COMPUTER SIMULATION MODELLING OF MIXED CHEMICAL/RADIOACTIVE WASTE DISPOSAL SYSTEMS

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ABSTRACT

As part of an investigation into the disposal of low level radioactive waste, the maximum solubilities of some important actinides (plutonium, americium and neptunium) in the presence of some organic complexing agents have been determined by a computer modelling technique. Predictions were made using an aqueous composition typical of a leached concrete pore water and by equilibration with the most likely actinide mineral phase. The effect of redox, pH and concentration of organic ligand, which were considered appropriate to a possible repository environment, have been evaluated.

INTRODUCTION

The safe disposal of radioactive waste requires a good understanding of the chemical interactions of the waste components with their respective environments, both in the near- and far-fields. Such interactions are of prime importance in determining the mobilization of the radionuclides present in the waste with respect to the conflicting processes of retardation and release.

Central to this issue will be the aqueous phase chemical speciation of the actinides with the inorganic and organic constituents of the waste matrix, the containment vault, and the surrounding geosphere. This is because chemical complexation reactions are pivotal in controlling the physico-chemical phenomena involved in retardation such as precipitation, sorption and colloid formation (1).

The maximum solubilities of some actinide elements (Pu, Am and Np) have been experimentally measured, and the resulting data used in validation exercises to assess the predictive capabilities of computer speciation models. Good agreement between computer predictions and experimental measurements was obtained in all cases (2). Although experimental measurements are essential in the assessment of radioactive waste disposal, time constraints and economic considerations restrict their application. However, given adequate thermodynamic data, computer simulation provides an alternative method for determining the effect of complex chemical equilibria over an extensive range of chemical conditions. Therefore, it may be necessary to resort to modelling of the metal-ligand interactions to provide a complementary method of investigation and, in addition, to optimize and direct any experimental program of work.

The Speciation Research Group at UWIST, Cardiff is one of the foremost laboratories in the chemical speciation simulation field in the United Kingdom and possesses fifteen computer programs and a library of associated thermodynamic databases for the simulation of chemical speciation in aqueous media. The programs range in sophistication from the relatively straightforward static modelling codes which can consider single solutions and may, or may not, include precipitation and redox reactions, to reaction pathway and chemical transport codes in which mixing and sorption may be considered (1). In the past, these programs have been used extensively to model a variety of systems, including groundwaters and biofluids (3, 4). The effects of speciation on flow have also been investigated by coupling a reaction pathway model with a chemical transfer model (5).

To date, these models have used thermodynamic data relating to the interactions of activation and fission products with the inorganic ligands present in the wastes and groundwaters. However, radioactive waste is not a purely inorganic system as it may contain a number of organic ligands which have been used in equipment decontamination procedures (e.g. $EDTA^{4-}$ and citrate) or are the decomposition products of waste materials such as cellulose, (e.g. D-glucoisosaccharate).

The work reported here refers, in part, to a preliminary study on the effects of the presence of EDTA, citrate and acetate in the waste matrix on the solubility and speciation of plutonium, americium and neptunium in concrete pore solutions.

MODELLING STUDIES

Methodology and Data Requirements

Migration of radionuclides from the intact vault will occur in the aqueous phase. Therefore, modelling requires consideration of the chemical composition of the leached pore water and the solubility limiting phase of the actinide under scrutiny. Obviously, the lower the solubility of the actinide, the less likely is the movement of that actinide from the repository into the biosphere.

The chemical composition of the pore water used in this study is given in Table I and is typical of soluble components of cementitious material as found by experimental analysis (2).

Corrosion of the steel canister containing the waste matrix and the iron components of the repository

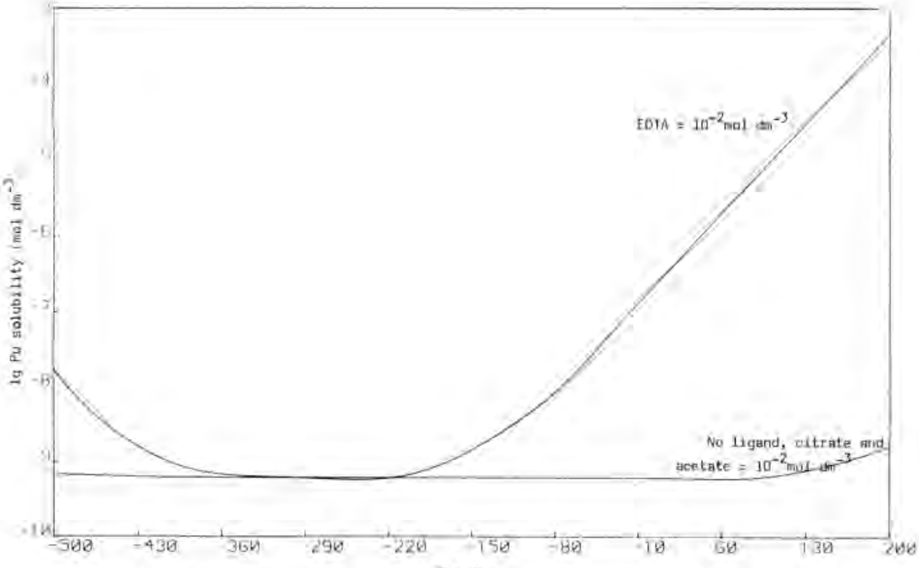

Fig. 1. Computed Solubility in a Concrete Solution at Different Redox Potentials (pH = 12.0).

will influence the redox potential of the system which may vary considerably. Therefore, a range of values should be considered in order to fully evaulate the possible implications of redox potential and the subsequent formation of different oxidation states of the components.

TABLE I

A Typical Concrete Pore Water Composition

Component	Concentration(mol dm^{-3})
Ca^{2+}	1.0×10^{-4}
Na^+	5.0×10^{-5}
Mg^{2+}	5.0×10^{-6}
CO_3^{2-}	3.0×10^{-5}
SO_4^{2-}	3.0×10^{-3}
Cl^-	2.0×10^{-3}

The existence of sodium, potassium and calcium hydroxides in a young concrete matrix produces a highly alkaline pore water. Aging effects by the depletion of calcium hydroxide will result in a gradual decrease in the pH, such that a range of values between pH 13.0 to 10.0 can be envisaged for the pore water. An arbitrarily chosen lower limit of 1×10^{-4} mol dm^{-3} was considered appropriate for the total calcium ion concentration for the present work. Although its concentration will be variable, calcium is considered the most likely cation to competitively complex with any organic ligand prior to the formation of any radionuclide-organic complexes. Evaluation of redox potential and pH effects on actinide solubility were also performed using an organic ligand concentration of 1×10^{-2} mol dm^{-3}, as this was expected to represent the maximum limit to be contained in the leached concrete water. The models are, therefore, assumed to represent the most pessimistic prediction for actinide solubility.

The solubility limiting phases chosen for this work for plutonium, neptunium and americium are amorphous $Pu(OH)_4$, $Np(OH)_4$ and $Am(OH)_3$, respectively. Under the pH conditions considered for this work, experimental results have validated modelled results have validated modelled results with good agreement (in the absence of organic ligands) and thus provide justification for their inclusion (2).

Dissolution/precipitation equilibria of the mineral phases of plutonium, americium and neptunium in the presence of EDTA, citrate and acetate were performed using the geochemical code MINEQL (6) and the reaction path code PHREEQE (7). In each model the total solubility of the actinide was determined under the chemical conditions specified.

In recent years, a large volume of experimentally determined (and estimated) thermodynamic data, including the formation of inorganic complexes of Pu, Np and Am has been collated (8, 9, 10, 11). A definitive description of the inorganic species, together with their numerical formation constants, is unlikely to satisfy all critics. It is possible that the inclusion of alternative or additional species and their thermodynamic data may have some effect on the speciation in any particular system. It is not within the scope of this paper to consider the merits of the choice of the individual inorganic species; nevertheless, the choice of species has been validated experimentally as described earlier. This compilation of inorganic species is essentially that based upon one used previously with a few improvements (11, 12).

More importantly, an extensive literature survey of thermodynamic data for organic complexes has been undertaken recently and incorporated into the UWIST database library. It is apparent that the number of experimentally determined formation constants compared to inorganic complexes is considerably fewer. Formation constant data relating to the systems considered in the present work are given in Table II after they have been corrected for temperature (25°C) and ionic strength (I=0).

RESULTS AND DISCUSSION

The solubilities of plutonium, americium and neptunium in the presence of three organic ligands

TABLE II

Thermodynamic Data for Actinide-Organic Ligand Species Used in Computer Simulations

(Correct to 25°C and Ionic Strength I = 0)

Aqueous Species	Oxidation State of Actinide	Formation Constant (lg β)	Source Reference
$PuEDTA^-$	(III)	17.52	13
$PuHEDTA$	(III)	22.33	13
$PuEDTA$	(IV)	28.95	14
PuO_2EDTA^{3-}	(V)	13.74	15
PuO_2HEDTA^{2-}	(V)	16.54	16
PuO_2EDTA^{2-}	(VI)	18.07	17
$AmEDTA^-$	(III)	20.58	18
$NpEDTA$	(IV)	27.75	19
NpO_2EDTA^{3-}	(V)	8.17	16
NpO_2HEDTA^{2-}	(V)	17.04	16
$NpO_2EDTA\ OH^{4-}$	(V)	-3.97	16
$PuCit$	(III)	10.66	20
$PuH_4Cit_2^+$	(III)	28.42	20
PuH_6Cit_3	(III)	42.43	20
$PuCit^+$	(IV)	14.71	21
$PuHCit^{2+}$	(IV)	16.26	21
PuH_2Cit^{3+}	(IV)	16.86	21
$PuCitOH$	(IV)	9.21	21
$PuCit(OH)_2^-$	(IV)	4.96	21
$PuCit_2^{2-}$	(IV)	19.92	21
PuH_2Cit_2	(IV)	29.52	21
$PuH_4Cit_2^{2+}$	(IV)	31.32	21
$PuH_5Cit_2^{3+}$	(IV)	31.42	21
$PuCit_2(OH)_2^{4-}$	(IV)	9.82	21
PuO_2Cit^{2-}	(V)	5.47	22
PuO_2HCit^-	(V)	9.48	23
PuO_2Cit^-	(VI)	10.59	24
$PuO_2Cit_2^{4-}$	(VI)	10.59	24
$AmCit$	(III)	8.76	25
$AmCit_2^{3-}$	(III)	12.10	25
$AmHCit^+$	(III)	11.67	25
$AmCitOH^-$	(III)	3.15	25
AmH_6Cit_3	(III)	12.49	26
NpO_2Cit^{2-}	(V)	5.47	22
NpO_2HCit^-	(V)	9.48	23
$PuAc^{2+}$	(III)	5.08	20
$PuAc_2^+$	(III)	9.11	20
$PuAc_3$	(III)	13.80	20
$PuAc_4^-$	(III)	16.91	20
$PuHAc^{3+}$	(III)	7.93	20
$PuAc^{3+}$	(IV)	6.15	27
$PuAc_2^{2+}$	(IV)	10.47	27
$PuAc_3^+$	(IV)	15.79	27
$PuAc_4$	(IV)	20.40	27
$PuAc_5^-$	(IV)	24.70	27
PuO_2Ac^+	(VI)	2.73	28
PuO_2Ac_2	(VI)	4.43	28
$PuO_2Ac_3^-$	(VI)	5.61	28
$AmAc^{2-}$	(III)	2.78	29
$AmAc_2^-$	(III)	4.60	29
$AmAc_3$	(III)	5.48	29
NpO_2Ac^+	(VI)	2.71	30
NpO_2Ac_2	(VI)	4.83	30
$NpO_2Ac_3^-$	(VI)	6.60	30

Notes:

(i) $EDTA^{4-}$ - Ethylenediaminetetraacetate
Cit^{3-} - Citrate
Ac^- - Acetate

(ii) All Formation Constants are expressed in the form:

$$pM + qL + rH = M_pL_qH_r\ ;\ \beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$$

except for the mixed hydroxy-ligand species which are expressed thus:

$$pM + qL + rH_2O = M_pL_qOH_r + rH;\ \beta_{pqr} = \frac{[M_pL_qOH_r][H]^r}{[M]^p[L]^q}$$

(EDTA, citrate and acetate) have been computed in a typical concrete solution under expected near-field conditions.

Plutonium

The total solubilities of plutonium in the presence of 1×10^{-2} mol dm^{-3} EDTA, citrate and acetate, at pH 12.0, are given as a function of redox potential in Fig. 1. Also shown, for comparison, are the computed values in the absence of these organic ligands. It is evident that the inclusion of both citrate and acetate have no significant effect on solubility over the range of E_h considered. The dominant aqueous species were computed as being $Pu(OH)_4$ and $Pu(OH)_5^-$ and, to a lesser extent, $Pu(OH)_3$ under reducing conditions. Under oxidizing conditions, the presence of $PuO_2(OH)_2^-$ and $PuO_2(CO_3)OH^-$ were more noticeable.

Considerable variation in the plutonium solubility is observed by the inclusion of EDTA. Under mildly reducing and oxidizing conditions, the formation of PuO_2EDTA^{3-} was computed as being significant. To a lesser extent, an increase in solubility is predicted due to the formation of $PuEDTA^-$ under strongly reducing conditions. Furthermore, over a finite redox potential (approx. -220 to -360 mV) no significant bange in solubility is observed.

To ensure consistency of results, verification exercises are necessary (30), and these were undertaken using MINEQL and PHREEQE codes and their respective databases. A typical comparison is given in Table III, and the results obtained appear to be in reasonable agreement. This simple approach ensures that any errors in the data input have been eliminated and that the solution of computer calculations by the

TABLE III

Comparison of Computed Solubilities Using PHREEQE and MINEQL (pH = 12.0, EDTA = 10^{-2} mol dm^{-3})

E_h(mV)	Pu Solubility(mol dm^{-3})	Dominant Aqueous Species	% Aqueous Pu
	MINEQL		
−500	1.65×10^{-8}	$PuEDTA^-$	95.8
		$Pu(OH)_4$	1.9
		$Pu(OH)_5^-$	1.7
0	2.01×10^{-7}	PuO_2EDTA^{3-}	99.7
+200	4.74×10^{-4}	PuO_2EDTA^{3-}	100.0
	PHREEQE		
−500	2.14×10^{-8}	$PuEDTA^-$	97.3
		$Pu(OH)_4$	1.3
		$Pu(OH)_5^-$	1.2
0	2.50×10^{-7}	PuO_2EDTA^{3-}	99.8
+200	5.83×10^{-4}	PuO_2EDTA^{3-}	100.0

TABLE IV

Effect of Citrate and Acetate as a Function of pH at Different Redox Potentials lg Pu Solubility (mol dm^{-3})

E_h(mV)	−500	−300	0
pH		NO ORGANIC LIGAND	
13	−8.55	−8.55	−8.55
12	−9.27	−9.29	−9.29
11	−9.47	−9.51	−9.51
10	−9.53	−9.35	−9.54
		CITRATE = 10^{-2} mol dm^{-2}	
13	−8.55	−8.55	−8.55
12	−9.25	−9.29	−9.29
11	−9.27	−9.51	−9.51
10	−5.73	−9.00	−9.54
		ACETATE = 10^{-2} mol dm^{-3}	
13	−8.55	−8.55	−8.55
12	−9.27	−9.29	−9.29
11	−8.72	−9.51	−9.51
10	−4.81	−8.19	−9.54

Figure 3 Computed plutonium solubility in a concrete solution at different EDTa Concentrations (pH = 11.0).

MINEQL and PHREEQE codes which use different convergence methods (Newton-Raphson and "continued fraction," respectively) are acceptable.

The influence of pH on plutonium solubility is given in Fig. 2 for EDTA, and in Table IV for citrate and acetate. It is evident that the solubility is increased by the inclusion of EDTA except with the coincidence of extremely alkaline pH values and reducing conditions. Therefore, any aging of the cement below pH 12.0 could result in some solubilization and possible migration of plutonium. Citrate and acetate, in comparison to EDTA, have little effect on solubility except under reducing conditions at the lower end of the pH range considered. Overall, it appears that the order of importance of organic complexing agents in determining plutonium solubility is EDTA acetate citrate.

The calculations described above have been performed from a worst case point of view with regard to the organic ligand concentration. The effect of EDTA concentration on plutonium solubility was evaluated and the results are given in Fig. 3. Under the conditions considered, it appears that the inclusion of EDTA will only affect the solubility subsequent to the near total chelation of aqueous calcium ions.

Americium

Unlike plutonium and neptunium, americium is only present in the trivalent oxidation state, in the near field. Since only one valence state is possible, the total solubilities of americium were determined as a function of pH. The computed values are given in Fig. 4, in the absence of organic ligand and in the presence of 1 x 10^{-2} mol dm^{-3} citrate and acetate, and 1 x 10^{-4} mol dm^{-3} EDTA.

As EDTA and citrate ligands have been shown to affect americium solubility, the effect of ligand concentration was evaluated at pH 11.0 and the computed results are given in Fig. 5. It is apparent that the solubilities computed for americium are increased over a greater EDTA concentration range than is observed for plutonium (Fig. 3). This effect is probably due to the greater magnitude of the $AmEDTA^-$ formation constant as compared with that for $PuEDTA^-$ (Table II).

Neptunium

The total solubilities of neptunium in the absence and presence of 1 x 10^{-2} mol dm^{-3} EDTA, citrate and acetate, as a function of redox potential, at pH 12.0, are given in Fig. 6. Solubilities were calculated using amorphorous $Np(OH)_4$ as the solubility limiting phase. Under the pH conditions considered, the computer simulations indicated that this mineral phase (as given by the saturation index) would control neptunium solubility.

Overall, only inclusion of acetate has no effect on solubility. The dominant aqueous species were computed as being $Np(OH)_4$ and $Np(OH)_5^-$ under reducing conditions while NpO_2OH became more prominent as the redox potential became more positive. It is not surprising that acetate had no effect on solubility since neptunium-acetate aqueous species with an oxidation state of five have not been included in the model. Increased solubilities resulting from the inclusion of EDTA and citrate are due to the formation of $NpO_2EDTA\ OH^{4-}$ and NpO_2EDTA^{3-}, and NpO_2Cit^{2-}, respectively. Similarly, the lack of neptunium-organic aqueous species with a valence state of three in the models results in no change in solubilities under reducing conditions.

CONCLUSIONS

This type of study provides useful information regarding the likely solubility of actinides present in radioactive wastes which contain organic complexing agents.

It should be appreciated that the measurement of formation constants for actinide species is very difficult because of the chemical complexity of their aqueous solution chemistry, with respect to hydrolysis. Furthermore, the constants are frequently

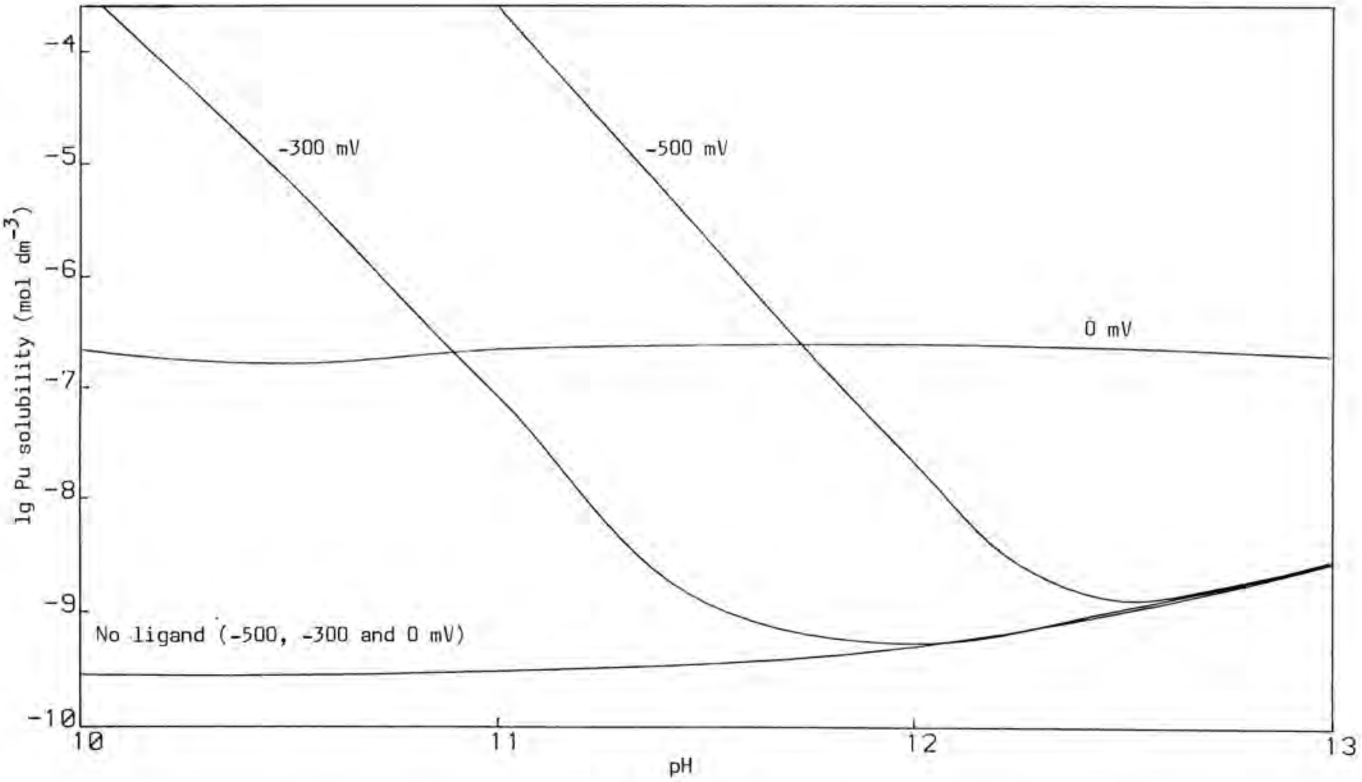

Fig. 2. Computed Plutonium Solubility in a Concrete Solution at Different pH Values (EDTA = 10^{-2} mol dm^{-3}).

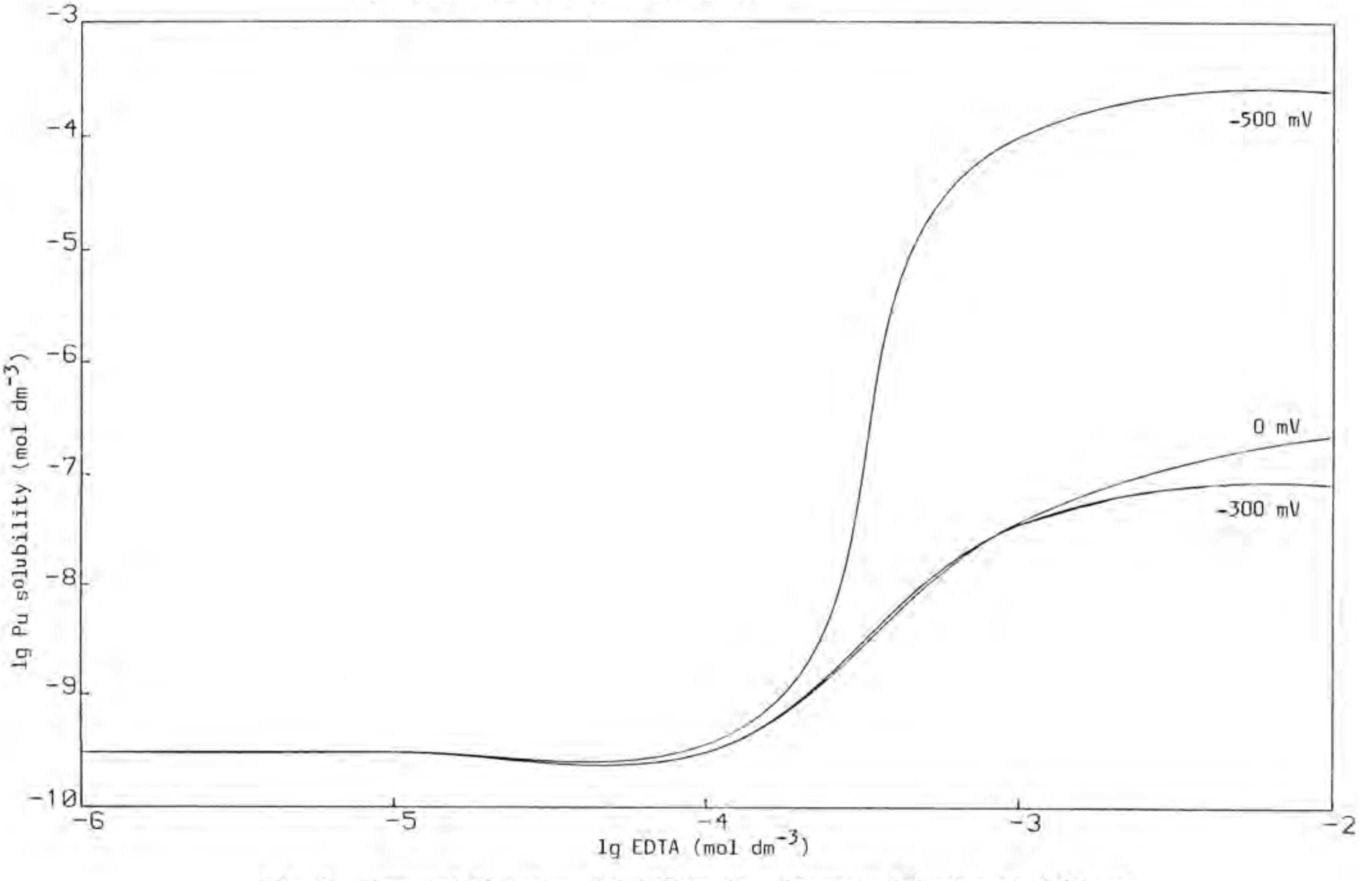

Fig. 3. Computed Plutonium Solubility in a Concrete Solution at Different EDTA Concentrations (pH = 11.0).

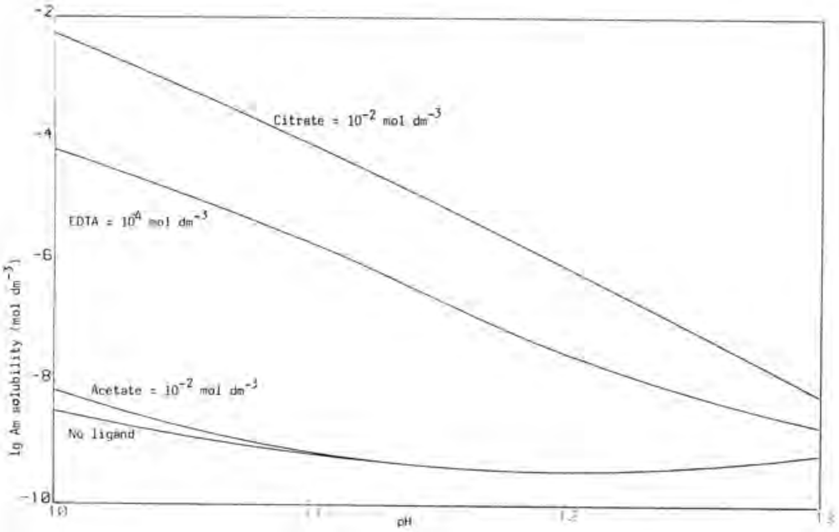

Fig. 4. Computed Americium Solubility in a Concrete Solution at Different pH Values.

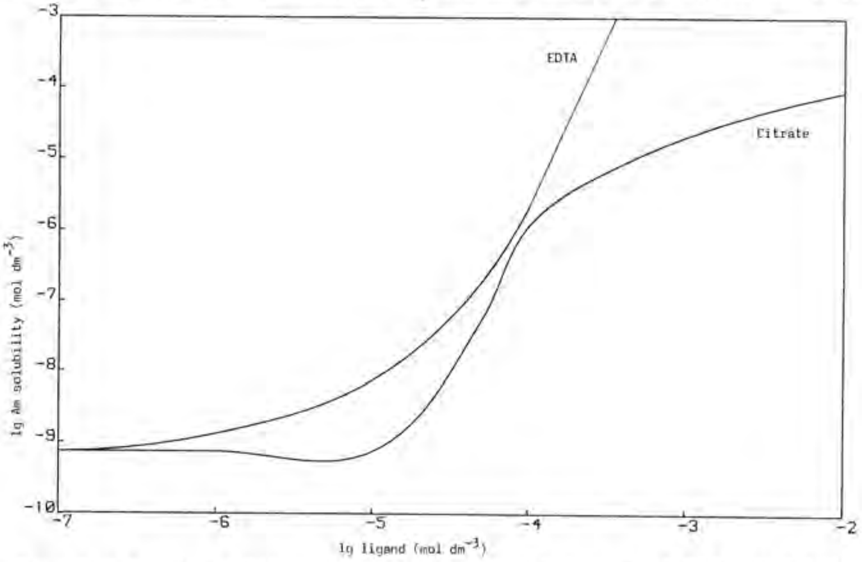

Fig. 5. Computed Americium Solubility in a Concrete Solution of Different EDTA and Acetate Concentrations (pH = 11.0).

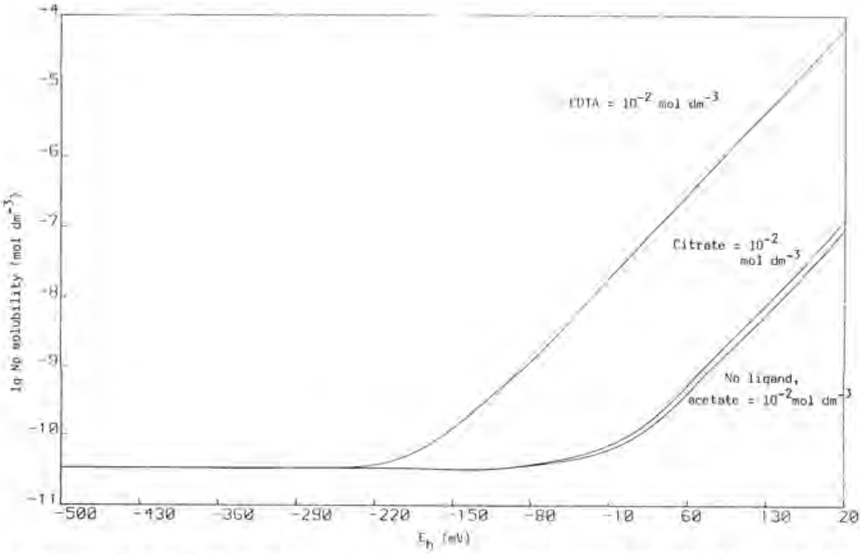

Fig. 6. Computed Neptunium Solubility in a Concrete Solution at Different Redox Potentials (pH = 12.0).

measured over a highly acidic pH range. In consequence, there is a lack of data available for the organic-actinide species that might exist under alkaline conditions which would be particularly relevant to this study.

It is acknowledged that the list of organic species is probably incomplete, as only experimentally determined thermodynamic data for EDTA, citrate and acetate have been included in the database. However, the models serve to identify and direct important areas of further investigation for experimentalists and indicate where it may be necessary to measure thermodynamic data for improvement of future models.

ACKNOWLEDGEMENTS

This work was funded by UK Nirex Limited and their permission to publish these results is gratefully acknowledged.

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