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# Criteria for compilation of a site-specific thermodynamic database for geochemical speciation calculations

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## Abstract

A methodology has been developed to establish a site-specific database appropriate to geochemical modelling the critical components and the wide range of near field conditions expected in the low level radioactive waste disposal site at Drigg in the UK. Several databases available in the public domain have been compared to select a foundation database. The foundation database was ‘trimmed-down’ and then customised to suit Drigg applications. The species dominant at Drigg have been identified and the thermodynamic constants of these species have been critically evaluated. The evaluated database has been validated for quality by comparing speciation calculations with plutonium and uranium experimental solubility results. © 1998 Elsevier Science S.A.

*Keywords:* Geochemical modelling/speciation; Thermodynamic databases; Uranium and plutonium solubility

## 1. Introduction

The current conceptual understanding of processes operating in the near field of the low level radioactive waste disposal site at Drigg in the UK are encapsulated within the DRINK (DRIgg Near field Kinetic) code [1]. The basis of chemical calculations within DRINK is an enhanced version of the USGS thermodynamic speciation code PHREEQE [2].

The prediction of near field speciation is dependent on the thermodynamic database that is used by PHREEQE. No one public domain database covered the full range of ligands, major elements and nuclides required for Drigg. A methodology has been developed to establish a site-specific database appropriate to modelling the critical components and the wide range of possible near field conditions.

## 2. Choice of a foundation database

As compilation of databases requires substantial effort and is normally managed within the context of multinational collaboration, the procedure chosen was to assess and modify data from existing database compilations.

The following three databases were compared to identify a foundation database: (1) CHEMVAL Version 6 database [3]; (2) BNFL internal database [4]; (3) HATCHES NEA Version 9 database [5].

The selection criteria were as follows. (1) The database must cover both aqueous and solid (mineral) phase equilibrium data. (2) All significant measured components of Drigg groundwater and leachates must be included. This includes components such as acetates. (3) Components must cover all of the nuclides that may be considered to be of major importance for Drigg [6]. This includes elements such as Pu, Th, U, Cs and Sr. (4) Components must cover all those involved in important processes. This includes components such as Fe, nitrate and sulphate from waste degradation and metal corrosion.

The NEA 9 database, which also contains some actinide data obtained from recent critical evaluation by NEA [7,8], mainly for uranium and americium, had the closest match to the selection criteria, and was therefore selected as the foundation database.

## 3. Customisation of the foundation database

NEA 9 is overspecified for Drigg modelling purposes. Many components were removed to aid computational efficiency.

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The evaluation of the Drigg near field is crucially dependent on microbial action [9]. Microbial activity impacts on the chemistry through substrate removal ($O_2$, $NO_3^-$, etc.), product generation ($CO_2$, acetic acid, etc.) and speciation and pH change. In addition, redox reactions are mediated by microbial activity, and are kinetically controlled. Therefore, to prevent equilibrium redox reactions occurring, the different oxidation states of the major elements have to be defined as independent master species, and any species containing these master species reconfigured. This allows the microbial module of DRINK to perform the relevant, kinetically controlled redox transformations.

Any subsequent speciation calculations described here were carried out using the customised database which will be referred to as the Drigg database.

## 4. Identification of dominating species

Computational efficiency during DRINK simulations is substantially improved if only those species of significant importance to near field behaviour are included in the database. Therefore species which could dominate at the Drigg site were identified through some PHREEQE runs for simulant solutions containing components expected in trenches and vaults under various conditions. From the resulting variations in leachate chemistry, speciation calculations were carried out using several databases (including the Drigg database) for the sake of comparison. This comparison highlighted any discrepancies in speciation arising solely from alternative database compilations.

The dominating species calculated from the foundation database were then critically evaluated in detail as outlined below.

## 5. Thermodynamic data evaluation

The thermodynamic data of the dominating species were critically evaluated to provide confidence in the quality of the data. The stability constants and solubility products of dominant species were critically evaluated based on the following criteria:

(1) Ionic strength corrections. Was there consistency in ionic strength extrapolation techniques used?

(2) Source of thermodynamic data. Has the thermodynamic data for the complexes of a metal with a given ligand been extracted from the same source?

(3) Estimated data. Quality of estimated data cannot be easily assessed. They have been highlighted and ‘warned’.

(4) Critically evaluated data. Has data been extracted, wherever possible, from data compilations which already have been critically evaluated?

(5) Missing data. Are there any dominating species at Drigg, which have not been included in the Drigg database?

## 6. Findings during evaluation, uncertainties

No uncertainties were found in the stability constants and solubility products of the species and minerals of major elements. Minor/trace elements such as Am, Cs, I, Tc, had minimal uncertainties given current understanding of their chemical behaviour. The species for which the data is considerably ambiguous or uncertain are listed in Table 1.

## 7. Confidence on Drigg database

As well as a critical evaluation of the thermodynamic

Table 1
The species for which the data is considerably ambiguous or uncertain

| Species/mineral | Comments |
|---|---|
| $Th(OH)_4(s)$ | Solubility product for thorium hydroxide has been calculated assuming that the free energy change for conversion of $ThO_2(s)$ to $Th(OH)_4(s)$ is zero, yielding identical solubility products for the two minerals [5,10]. |
| $RaHCO_3^+(aq)$ | This species has been observed only in one investigation [11]. All other investigators reported only the presence of carbonate complex, $RaCO_3(aq)$ [12]. |
| $Np(OH)_4(aq)$ | Log stability constant for $Np(OH)_4(aq)$ in NEA 9 is −9.00 [5], whereas CHEMVAL 6 lists a value of −9.89 [3]. NEA 9 value has been reported as adjusted to fit experimental data. |
| $Np(OH)_3(CO_3)^-(aq)$ and $Pu_3(OH)_5^{4+}(aq)$ | For these two species only estimated stability constants, as general to all actinides [13], are available. |
| $NpO_2(s)$ | Values available in the literature vary over a wide range ($\log K_{sp}$ varies from −2.68 to −7.85) [3,14]. |
| $Pu(OH)_4(aq)$ | Several original source publications have significantly different values ($\log \beta = -9.2$ to $-10.54$) [15,16]. |
| $Pu(CO_3)^{2+}$, $Pu(CO_3)^{2-}$ and $Pu(CO_3)_3^{3-}$ | Two sets of estimated data are available and they are different by two orders of magnitude [13,17]. |
| Sr(OH)2(s) | Source publication values are different by four orders of magnitude ($\log K_{sp} = 24.20$ to 28.79) [18,19]. |
| $U(OH)_4(aq)$ | Values listed in different databases are significantly different ($\log \beta = -4.53$ to $-10.50$) [3,20]. |
| $U(OH)_5^-$ | There is a difference of opinion regarding the existence of this species [10,21]. |
| Uraninite | It is unclear if uraninite is the same as or different to, crystalline uranium oxide [3,20]. However the solubility products of uraninite and $UO_2$ (crystalline) are not significantly different. |
| Swartizite, $CaMg(UO_2(CO_3)_3$, and Liebigite, $Ca_2UO_2(CO_3)_3$ | These two minerals were not found in NEA 9, but may be formed in carbonate water under oxidising conditions expected in Drigg. |

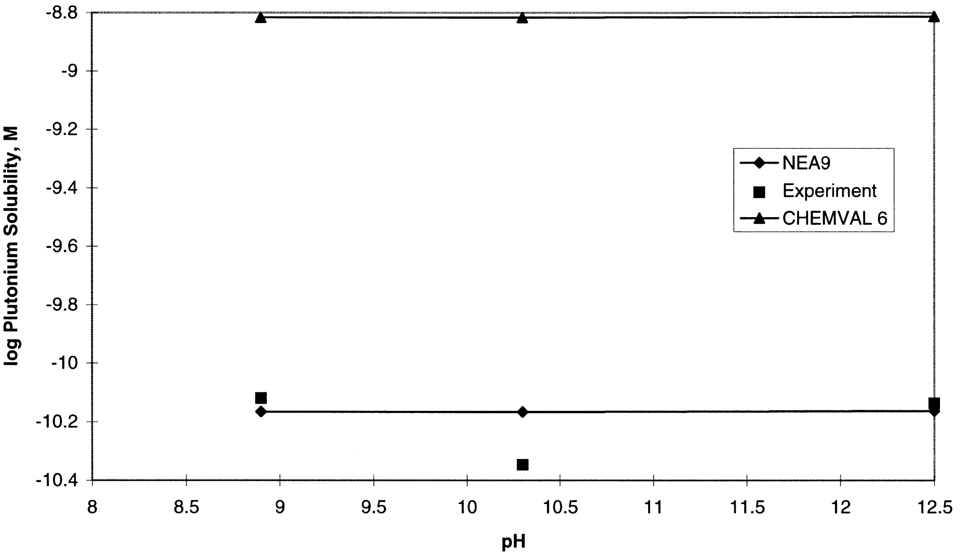

Fig. 1. Plutonium solubility in a cementitious environment.

data, it is also vital to test the database against experimental data. In addition, sensitivity analysis can perform an important role in the determination of a site-specific database, and is in the process of being performed.

BNFL has, over the years, performed a number of solubility experiments, and the result of some of these is shown here. The illustrated examples are investigations of the uncertainties in thermodynamic data discussed above, and also those systems where solubility is likely to be the limiting factor in the migration of the radionuclides.

Fig. 1 shows the solubility of Pu in a cementitious, reducing (Portland cement 300) environment, as well as the results of modelling work, with $Pu(OH)_4(s)$ as the solubility controlling solid [22]. $Pu(OH)_4$ was precipitated

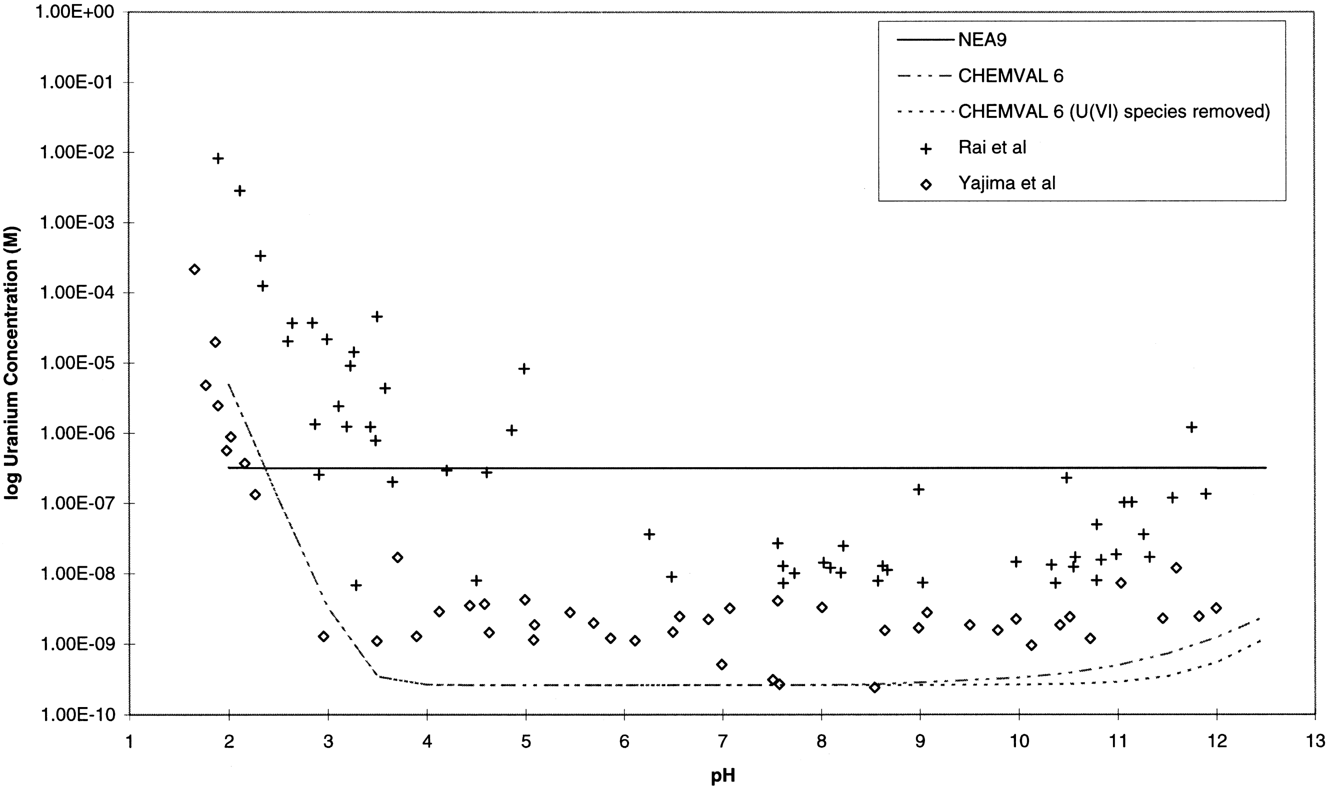

Fig. 2. Uranium solubility in the pH range from 2 to 12.

from a Pu-238 in 0.1 M $HNO_3$ solution with pH being controlled by adding either $HNO_3$ or NaOH. Pu left in the solution was measured radiometrically after separating the solid by dialysis.

As discussed above, $Pu(OH)_4$(aq) has an associated equilibrium constant that varies by over an order of magnitude. However, Fig. 1 reveals that use of a log $\beta$ for $Pu(OH)_4$(aq) of −10.54 (NEA 9 value) gives a much better fit than a value of −9.2 (CHEMVAL 6), thus providing confidence in the NEA 9 value.

Fig. 2 shows a comparison of solubility of U(IV), experimentally measured by Rai et al. [21] and Yajima et al. [23] in the pH range from 2 to 12, with the modelling results obtained with CHEMVAL 6 and NEA 9. As can be seen from Fig. 2, NEA 9 does not predict the solubility behaviour, particularly at low pH. Also at high pH the solubility predicted is over an order of magnitude higher than the experimental values. The solubility predicted with CHEMVAL 6 is in excellent agreement with the data obtained by Yajima et al. [23] and predicts the trend observed by Rai et al. [21] over the whole pH range.

Finally, Fig. 3 investigates the solubility of U in simulant Drigg groundwater [24]]. Uranyl solution was added to a simulant Drigg groundwater solution (pH 8.2) in batches, and each time pH was brought back to the original value by adding NaOH [25]. Uranium in solution was measured after removing colloidal materials by filtration. At the end of the experiment the solid was recovered and re-equilibrated with simulant groundwater to determine the solubility by undersaturation. The results of oversaturation (stepwise addition of uranyl solution) and undersaturation experiments are shown, and are in excellent agreement. The modelled uranium solubility using two uranyl hydroxides, β-$UO_2(OH)_2$ (log $K_{sp}$=4.94) and $UO_32H_2O$ (log $K_{sp}$=4.82) from the NEA 9 database is also shown to be in excellent agreement.

The uranyl system is likely to be solubility controlled in Drigg, and these results provide confidence that the published thermodynamic data can be used to model the solubility of uranium at Drigg.

## 8. Conclusions

This study has illustrated that values within many thermodynamic database compilations are still not completely traceable and self consistent. When applying such databases to radioactive safety assessments it is recommended that data for significant species and solids are critically assessed in the manner presented here. This study also emphasises the importance of independent database validation, in this case by comparison with experimental solubility studies.

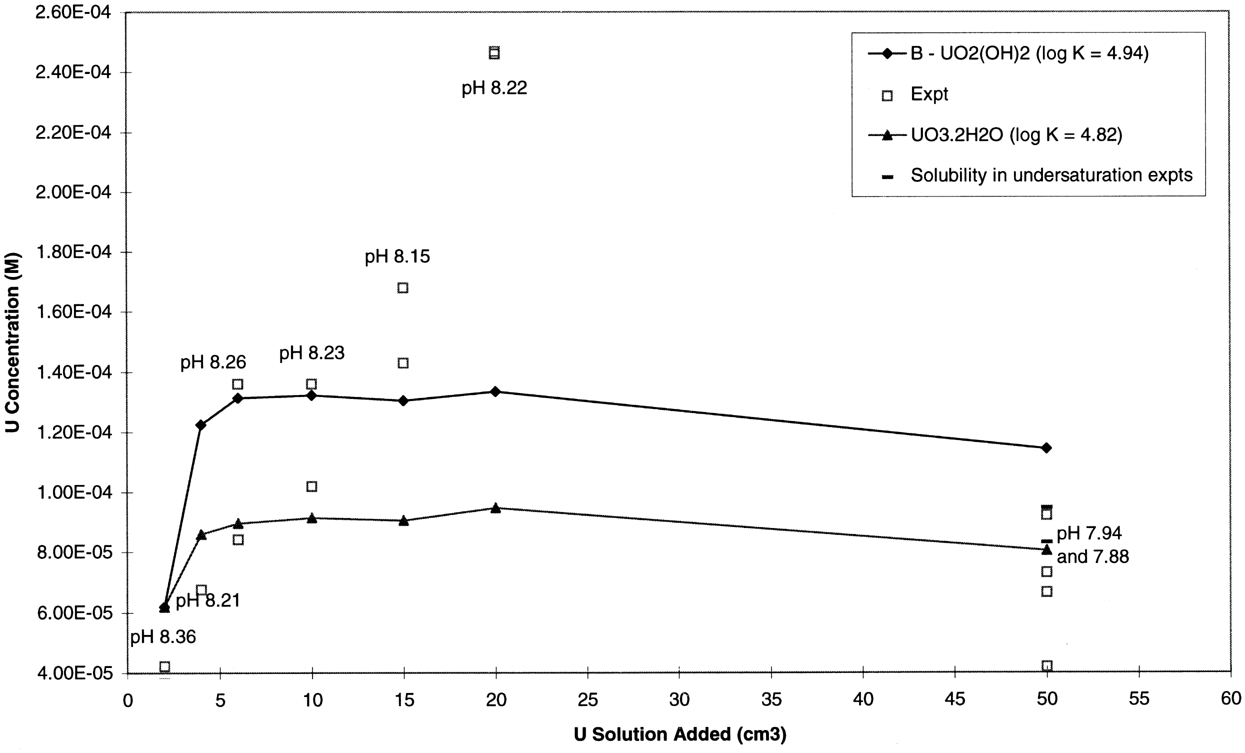

Fig. 3. Uranium solubility in Drigg groundwater (pH~8).

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