0.36 ± 0.04	27 ± 3	86 ± 9
	0.4	7.4	-510	2.6 ± 0.3	86 ± 13	200 ± 40
	0.4	7.3	-510	3.0 ± 0.4	10 ± 2	130 ± 20
	2.0	6.6	-370	9.2 ± 1.1	580 ± 140	1000 ± 200
	2.0	6.6	-380	8.0 ± 0.9	680 ± 80	1000 ± 100
Mudstone	0.0	9.1	-370	2.4 ± 0.2	25 ± 3	52 ± 7
	0.0	9.1	-390	1.3 ± 0.1	21 ± 2	39 ± 5
	0.4	7.1	-380	0.9 ± 0.1	13 ± 2	110 ± 20
	0.4	7.2	-370	1.6 ± 0.2	23 ± 3	40 ± 9
	2.0	6.4	-360	0.58 ± 0.07	11 ± 1	14 ± 2
	2.0	6.4	-360	1.5 ± 0.2	44 ± 4	47 ± 6
Sandstone	0.0	10.0	-590	0.71 ± 0.07	16 ± 2	37 ± 4
	0.0	10.0	-550	0.92 ± 0.09	17 ± 2	40 ± 6
	0.4	7.1	-330	3.8 ± 0.5	240 ± 40	260 ± 60
	0.4	7.1	-330	5.3 ± 0.7	190 ± 40	300 ± 90
	2.0	6.4	-380	8.3 ± 1.0	650 ± 70	>310
	2.0	6.3	-370	3.6 ± 0.4	210 ± 20	260 ± 30

RESULTS AND DISCUSSION

Results of sorption experiments using equilibrated de-ionised water and seawater are shown in Tables II and III respectively. Uncertainties on R_D values shown in these Tables are $\pm 2\sigma$ and are based on counting statistics alone. R_D was defined by:

$$R_D = V/M \times (C_o - C_i)/C_i$$

where V = volume of solution, M = mass of rock, C_o and C_i = initial and final concentrations of plutonium in solution.

Most of the measured R_D values after filtration are very high ($>10 \text{ m}^3 \text{ kg}^{-1}$). In all cases, strong sorption is maintained in the presence of carbonate. To assist with interpretation of the experimental data, thermodynamic modelling was carried out. The geochemical speciation program HARPHRQ [5] was used, along with the associated HATCHES thermodynamic database (version NEA11) [6] and additional plutonium data supplied by JNC.

In developing the model, there were a number of key uncertainties to consider. Firstly, there is uncertainty as to the thermodynamic stability of key plutonium(III)/(IV) species in solution and the role that carbonate plays in influencing the relative stability of these oxidation states. Secondly, within the literature, there is an incomplete understanding of the effect of carbonate on plutonium sorption. Available data give conflicting results; some suggest high carbonate concentrations are associated with a reduction in sorption [7], whereas other data (AEA Technology unpublished results) suggest sorption is either unaffected or enhanced. As a result, the approach has been to derive a thermodynamic sorption model that is chemically plausible. This provides a valuable interpretative tool with some predictive capability for this complex natural system. The model is based on haematite. This iron oxide phase is of similar crystallinity to the magnetite observed in some of the samples and has an independently parameterised sorption dataset. The authors are not aware of any such datasets for iron(II) oxide mineral phases. Also, the role of iron-bearing minerals such as chlorite and biotite could not be fully assessed in this work due to lack of appropriate data.

TABLE III: PLUTONIUM SORPTION ONTO BASALT, MUDSTONE AND SANDSTONE FROM SYNTHETIC ROCK-EQUILIBRATED SEAWATER

Rock	% CO ₂ in atmosphere	Final pH	Final Eh / mV vs S.H.E.	$R_D / \text{m}^3 \text{ kg}^{-1}$		
				Centrifuged	0.45 μm filtered	10000 MWCO filtered
Basalt	0.0	8.4	-520	0.84 ± 0.09	130 ± 20	240 ± 40
	0.0	8.4	-520	0.63 ± 0.06	120 ± 20	97 ± 3
	2.0	7.5	-400	5.7 ± 0.9	96 ± 13	150 ± 20
	2.0	7.5	-410	7.8 ± 1.1	120 ± 20	890 ± 740
Mudstone	0.0	8.4	-470	1.3 ± 0.1	3.5 ± 0.7	3.6 ± 0.6
	0.0	8.3	-480	1.4 ± 0.1	7.3 ± 0.9	140 ± 30
	2.0	7.6	-390	4.7 ± 2.4	1900 ± 500	5800 ± 900
	2.0	7.5	-400	6.6 ± 1.8	790 ± 190	1200 ± 200
Sandstone	0.0	8.4	-510	1.4 ± 0.1	30 ± 5	36 ± 4
	0.0	8.4	-510	2.1 ± 0.2	22 ± 2	23 ± 4
	2.0	7.5	-430	4.3 ± 0.5	11 ± 1	19 ± 2
	2.0	7.5	-430	3.9 ± 0.5	7.0 ± 0.8	9.8 ± 1.2

TABLE IV: PREDICTED AQUEOUS SPECIATION OF PLUTONIUM IN ROCK-EQUILIBRATED DE-IONISED WATER AND SEAWATER / %

	0% CO ₂		0.4% CO ₂	2.0% CO ₂	
	DI Water	Seawater	DI Water	DI Water	Seawater
Basalt					
Pu(OH) ₄	58				
Pu ³⁺		1	2	9	
Pu(OH) ²⁺		48	11	11	2
Pu(OH) ₂ ⁺	36	25	5		
Pu(OH) ₃	5				
Pu(CO ₃) ⁺		22	79	78	61
Pu(CO ₃) ₂ ⁻		2	3		29
Pu(CO ₃) ₃ ³⁻					4
Mudstone					
Pu(OH) ₄	37				
Pu ³⁺		1	3	18	
Pu(OH) ²⁺	2	27	15	13	2
Pu(OH) ₂ ⁺	51	52	4		
Pu(CO ₃) ⁺	5	16	75	63	56
Pu(CO ₃) ₂ ⁻	3		1		34
Pu(CO ₃) ₃ ³⁻					6
PuSO ₄ ⁺			1	6	
Sandstone					
Pu(OH) ₄	3				
Pu ³⁺		1	4	17	
Pu(OH) ²⁺		25	17	14	
Pu(OH) ₂ ⁺	91	49	4		
Pu(OH) ₃	2				
Pu(CO ₃) ⁺		20	74	66	62
Pu(CO ₃) ₂ ⁻	2	2			29
Pu(CO ₃) ₃ ³⁻					4

Values of pH and Eh used in the calculations are those given in Tables II and III.

The predicted aqueous speciation is shown in Table IV. No experimental technique is presently capable of measuring the speciation or oxidation state of plutonium in neutral or alkaline pH solutions because of the very low solubility of plutonium compounds under these conditions. The predicted speciation under the experimental conditions was a mixture of Pu(III) and Pu(IV). A preliminary model based on an independently parameterised Pu(IV) sorption dataset did not adequately reproduce experimental trends. A model based on the sorption of plutonium(III) hydrolysis products and carbonate species was therefore developed. No independent data for plutonium(III) sorption onto haematite were available. The dataset was thus derived by fitting to the de-ionised water data obtained in the current work.

Modelled results for the de-ionised water experiments are compared with the experimental data in Figure 1. The model gave generally good agreement with observed results. The ability of the model to simulate the experimental trends for all three rocks supports the assumption that a similar phase dominates sorption in all three cases. Similar agreement was obtained for the seawater experiments; however in the case of sandstone, the model does not reproduce the observed decrease in sorption as the carbonate concentration is increased. Interestingly, there was no need for rock-specific model refinements e.g. to account for different surface areas or amounts of iron oxide at the surface for each rock type. The modelling illustrates that the observed sorption can be interpreted in terms of strong sorption of both plutonium(III) hydrolysis products and carbonate species onto iron oxide surfaces present in the rocks.

CONCLUSIONS

Results from batch sorption experiments have shown that under reducing conditions, plutonium is generally strongly sorbed onto samples of JNC basalt, mudstone and sandstone. This strong sorption is maintained in the presence of carbonate. The successful application of an iron oxide-based model illustrates that the observed sorption can be interpreted in terms of strong sorption of both plutonium(III) hydrolysis products and carbonate species.

ACKNOWLEDGEMENT

This work was funded by the Japan Nuclear Cycle Development Institute (JNC), Tokai, Japan. Their permission to publish the results is gratefully acknowledged.

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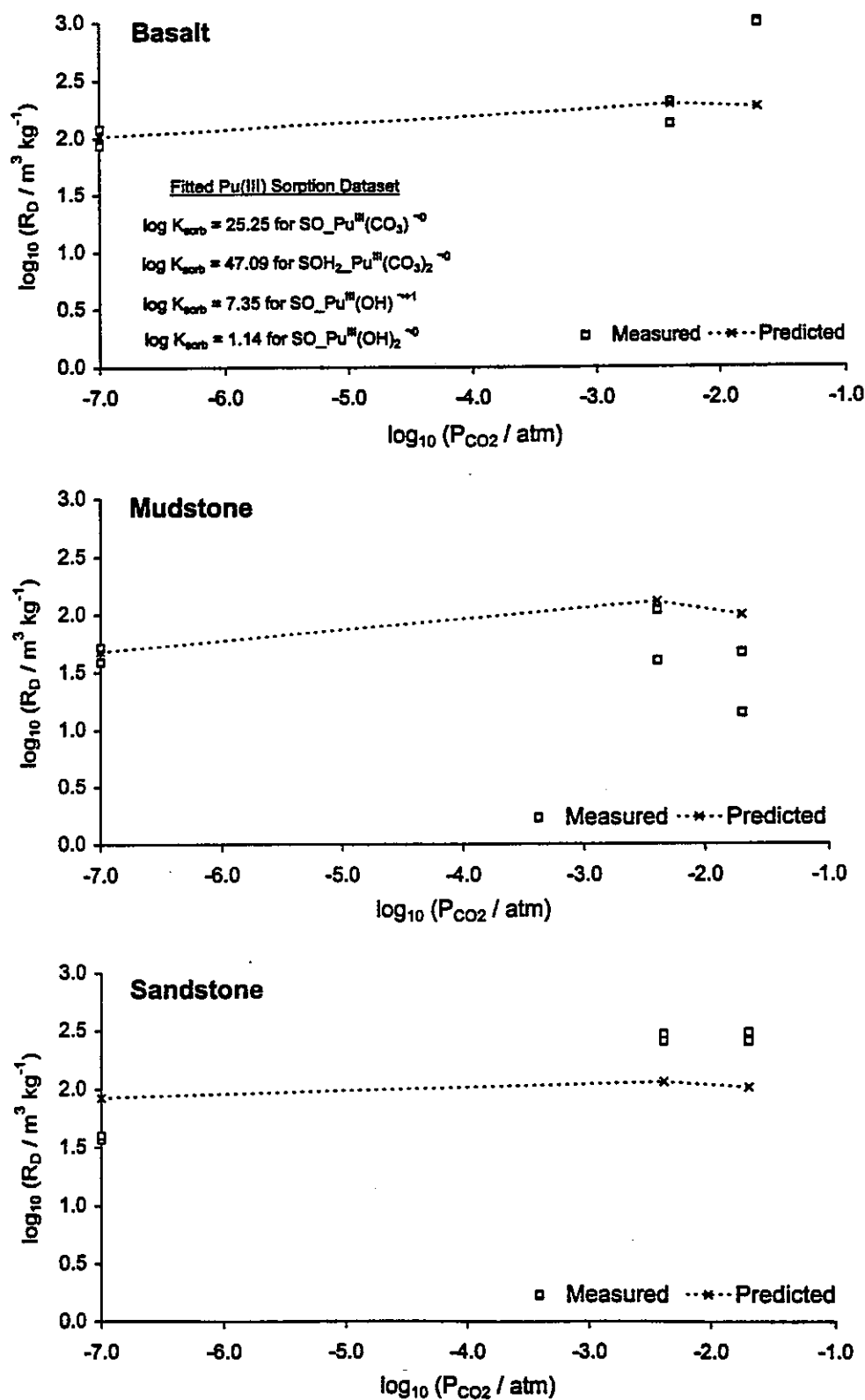


Figure 1 Comparison of the Predicted and Observed Sorption of Plutonium onto Basalt, Mudstone and Sandstone from rock-equilibrated deionised water in the presence of carbonate.

APPENDIX 2

Sorption of Plutonium onto Bentonite, Tuff and Granodiorite at 60°C

1. INTRODUCTION

This study was reported previously to JNC [1] in the Report 'Sorption Studies of Radioelements on Geological Materials - Year 7 Final Report to PNC', Report AEAT-3142 (Issue 3, 1998). The work is summarised here for JNC's convenience.

2. EXPERIMENTAL

2.1 Preparation of Solutions for Batch Sorption Studies

Table 1 shows the concentrations of cations and anions present after 4 weeks equilibration of de-ionised water with respectively bentonite (at room temperature) and tuff and granodiorite at 60°C. It proved impractical to filter the bentonite-equilibrated de-ionised water at 60°C. There was, however, little difference between the tuff and granodiorite-equilibrated waters equilibrated at room temperature and 60°C. The recipe for the bentonite-equilibrated de-ionised water equilibrated at room temperature was therefore used. Synthetic solutions based on these analyses were prepared. All solutions were de-oxygenated by bubbling an argon (96%)/hydrogen (4%) mixture through them before posting into the glovebox.

2.2 Execution of Batch Experiments

The bentonite sample was used as received from PNC, and the tuff and granodiorite samples were ground in an automatic mortar and pestle under a nitrogen atmosphere until the entire samples passed through a 250µm sieve.

Sorption experiments were carried out inside a shaker / incubator at 60°C in a nitrogen-atmosphere glovebox suite with an oxygen level of less than 1 ppm.

Plutonium-238 solution was added to appropriate volumes of synthetic rock-equilibrated water, and sodium dithionite (2.5×10^{-3} M) added in order to provide the required strongly-reducing conditions. A water-to-rock ratio of 20:1 was used in the case of bentonite, whilst a ratio of 5:1 was used in the case of tuff and granodiorite. Each pH value was then adjusted to the appropriate value shown in Table 1, and the solutions filtered using 0.45µm filters. Aliquots of 40 cm³ were then taken and mixed with rock at the appropriate water-to-rock ratio in previously-washed polypropylene centrifuge tubes, and equilibrated for 4 months.

Sodium dithionite 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, the Eh value was monitored every 7 days, and when it increased towards -300mV (vs the Standard Hydrogen Electrode,

SHE) more dithionite was added and the pH adjusted back to the appropriate value. pH and Eh measurements were carried out at 60°C.

The experiments were carried out in duplicate. At the end of the four month equilibration period, three liquid/solid separation techniques were employed:

- (i) For tuff and granodiorite, centrifugation at 1100g for 15 minutes, and for bentonite, for 2.5 hours, 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 10000 MWCO filter (Millipore "TGC").

In the case of bentonite, the centrifugation was carried out for 2.5 hours at 1100g since past experience with bentonite has demonstrated that shorter centrifugation times give poorer phase separation and resulted in blockage of pores in the membranes of filters used subsequently. Each tube was removed from the shaker/incubator, centrifuged in a heated centrifuge operating at 60°C, and then transferred to a heating block at 60°C. An aliquot of liquid was quickly removed and pipetted into 1 cm³ dilute acid. This acidification 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 then filtered through a Millipore 'Millex HV' 0.45µm filter which had been pre-heated, washed and pre-conditioned at 60°C prior to use [2]. This operation was carried out inside the shaker/incubator, which was maintained at 60°C. Whenever possible, the transparent lid of the shaker/incubator was kept in place in order to minimise 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' (10000 MWCO) filters. These were pre-treated in a similar manner to the 0.45µm filters used earlier. Aliquots of filtrate were then acidified and taken for analysis. 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) in July 1997.

The vessel walls from one of each duplicate experiment were investigated for sorption. In order to determine the amount of radionuclide sorbed onto the vessel walls, 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 cm³ volumes of rock-equilibrated water. The vessel walls were then washed with 10.0 cm³ 4M HNO₃. Aliquots of this acidic solution were then transferred to plastic vials for analysing.

2.3 Results of Batch Sorption Studies of Plutonium on Bentonite, Granodiorite and Tuff at 60°C

Table 2 shows the results obtained for the sorption of plutonium onto the three geological materials at 60°C. Sorption is strongest in the case of bentonite ($R_D = 2.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ to $8.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ after 10000 MWCO filtration). For granodiorite, R_D values are in the range 9.8×10^3 to $5.7 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$, and for tuff, 6.7×10^3 to $1.2 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$. There is evidence of colloid formation in the cases of granodiorite and tuff, but not in the case of bentonite.

2.4 Vessel Wall Sorption

The amount of plutonium sorbed onto the vessel walls was determined as outlined in Section 2.1. The maximum amount adhering to the vessel walls in the experiments containing geological material was 5.7%. In other words, in the presence of polypropylene and geological material, the plutonium is preferentially sorbed onto the geological material. No allowance was made for the small degree of wall sorption in the R_D calculations, because this factor is small by comparison with errors based on the statistics of counting.

3. MATHEMATICAL MODELLING OF BATCH SORPTION EXPERIMENTS

3.1 Introduction

Thermodynamic modelling has been carried out in support of the batch sorption experiments using the aqueous speciation code HARPHRQ (version 1.41) [3, 4] in conjunction with the HATCHES database (versions NEA9 and NEA10) [5]. The sorption module HARSORB has been used to aid interpretation of the batch sorption experiments.

The refined goethite-based triple layer sorption model developed in Year 4 [6] has been used to interpret the extent of sorption onto bentonite, granodiorite and tuff. The model was originally developed to examine sorption onto bentonite, with the assumption that the sorption behaviour was dominated by small quantities of goethite present in the form of a surface coating on the montmorillonite. The present refined model is based on the original triple layer model developed for PNC in Year 1 [7], but with a number of modifications:

- the aqueous methane species ($\text{CH}_4(\text{aq})$) has been removed from the calculations because the reduction of carbonate species to methane under strongly-reducing conditions, although predicted to occur thermodynamically, is not observed on the experimental laboratory timescale;
- a more sophisticated treatment of sorption of groundwater ions has been implemented in the refined model, with the aqueous concentrations remaining constant at the experimentally determined values;

- the density of sorption sites has been refined to improve predictions at the various water:rock ratios.

The reasons for making these model refinements were discussed in more detail in the Year 4 progress report [6]. Details of the refined model used in Year 5 [8] for the sorption of neptunium are presented in Tables 3 - 4. Table 3 gives the refined triple layer model parameters used in these calculations. The concentration of sites and surface areas for each rock type are those used previously for calculations in Year 4. It should be noted that although there are differences between these parameters for each rock type, they yield the same surface site density for goethite in each case.

The concentration of sites and surface area values, used in this work and in Year 4, are significantly higher than those reported in the original model [7, 9, 10]. In the original model, the concentration of sites corresponded to that expected for a 40% covering of goethite on the extended montmorillonite surface. The concentration of surface sites for the refined model is greater than that expected for a complete goethite covering of the available montmorillonite surface. This might be explained by the presence of a less crystalline hydrous ferric oxide phase, which has a significantly higher site density [11], or by uncertainties in the experimental literature values used to derive the values for the percentage of montmorillonite loading.

The sorption equilibria and log K values for the sorption of groundwater ions onto goethite [12, 13], shown in Table 4, remain unchanged from the previous studies.

3.2 Predicted Speciation of Plutonium

The predicted speciation of plutonium in de-ionised water equilibrated with bentonite, granodiorite and tuff is shown in Table 5 under the strongly-reducing conditions. The predictions at 25°C were carried out at the reported Eh values for the room temperature neptunium sorption experiments reported in Year 5 [8].

The major aqueous species were predicted to be $\text{Pu}(\text{CO}_3)_3^{2-}$ in the bentonite and tuff waters and $\text{Pu}(\text{OH})_4(\text{aq})$ 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. Predictions at 60°C were hindered by a lack of enthalpy data for Pu(III) species and for Pu(IV) carbonate species.

3.3 Modelling of Plutonium Sorption onto Bentonite, Tuff and Granodiorite

For the interpretation of the sorption data for plutonium it has been assumed that the extent of sorption at room temperature is the same as that measured at 60°C for each of the systems studied. This assumption was made due to the incomplete enthalpy dataset for plutonium species and the need to parameterise a room temperature model for the diffusion modelling studies.

The experimental sorption data for plutonium have been fitted by assuming sorption occurs by the formation of surface complexes between surface goethite-type sites and the major aqueous species. Table 6 shows the sorption equilibria and the log K values derived in this work.

The average measured R_D value for plutonium onto bentonite under strongly-reducing conditions at 60°C was $6 \times 10^4 \text{ cm}^3\text{g}^{-1}$. Under aerobic conditions, values in the range 10^3 - $10^5 \text{ cm}^3\text{g}^{-1}$ have been reported in the pH range 5 to 9 [33]. At the highest pH values, the sorption is comparable to that reported here although the oxidation state is likely to be Pu(V) under aerobic conditions.

4. CONCLUSIONS

At 60°C, under reducing conditions, plutonium is strongly sorbed onto all three geological materials, R_D values following 10000MWCO filtration being in the region of 6.7×10^3 to $1.1 \times 10^5 \text{ cm}^3\text{g}^{-1}$. There is evidence for particulate or colloid formation, but only for granodiorite and tuff. In general, sorption is strongest in the case of bentonite.

An existing goethite-based triple-layer model for sorption was applied to the plutonium data, under the assumption that the extent of sorption is not sensitive to temperature between room temperature and 60°C. Differences in the predicted speciation in the three rock-equilibrated waters meant that the model could only be used to fit an equilibrium constant for a single sorption reaction for each rock studied.

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TABLE 1**ANALYSIS OF DE-IONISED WATER AFTER EQUILIBRATION FOR FOUR WEEKS
WITH BENTONITE, TUFF AND GRANODIORITE AT 60°C**

Species	Concentration / $\mu\text{g cm}^{-3}$		
	After Equilibration at 60°C with Bentonite*	After Equilibration at 60°C with Tuff	After Equilibration at 60°C with Granodiorite
Al	< 0.3	0.36	1.6
B	< 0.02	0.33	0.03
Ca	0.49	5	2.8
Fe	0.04	0.08	< 0.003
K	0.66	9	11
Mg	0.07	< 0.05	< 0.05
Na	110	97	11
Si	5.3	10	14
Sr	0.005	0.01	< 0.002
F ⁻	< 0.1	2.6	0.78
Cl ⁻	< 0.1	8.7	1.2
Br ⁻	< 0.05	< 0.02	< 0.02
PO ₄ ³⁻	< 0.1	< 0.05	< 0.05
SO ₄ ²⁻	9.2	160	0.55
CO ₃ ²⁻	28	47	< 10
Final pH	9.4	9.2	9.6

Samples were filtered using a 10000MWCO filter prior to analysis. *Analysis from 20°C equilibration used, but at different pH

TABLE 2

PLUTONIUM SORPTION ONTO BENTONITE, GRANODIORITE AND TUFF AT 60°C UNDER STRONGLY-REDUCING CONDITIONS

Geological Material	Final pH	Final Eh mV vs. SHE	$R_D / \text{cm}^3\text{g}^{-1}$		
			Centrifuged	0.45 μm	10000 MWCO
Bentonite	9.4	-410	$1.3 \times 10^4 \pm 0.3 \times 10^4$	$1.1 \times 10^4 \pm 0.1 \times 10^4$	$8.7 \times 10^4 \pm 1.4 \times 10^4$
	9.4	-410	$1.6 \times 10^4 \pm 0.3 \times 10^4$	$2.1 \times 10^4 \pm 0.3 \times 10^4$	$2.7 \times 10^4 \pm 0.3 \times 10^4$
Granodiorite	9.6	-580	$1.7 \times 10^2 \pm 0.2 \times 10^2$	$1.2 \times 10^3 \pm 0.2 \times 10^3$	$5.7 \times 10^4 \pm 0.8 \times 10^4$
	9.6	-590	$2.2 \times 10^2 \pm 0.3 \times 10^2$	$1.3 \times 10^3 \pm 0.2 \times 10^3$	$9.8 \times 10^3 \pm 1.3 \times 10^3$
Tuff	9.2	-520	$8.4 \times 10^2 \pm 1.0 \times 10^2$	$1.4 \times 10^3 \pm 0.2 \times 10^3$	$6.7 \times 10^3 \pm 0.39 \times 10^3$
	9.2	-530	$7.6 \times 10^2 \pm 1.0 \times 10^2$	$8.3 \times 10^2 \pm 2.0 \times 10^2$	$1.2 \times 10^4 \pm 0.3 \times 10^4$

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

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

TABLE 3

TRIPLE LAYER SORPTION PARAMETERS ASSUMED IN THE BENTONITE, TUFF AND GRANODIORITE SORPTION MODEL (WATER:ROCK RATIOS 20:1 FOR BENTONITE, 5:1 FOR TUFF AND GRANODIORITE)

Parameter		Value
Triple layer parameter ^[12]	C ₁	140 $\mu\text{F cm}^{-2}$
	C ₂	20 $\mu\text{F cm}^{-2}$
Bentonite		
Surface area	50g l ⁻¹	6.80 x 10 ³ m ² kg ⁻¹
Concentration of sites	50g l ⁻¹	2.88 x 10 ⁻² mol dm ⁻³
Tuff		
Surface area	200g l ⁻¹	5.44 x 10 ⁴ m ² kg ⁻¹
Concentration of sites	200g l ⁻¹	2.31 x 10 ⁻¹ mol dm ⁻³
Granodiorite		
Surface area	200g l ⁻¹	2.72 x 10 ⁴ m ² kg ⁻¹
Concentration of sites	200g l ⁻¹	1.16 x 10 ⁻¹ mol dm ⁻³

TABLE 4

**REACTION CONSTANTS FOR THE SORPTION OF
INACTIVE SOLUTES ONTO GOETHITE SITES (SOH)**

Reaction(a)	LogK(b)
$\text{SOH} = \text{SO}^- + \text{H}_s^+$	-9.52
$\text{SOH} + \text{H}_s^+ = \text{SOH}_2^+$	5.57
$\text{SOH} + \text{Na}_s^+ = \text{SONa} + \text{H}_s^+$	-8.40
$\text{SOH} + \text{K}_s^+ = \text{SOK} + \text{H}_s^+$	-8.40
$\text{SOH} + \text{Ca}_s^{2+} = \text{SOCa}^+ + \text{H}_s^+$	-5.00
$\text{SOH} + \text{Ca}_s^{2+} + \text{H}_2\text{O} = \text{SOCaOH} + 2\text{H}_s^+$	-14.50
$\text{SOH} + \text{Mg}_s^{2+} = \text{SOMg}^+ + \text{H}_s^+$	-5.45
$\text{SOH} + \text{Mg}_s^{2+} + \text{H}_2\text{O} = \text{SOMgOH} + 2\text{H}_s^+$	-14.25
$\text{SOH} + \text{SO}_4^{2-}{}_s + \text{H}_s^+ = \text{SOH}_2\text{SO}_4^-$	9.10
$\text{SOH} + \text{SO}_4^{2-}{}_s + 2\text{H}_s^+ = \text{SOH}_3\text{SO}_4$	14.40
$\text{SOH} + \text{CO}_3^{2-}{}_s + \text{H}_s^+ = \text{SOH}_2\text{CO}_3^-$	15.90
$\text{SOH} + \text{CO}_3^{2-}{}_s + 2\text{H}_s^+ = \text{SOH}_3\text{CO}_3$	22.30
$\text{SOH} + \text{H}_s^+ + \text{Cl}_s^- = \text{SOH}_2\text{Cl}$	7.00

- a) The subscript 's' denotes the surface activity of the solute. The surface activity is related to the bulk solution activity through the expression:

$a_s = a_b \exp (-ze\psi/kT)$ where z is the charge of the species, e is the electronic charge, Ψ the potential at the surface, K the Boltzmann constant and T the absolute temperature.

- b) All the above data are taken from reference [12] except for the reactions involving the carbonate species which were taken from reference [14].

TABLE 5

**PREDICTED SPECIATION OF PLUTONIUM IN BENTONITE, GRANODIORITE
AND TUFF EQUILIBRATED DE-IONISED WATERS AT ROOM TEMPERATURE
UNDER STRONGLY-REDUCING CONDITIONS**

a) ROOM TEMPERATURE

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	7.30 %
			Pu(OH) ₃	0.2 %
Granodiorite	-460	10.1	Pu(OH) ₄	91.1 %
			Pu(OH) ₃	4.7 %
			Pu(OH) ₄ ⁻	1.9 %
			Pu(OH) ₂ ⁺	1.2 %
Tuff	-310	9.4	Pu(CO ₃) ₃ ²⁻	93.3 %
			Pu(CO ₃) ₄ ⁴⁻	6.6 %

TABLE 6

**FITTED EQUILIBRIUM CONSTANTS FOR THE SORPTION OF PLUTONIUM
SPECIES ONTO GOETHITE-TYPE SITES (SOH)**

Reactions*	LogK	Experimental R _D cm ³ g ⁻¹ †
Onto bentonite		
$\text{SOH} + 4\text{H}_s^+ + \text{Pu}_s^{4+} + 3\text{CO}_3^{2-} = \text{SOH}_2\text{Pu}(\text{CO}_3)_3^-$	59.81	5.7×10^4
Onto tuff:		
$\text{SOH} + 4\text{H}_s^+ + \text{Pu}_s^{4+} + 3\text{CO}_3^{2-} = \text{SOH}_2\text{Pu}(\text{CO}_3)_3^-$	58.39	9.3×10^3
Onto granodiorite:		
$\text{SOH} + \text{Pu}_s^{4+} + 4\text{H}_2\text{O} = \text{SOHPu}(\text{OH})_4 + 4\text{H}_s^+$	-5.52	3.3×10^4

† LogK values fitted to average experimental values determined at 60°C after 10000 MWCO filtration.

* The subscript 's' denotes the surface activity of the solute. The surface activity is related to the bulk solution activity through the expression:

$a_s = a_b \exp (-ze\psi/KT)$ where z is the charge of the species, e is the electronic charge, Ψ the potential at the surface, K the Boltzmann constant and T the absolute temperature.