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# Understanding the Behaviour of the Actinides under Disposal Conditions: A Comparison between Calculated and Experimental Solubilities

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*Actinides / Solubility / Repository / Modelling*

## Abstract

The solubilities of plutonium, americium and neptunium measured in simulated near-field waters have been compared with those predicted using the simple thermodynamic model NearSol. The dependence of solubility on pH and redox potential is examined in an effort to understand the behaviour of actinides in disposal.

The agreement was variable. Differences could be appreciable, in particular for neptunium under oxidizing conditions; conversly, the model successfully predicted the behaviour of neptunium under reducing conditions. Such comparisons pinpointed deficiences in the thermodynamic data base and showed the sensitivity of solubilities to certain experimental parameters such as Eh and the concentration of carbonate ions.

A comparison between NearSol and the reaction pathway program PHREEQE gave generally good agreement. NearSol was quicker and easier to use, requiring only limited preselection of participating species; however it did not account for the behaviour of bulk inactive species in solution; this feature will be built into an updated version.

## Introduction

Much effort is presently being spent in developing an understanding of the behaviour and fate of long-lived radionuclides under the disposal conditions favoured for intermediate level nuclear wastes. The combination of experimental simulation and theoretical modelling provides essential information in an area which presents many difficulties, particularly given the long time periods involved in any radiological effects of disposal. Agreement between the two helps to build confidence in the experimental techniques and the models.

The presently accepted option for the disposal of intermediate level wastes arising from the nuclear industry is their encapsulation in a suitable matrix followed by burial in stable geological formations.

One of the major pathways to man from this form of disposal is the release of radionuclides into repository waters and their migration through the geosphere to the biosphere. As a consequence of using the concept of multiple barriers and adopting the philosophy of some redundancy in their engineering, it has been proposed that the materials present in a waste repository, the matrix used to encapsulate the waste, canister and backfilling agents, will provide the bulk of the protection [1]. These materials constitute the so-called near field. This protection is defined in terms of a near-field source term, a general description of the release of radioactivity from the repository. Under the envisaged conditions of very low water flow, the source term is effectively determined by the availability and solubility of the radionuclide and the sorption of radionuclide species on to the surfaces of the near field [2]. A thorough understanding of these processes is therefore desirable before the long-term release rate can be predicted and the method of disposal shown to be acceptable.

Immobilisation studies have shown some cements and concretes with various modifiers to be acceptable matrices for the encapsulation of wastes and backfilling of repositories [3]. Groundwaters flowing through the repository will have pH and composition strongly influenced and buffered by the leaching of the cement solid phases. On sealing a deep repository oxygen levels will fall to very low levels, resulting in a reducing environment with the redox potential being governed by the corroding iron canister and ferrous minerals present in the groundwater [4].

A model has been developed from a simple one devised by ALLARD [5, 6, 7] and a computer program, NearSol [8], written to predict the solubility and speciation of key actinides in repository waters as part of a programme to interpret simulated near-field experiments for intermediate level wastes. The full NearSol thermodynamic data base is given in reference 8; Table 1 gives selected data for the major species predicted in this comparison. Solubilities of plutonium, americium and neptunium have been measured by EWART *et al.* in cement-equilibrated water and the dependence of solubility on redox potential (Eh, which is measured relative to the standard hydrogen electrode) and pH was examined [9, 10]. This is part of a programme being carried out for UK NIREX Ltd. to evaluate the performance of the near-field. These studies were not site specific. Solubility effectively sets an upper limit to the concentrations of a radionuclide in repository waters.

In NearSol, the influence of repository waters on actinide solubilities is modelled using pH, Eh, concentration of complexing ions, and the solubility products of sparingly soluble calcium salts (carbonate, phosphate, etc.) that buffer the concentrations of the anions to low values.

Several comprehensive geochemical models are being used for this type of calculation, in addition to more detailed modelling of the behaviour of the repository and its surroundings. One of these, the reaction pathway program PHREEQE, is extensively used at Harwell [11]. NearSol was written as a rapid response to near-field modelling requirements at a time when the more complex geochemical programs were not readily available at Harwell. Whilst a general near-field model, based on PHREEQE, is now being developed, NearSol still has a role in giving immediate and important information on the speciation and solubility of the actinides.

Table 1. Selected NearSol thermodynamic data base for the actinides ($I = 0$, 25°C)

(i) Solid phases

$$M_xL_y = xM^{m+} + yL^{n-\,(a)} \qquad K_{sp} = [M]^x[L]^y$$

where M is any actinide

| Solid phase | Solubility product ($\log_{10} K_{sp}$) | Reference |
|---|---|---|
| $Am(OH)_3$ | − 25.5 | 13 |
| $Am(OH)CO_3$ | − 23 | 13, 14 |
| $M(OH)_4 \cdot xH_2O$ | − 54 | 5 |
| $MO_2(OH)$ | − 8.8 | 5 |

(ii) Complexes

$$xM^{m+} + yL^{n-} = M_xL_y^{(xm-yn)\,(a)} \qquad K = \frac{[M_xL_y]}{[M]^x[L]^y}$$

| Solution species | Formation constant ($\log_{10} K$) | Reference |
|---|---|---|
| $M(OH)^{2+}$ | 6 | 5 |
| $Am(OH)_3$ | 15.5 | 5 |
| $Am(OH)_2CO_3^-$ | 17.6 | 14 |
| $Am(OH)(CO_3)_2^{2-}$ | 19.8 | 14 |
| $MSO_4^+$ | 3.5 | 5 |
| $M(SO_4)_2^-$ | 5.2 | 5 |
| $M(OH)_3^+$ | 36 | 5 |
| $M(OH)_4$ | 45.5 | 5 |
| $M(OH)_3CO_3^-$ | 42 | 5 |
| $MO_2OH$ | 4.6 | 5 |

(a) Similar equations can be written for solid phases and solution species where two anions are present.

A comparison between NearSol and PHREEQE running NearSol with the PHREEQE data base for the actinides was made to determine whether the chemical features built into the former model were in fact the important ones.

## Methodology for calculating actinide solubilities

In NearSol, actinides are allowed to dissolve according to the solubility products of the various solid phases potentially present; the different oxidation states equilibrate as determined by the standard potentials for redox processes in solution. Dissolution-precipitation reactions continue until the free energy of the system is at a minimum and the solubility product of one solid is achieved (i. e. the solution is saturated with respect to that particular solid); this identifies the solubility-limiting solid phase. In turn, free, uncomplexed actinide will complex extensively with anions in the system as defined by the appropriate stability constants and concentrations of complexing ions. Complexing ions may be involved in further equilibria with bulk, inactive species which may limit their concentrations by precipitation and complex formation. No mass balance between metal and complexant is made during the calculation.

## Experimental data used in the calculations

The experimental methods and other source data of EWART *et al.* are given in references 9 and 10.

### Water composition

Simulated pore water was prepared by equilibrating demineralised water with crushed concrete for several months, after which waters were ultrafiltered to remove the bulk of the colloidal material. The pH was varied by addition of sodium hydroxide or hydrochloric acid. The chemical analysis was as follows:

| Ion | $Ca^{2+}$ | $Na^+$ | $Mg^{2+}$ |
|---|---|---|---|
| Concentration ($M$) | $1 \times 10^{-2}$ | $5 \times 10^{-5}$ | $5 \times 10^{-6}$ |

| Ion | $Cl^-$ | $SO_4^{2-}$ | $CO_3^{2-}$ | pH |
|---|---|---|---|---|
| Concentration ($M$) | $2 \times 10^{-3}$ | $3 \times 10^{-3}$ | $3 \times 10^{-5}$ | 12 |

(Ionic strength = 0.04 $M$)

### Redox potential

For the studies with americium and neptunium the concrete water was allowed to equilibrate in a glove box under a nitrogen atmosphere resulting in an Eh of approximately 200 mV. To examine plutonium in a reducing environment, waters were sparged with argon/5% hydrogen, effectively removing oxygen to below the limit of detection. This gave a redox potential of approximately 50 mV. Further reduction gave a measured Eh for the plutonium solubilities of −300 mV. In the subsequent neptunium solubility experiments the Eh measured was −400 mV or less.

Actinides were added in small volumes as chloride in solution. Samples were analysed after ultrafiltration to remove the colloidal fraction after thirty minutes (Pu and Am) or twenty-four hours (Np) equilibration time.

## Results

Comparisons of predicted and experimental solubilities for americium under oxidizing conditions and plutonium and neptunium under reducing conditions against pH are shown in Figures 1 to 3.

Americium solubilities (Fig. 1) were independent of Eh under the experimental conditions, Am(III) being the only oxidation state present. The experimental solubilities gradually decreased from $10^{-5}$ $M$ at pH 8 to $10^{-11}$ $M$ at pH 13. The solubility limiting solid phase was predicted to change from the mixed hydroxycarbonate to the trihydroxide at about pH 10.5. The mixed hydroxycarbonate species $Am(OH)_2CO_3^-$ is expected to dominate the solubility at high pH, but as the pH decreases $Am^{3+}$ should gradually become dominant and give a rapid in-

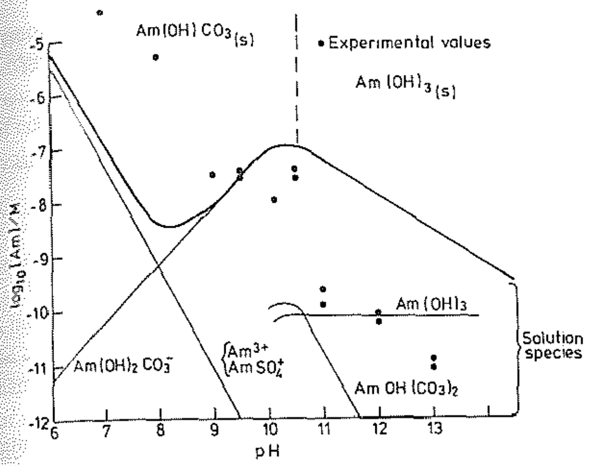

Fig. 1. Predicted and experimental solubilities of americium

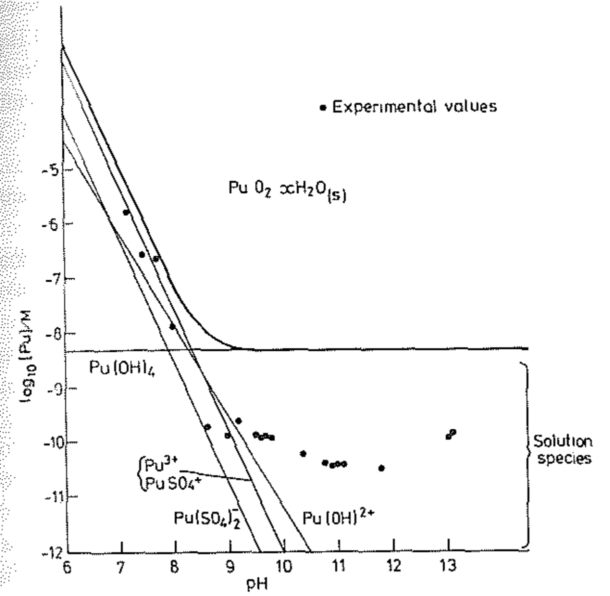

Fig. 2. Predicted and experimental solubilities of plutonium under reducing conditions

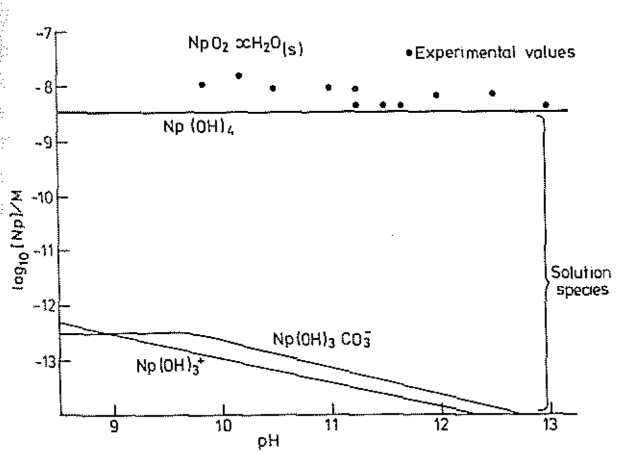

Fig. 3. Predicted and experimental solubilities of neptunium under reducing conditions

crease in solubility below pH 8. Sulphate complexation at near-neutral pH could be significant if the concentration of free sulphate ion is not reduced by other competing reactions e. g. the formation of the calcium sulphate complex. No evidence for the anionic species $Am(OH)_4^-$ was obtained; if important, it would result in an increase in solubility at high pH. Agreement was fair between pH 9–10.5 but discrepancies of up to two orders of magnitude were observed at higher and lower pH values.

The expected precipitating solid phase for plutonium was hydrated plutonium(IV) dioxide. The measured solubility was independent of pH above 8.5 at about $10^{-10}$ *M*, the predicted solution species being the neutral hydroxide $Pu(OH)_4$. At lower pH, plutonium(III) species could explain the rapid increase in solubility ($10^{-6}$ *M* at pH 7.5). As with americium, $Pu^{3+}$ is expected to be the main species at neutral pH; sulphate species could increase solubility if the free concentration was not suppressed. The general shape of the predicted solubility curve followed experimental trends, but above pH 8.0 there were significant differences of up to two orders or magnitude. The anionic species $Pu(OH)_5^-$ which could increase solubility at high pH did not appear to be significant.

Excellent agreement for neptunium under reducing conditions was obtained between theory and experiment. No pH dependence was observed, the solubility being about $10^{-8}$ *M* throughout. The precipitating solid phase was predicted to be the hydrated neptunium(IV) dioxide and the main aqueous species $Np(OH)_4$. No increase in solubility was observed at high pH; there was no evidence of the anionic species $Np(OH)_5^-$.

The solubility of neptunium was also measured in more oxidizing waters (about 200 mV). The modelled results are not given here due to uncertainties over the exact Eh; the solubility is very sensitive to Eh in this region due to the position of the $NpO_2^+/Np^{4+}$ redox couple. Predicted solubilities bore little resemblance to experimental results. Figure 4 shows the theoretical dependence of solubility on

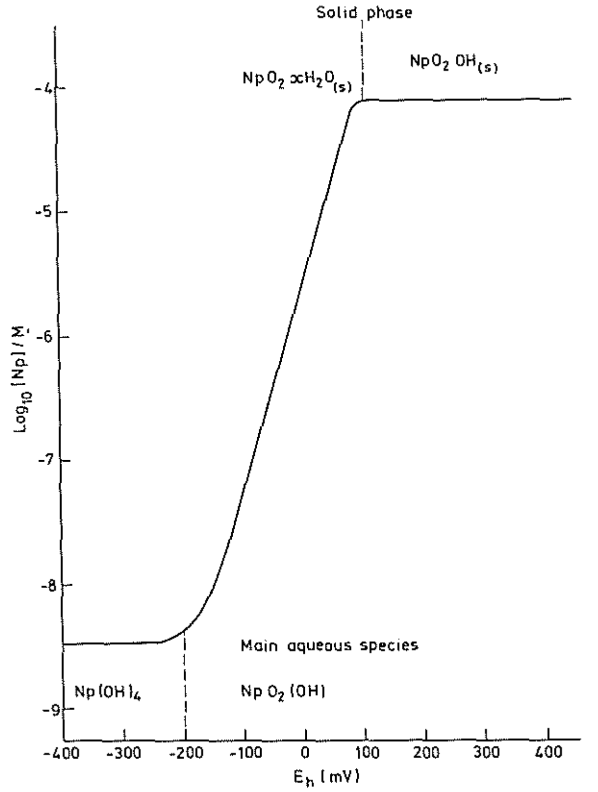

Fig. 4. The effect of Eh on the solubility of neptunium at pH 12.0

Eh at a fixed pH 12 and the water composition given earlier. A rapid increase in solubility is expected as the soluble species change from hydrolysed Np(IV) to Np(V) and a similar change occurs in the solid phase.

## Intercode comparison: NearSol vs PHREEQE

The solubility and speciation of americium was remodelled by the reaction pathway program PHREEQE and by an adapted version of NearSol using the PHREEQE americium data base; the comparison of the two is shown in Figure 5.

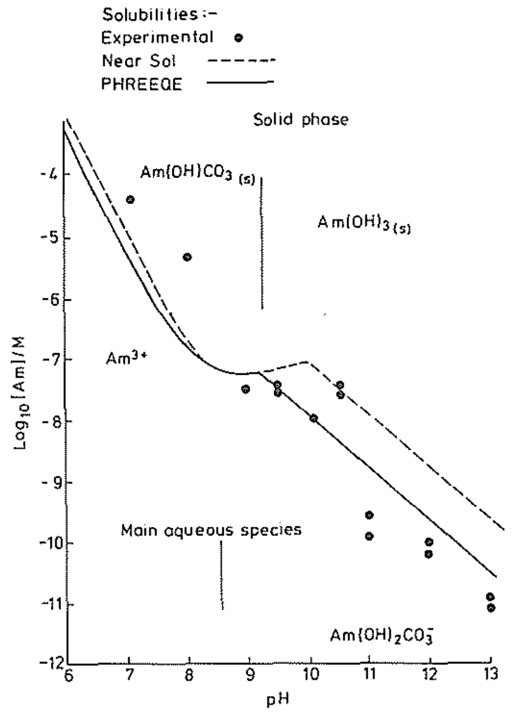

Fig. 5. Comparison between americium solubilities and speciation predicted by NearSol and PHREEQE

Both models show a similar trend in solubility with respect to pH; however PHREEQE solubilities were up to one order of magnitude lower. These discrepancies in solubility and speciation were due to the inability of NearSol to evaluate the role of complexes formed by inactive cations, in particular calcium, introduced by the concrete. This will lower the concentration of free anions available to complex with the actinides. This point is discussed further in the next section.

There was no difference in predicted solubilities when a similar comparison was made with plutonium and neptunium.

## Discussion

### Americium

The comparison between predicted and experimental solubilities gave only limited agreement: this may be explained by two main factors. Competition for the strong complexing anions carbonate and sulphate by cations leached from the concrete, in particular calcium, will effectively reduce their free concentrations available to interact with americium and may alter the position of equilibrium with the solid phase. This can suppress complex formation but may increase the solubility of the solid phase; NearSol does not at present consider this important effect. The quality of the data base can give further discrepancies. Increasing the solubility product for $Am(OH)_3$ and the formation constant for $Am(OH)_2CO_3^-$ gives better agreement [9].

The point of inflection at about pH 10 as the solid phase is predicted to change from the hydroxide to hydroxycarbonate was not obvious from the experimental data. This comparison highlights the sensitivity of americium solubility to carbonate concentration throughout the pH range and the need for accurate analytical data for each run, and a reliable data base for the carbonate species.

### Plutonium

The predicted solubilities followed the experimental trend but were two orders of magnitude too high at pH 9 and above. The only solution species predicted in the high pH range was $Pu(OH)_4$, which results in solubility being independent of pH; the solubility product used may be rather high.

### Neptunium

Under reducing conditions very good agreement between calculated and measured solubilities was achieved. It should be emphasized, however, that lowering the solubility product and increasing the formation constant for $NpO_2 \cdot x H_2O_{(s)}$ and $Np(OH)_{4(aq)}$ respectively, and vice-versa, would give a similar solubility; any assumption that the data base has been validated must be treated with caution.

These modelling studies have confirmed that Eh is a key parameter in determining the solubility of neptunium. This has been observed in a comparison between some of the solubilities measured by EWART *et al.* [9] and those of KIM [12], both nominally under oxidizing conditions. Variations in solubility amount to some orders of magnitude, and this suggested that the British measurements were carried out at a somewhat lower Eh than originally estimated. Reliable thermodynamic data are needed for the hydrolysis products $NpO_2(OH)_x^{(1-x)+}$. The first hydrolysis product $NpO_2OH$ is included in the model but KIM has recently identified the anionic species $NpO_2(OH)_2^-$ [12], which would result in increased solubilities at high pH.

### Colloids

Colloids are not considered in the model although the formation constants for some small polynuclear species ($n \leqslant 6$) are included. In the experiments colloids were removed by ultrafiltration but small polynuclear species which would pass through the filter membranes could enhance the 'apparent' solubility. The role and importance of colloidal species in the near field has still to be fully evaluated.

## Comparison between models

A major disadvantage of NearSol is the inability to model the complexation behaviour of near-field cations other than the actinides. This was found to be important only for americium. Although solubility products of calcium salts were included in the data base there is no provision for evaluating the formation of carbonate, sulphate and phosphate complexes. PHREEQE showed that above pH 10 the formation of the dominant species $Am(OH)_2CO_3^-$ would be suppressed due to competition for carbonate by $Ca^{2+}$ forming $CaCO_{3(aq)}$ and $CaHCO_{3(aq)^+}$; at high pH the formation of $Ca(OH)^+_{(aq)}$ reduces this effect. At pH below 10 NearSol predicted that $AmSO_4^+$ would influence solubility; however, the formation of $CaSO_{4(aq)}$ would effectively reduce the concentration of this species. An advanced form of NearSol will include such calcium complexation. Other near-field cations such as $Na^+$ and $Mg^{2+}$ will not be modelled as expected concentrations would be too low to influence solubility.

NearSol has no capability for interpreting the effect of high actinide inventories and assumes that the amount of actinide just exceeds the solubility product, as would be found in a solubility experiment where just sufficient actinide is added to form a precipitate. For example, at intermediate pH with an excess of americium over carbonate, sufficient of the latter would be precipitated as $Am(OH)CO_3(s)$ to result in a change of solid phase to $Am(OH)_3$ (s) and an increase in solubility. Other more complex models can examine inventory and a variety of other parameters such as temperature and kinetics; however the objectives of NearSol are to remain simple and flexible and to be limited to modelling solubility in the near-field and simulated experiments where both actinide and complexing anions are in equilibrium with their solid phases.

NearSol has the advantages of simplicity and ease in use. The complex geochemical models require a thorough operator knowledge of the system to reduce the time of calculation and eliminate trial and error calculations; data screening may be necessary to identify important aqueous species and limiting solids [11]. Whereas such programs are preferred for detailed modelling, NearSol should be satisfactory for many near-field solubility calculations and could be used to preselect the significant species to increase the efficiency of operation of programs such as PHREEQE.

Much effort is presently being directed towards a general near-field model based on PHREEQE which will ultimately be superior to such simple models as NearSol; however valuable understanding of the near-field chemistry of the actinides can still be obtained using the latter.

## Conclusions

The conclusions of this study are as follows:

(a) NearSol has been valuable in predicting speciation and trends in solubility of actinides but does not give consistently good agreement with experimental determinations of the solubilities of Pu, Am and Np in simulated repository waters.

(b) From these studies it has been shown that there is a need to define certain experimental data used in modelling accurately. Examples include Eh with Np and concentrations of carbonate ions when modelling the behaviour of Am.

(c) Inadequacies in the thermodynamic data base identified from using NearSol include:

- (i) the standard redox potential for the Np(IV)/Np(V) couple.
- (ii) stability constants for americium hydroxycarbonate complexes.
- (iii) the solubility product of hydrated $PuO_2$.

(d) Calculations with NearSol (run with the PHREEQE data base for the actinides) and the geochemical model PHREEQE are similar. The major difference is that NearSol does not, at present, allow for complex formation between calcium ions and complexing anions.

(e) NearSol has made an important contribution to the understanding of the chemistry of the near-field.

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