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Review Report on the WIPP Thermodynamic Model for Trivalent Actinides An(III)

Thomas Fanghänel

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Prepared for:

E. James Nowak
MS 1320/Org. 6831
Sandia National Laboratories
PO Box 5800
Albuquerque, New Mexico 87185-1320 USA

Copy to: C.F. Novak
           R.V. Bynum
           C.E. Palmer

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Introduction

This report presents the results of a review of the WIPP thermodynamic model for trivalent actinides. The review was performed at LLNL during April 30 to May 5, 1996. The following manuscripts, reports, memos, etc., were made available to the reviewer and were used for the review:

- Novak, C.F.; Moore, R.; Bynum, R.V. Prediction of dissolved actinide concentrations in concentrated electrolyte solutions: A conceptual model and model results for the Waste Isolation Pilot Plant (WIPP).
- Novak, C.F.; Crafts, C.C.; Dhooge, N.J. A data base for thermodynamic modeling of +III actinide solubility in concentrated Na-Cl-SO$_4$-CO$_3$-PO$_4$ electrolytes.
- Rao, L.; Rai, D.; Felmy, A.R.; Fulton, R.W.: Solubility of NaNd(CO$_3$)$_2$*6H$_2$O(c) in concentrated sodium carbonate and sodium bicarbonate solutions.
- Rao, L.; Rai, D.; Felmy, A.R.: Solubility of Nd(OH)$_3$(c) in the aqueous NaCl solution at 25°C and 90°C. Report PNL-SA-26137
- Rai, D.; Felmy, A.R.; Fulton, R.W.: Nd^{3+} and Am^{3+} ion interactions with sulfate ion and their influence on NdPO$_4$(c) solubility. J. Solution Chem. 24(1995)879
- Felmy, A.R.; Rai, D; Schramke, J.A.; Ryan, J.L.: The solubility of plutonium hydroxide in dilute solution and high-ionic-strength chloride brines. Radiochim. Acta 48(1989)29
- Rai, D.; Felmy, A.R.; Fulton, R.W.: Solubility and ion activity product of AmPO$_4$*xH$_2$O(am). Radiochim. Acta. 56(1992)7
- Felmy, A.R.; Rai, D; Fulton, R.W.: The solubility of AmOHCO$_3$(c) and the aqueous thermodynamics of the system Na$^+$-Am^{3+}-HCO$_3$$^{2-}$-CO$_3$$^{2-}$-OH$^-$-H$_2$O. Radiochim. Acta 50(1990)193
- Kahalili, F.I.; Symeopoulos, V.; Chen, J.-F.; Choppin, G.R.: Solubility of Nd in brine. Radiochim. Acta 66/67(1994)51
- Novak, C.F.: Estimates of Dissolved Concentrations for +III, +IV, +V and +IV actinides in a Salado and a Castile brine under anticipated repository conditions. Memo, 28 March 1996
- Novak, C.F.: Confirmatory testing of the inorganic +III actinide dissolved concentration model for Pu(III) and Am(III) in complex brines. Memo, 9 April 1996

The review concerns the model developed for trivalent actinides in the system H-Na-K-Mg-Ca-Cl-SO$_4$-HCO$_3$-CO$_3$-OH-B-H$_2$O. Organic ligands are not within the scope of this review.

The goal of the WIPP thermodynamic model is the development of a model capable of predicting dissolved actinide concentrations in WIPP brines. The model is based on the principles of equilibrium thermodynamics.

The system under consideration is very complex and necessitates several key assumptions. These assumptions are:

- Complexation, precipitation and dissolution reactions, except redox reactions, are described within the framework of equilibrium thermodynamics.
- Actinides do not sorb on immobile substrates.
- Redox reactions (actinide conversion among the oxidation states) are not equilibrium processes.

These assumptions simplify the model and are conservative. In particular the exclusion of sorption is conservative and leads to an overestimation of the mobile actinide concentrations. Actinides are strongly sorbed on solid surfaces. Applying these assumptions the solubility of actinides and hence the maximum concentration of the actinides in the mobile phase can be estimated by using thermodynamic models. (The formation of colloids is considered in a separate study and not included in the model reviewed.)

Development of a thermodynamic model

The development of a thermodynamic model for actinides in concentrated electrolyte solutions includes two submodels:

- A chemical model which defines the homogeneous and heterogeneous equilibrium reactions and the species that have to be considered.
- An activity coefficient model which is a formalism for calculating activity coefficients of the species defined in the chemical model as function of composition (temperature, pressure).

For the WIPP thermodynamic model the ion interaction approach (Pitzer equations) was chosen for modeling the excess properties of the aqueous solution (activity coefficient model). At present the Pitzer approach is the most sophisticated semiempirical approach for the Gibbs excess energy of a concentrated electrolyte solution. It is widely used and a data base with ion interaction parameters covering a

large variety of different solution species is available. All other known semiempirical extensions of the Debye-Hückel theory are inadequate for modeling the thermodynamic properties of the high concentrated complex brines of the WIPP disposal.

For calculating the properties of the brines a combination of the data bases published by Harvie et al. [1] and by Felmy and Weare [2] are employed. The resulting data base was successfully applied in numerous model calculations of thermodynamic properties of complex brines of the six component sea water system Na-K-Mg-Ca-Cl-SO_4-H_2O including borate and CO_2 at room temperature.

The data base had to be extended for the interaction of actinides in complex concentrated brines.

The applied methodology

- evaluate existing literature data
- design and perform additional experiments
- parameterize the model
- test the predictive capability of the model by predicting properties of given system and comparing the predictions with independent experimental results (not used for the parameterization of the model)

is based on scientific principles and is best suited for the model development.

Oxidation state analogy

In order to simplify the model an oxidation state analogy is applied for the trivalent actinides in the WIPP thermodynamic model. This oxidation state analogy claims that the trivalent actinides under consideration (Pu(III), Am(III)) and the lanthanide Nd(III) have the same or at least very similar thermodynamic and solution chemical properties. This analogy is in general reasonable, but care should be taken when the analogy is extended to other trivalent lanthanides, in particular to the lower lanthanides.

Oxidation state analogy is applied to the following three quantities:

- ion-interaction (Pitzer) parameters
- chemical potentials of aqueous species
- chemical potentials of solid compounds

The first analogy is certainly reasonable. There is no evidence that the parameters accounting for the interaction of Nd(III) species with the major constituents of the brines are different from those of the equivalent An(III) species.

Similar arguments could be applied to the analogy of the equilibrium constants of the aqueous species. The structure of the actinide species is expected to be the same as those of the analog Nd species.

More care has to be taken when the oxidation state analogy is applied to chemical potentials of analog solids. The chemical potentials of solid phases are governed by their structure. Even very small changes in the diameters of different ions could cause a change in the structure and those solids could have different solubilities. It follows that this analogy is not necessarily conservative. A good example for illustration are the two homologue solid compounds $NaNpO_2CO_3*2H_2O$ and $KNpO_2CO_3*2H_2O$. These compound have different structures and the solubility of the sodium compound is about two orders of magnitude higher than that of the homologue potassium compound. Although the differences in the ionic diameters between Na^+ and K^+ are larger than between trivalent actinides and lanthanides and this kind of analogy is not used in the WIPP thermodynamic model, the example demonstrates that solids could have much larger differences in their thermodynamic properties than one would expect from a simple analogy consideration. Thermochemical investigations and comparison with results of other equilibrium thermodynamic studies on $Ln(OH)_3$ and $An(OH)_3$ by Morss at al. [3] clearly demonstrate that there are differences in the solubility products of actinide hydroxides of more than one order of magnitude. The reviewer recommends that individual solubility products be used for the different actinides in the thermodynamic model if they are available in the literature. This will not cause a remarkable increase in the complexity of the model.

Model for trivalent actinides

The WIPP thermodynamic model takes into consideration the interaction or complexation of the trivalent actinides with the following ions/species:

- H^+, Na^+, K^+, Mg^{2+}, Ca^{2+} / Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, OH^-

and several organic substances, which are outside the scope of the present review.

One of the key problems for the modeling of the behavior of actinides in concentrated aqueous solutions is to decide whether the interaction of a trivalent actinide with a certain ion should be treated as ion-ion interaction or as complex formation (ion

association). In the later case appropriate complex formation equilibria have to be formulated and new species and their interactions with other solution species have to be introduced into the model. This complicates the model and makes it necessary to determine additional chemical potentials and interaction parameters. On the other hand the model becomes more realistic with respect to aqueous chemistry (structural considerations) and from the point of view of electrolyte thermodynamics strong complexes can not be treated as ion-ion interaction without invoking the formation of complex species.

Among the anions considered in the model there are the following potential ligands for trivalent actinides:

- Cl^-
- SO_4^-
- HCO_3^-
- CO_3^-
- OH^-
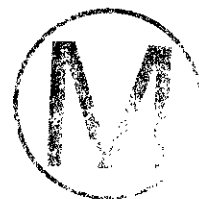
It is known from numerous investigations that CO_3^- and OH^- form strong complexes with trivalent actinides, while complexes with the other ligands are much weaker or are questionable (e.g. bicarbonato complexes). There is experimental evidence for chloro complexes at very high chloride concentrations (above 4 molal) [4] and for relatively weak sulfate complexes at sulfate concentrations of 0.05 molal and higher [5]. The hydrolysis of trivalent actinides in brines was investigated by several authors. A thermodynamic model for the first and second hydrolysis equilibrium of Cm(III) in 0-6 molal NaCl solution is published [6]. Experimental data for the CO_3^- have been published and new spectroscopic investigations are in progress in our institute in Karlsruhe.

The WIPP model treats the interaction of An(III) with Cl^- and SO_4^- as strong ion-ion interaction without invoking the formation of complex species. Within the composition range of the WIPP brines this is a reasonable approach which was demonstrated in several comparisons between model calculations and data. Both interactions can also be treated within the framework of the PITZER formalism by taking into account spectroscopically confirmed chloro and sulfato complexes, which is a more realistic approach regarding aqueous solution chemistry and increases the range of applicability of the model to other process such as sorption or ion exchange equilibria. Thermodynamic models for those systems are in preparation at Karlsruhe and will be available soon.

In the WIPP model the carbonato complexes $AnCO_3^+$, $An(CO_3)_2^-$ and $An(CO_3)_3^-$ are considered. Pitzer parameters have been derived only for the interaction of $An(CO_3)_3^-$

with Na^+ (binary parameters) and with Cl^- (mixing parameters). All other parameters for example those accounting for the interaction of $An(CO_3)_2^-$ with the main cations (Na^+ or Mg^{++}) and of $AnCO_3^+$ with chloride are set to zero. This is mainly caused by the limited number of reliable experimental data available in the concentration range where those species are important. The consequence is that predictions for conditions where the mono and dicarbonato complex govern the aqueous chemistry of the trivalent actinides has to be used with care. With new experimental results the model could certainly be improved. Such investigations are in progress at Karlsruhe. The present model predicts the solubility of $NaAm(CO_3)_2*xH_2O$ in carbonate solutions in reasonable good agreement with independent experimental results. Predictions should be restricted to conditions that are similar to those where the experiments for the parameterization of the model were performed. If the model predictions are extended to CO_2 partial pressures of up to 100 bar the reviewer doubts that reliable results can be expected from the model. Additional experimental data are necessary for those conditions.

A weak point of the present model is neglecting the hydrolysis of trivalent actinides. Hydrolysis species are very strong complexes. They form at pH>7 and are very important in systems with low concentrations of other strong ligands and high pH. Such conditions are realistic for WIPP brines if for example portlandite/calcite are used as backfill materials. Neglecting the hydrolysis in those brines leads to completely wrong predictions of the total An(III) concentration stable in solution. The predicted An concentrations are at least 10 orders of magnitude too low. Under those conditions all of An(III) is stabilized as hydroxo complexes (mainly as $An(OH)_3(aq)$), while the model predicts only the An^{3+} concentration which is negligible under those conditions. Consequently, if pH is high and other strong ligand concentrations like that of CO_3^- are low the model predicts An(III) concentrations that are several orders of magnitude too low. When hydrolysis is considered the model predictions would be reliable as is demonstrated for the solubility of Np(V). The WIPP model takes into account the hydrolysis of Np(V) and predicts a slight increase of the Np(V) solubility when portlandite/ calcite are added to the brines, although Np(V) hydrolysis is much weaker than An(III) hydrolysis and is important only above pH 10. While the model predicts reliable Np(V) solubilities under these conditions the predicted An(III) concentrations are total unrealistic and at least 10 orders of magnitude too low. The WIPP model has to be improved by taking into account the formation of hydrolysis species. Appropriate information is available from the model published for the hydrolysis of Cm(III) in NaCl solutions [6]. This model could easily be incorporated into the present WIPP thermodynamic model.

Conclusions

The applied assumptions for the development of the WIPP thermodynamic model are conservative and simplify the overall model. This is a prerequisite for calculating dissolved actinide concentrations in the very complex repository system.

In general the model represent the present state of the knowledge of aqueous solution thermodynamics. The chosen activity coefficient model and the applied data base are, with a few exceptions, suitable for calculating maximum trivalent actinide concentrations in WIPP brines. The model needs to be improved in some parts. This concerns in particular the hydrolysis equilibria of trivalent actinides which have to be introduced into the model. Moreover the reviewer recommends that the model regarding the interaction of carbonate complexes in concentrated electrolyte solutions be refined.

The development of realistic models based on both our knowledge on aqueous solution chemistry and electrolyte thermodynamics is one of the key issues for the performance assessment of a waste repository. This is not only a matter of the accuracy of the model predictions. Realistic and accurate models give confidence that the basic principles of the behavior of the system are understood which is probably more important for the performance assessment than to predict solubilities with an higher accuracy.

References

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