

CHEMICAL EQUILIBRIUM MODELING OF HANFORD WASTE TANK PROCESSING: APPLICATIONS OF FUNDAMENTAL SCIENCE

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ABSTRACT

The development of computational models based upon fundamental science is one means of quantitatively transferring the results of scientific investigations to practical application by engineers in laboratory and field situations. This manuscript describes one example of such efforts, specifically the development and application of chemical equilibrium models to different waste management issues at the U.S. Department of Energy (DOE) Hanford Site. The development of the chemical models is described with an emphasis on the fundamental science investigations that have been undertaken in model development followed by examples of different waste management applications. The waste management issues include the leaching of waste slurries to selectively remove non-hazardous components and the separation of Sr⁹⁰ and transuranics from the waste supernatants. The fundamental science contributions include: molecular simulations of the energetics of different molecular clusters to assist in determining the species present in solution, advanced synchrotron research to determine the chemical form of precipitates, and laser based spectroscopic studies of solutions and solids.

INTRODUCTION

The high-level radioactive waste tanks at the U.S. Department of Energy (DOE) storage site at Hanford contain extremely complex solutions containing high concentrations of electrolytes ions, radioactive species, other metal ions, and, in selected tanks, high concentrations of organic chelating agents (see Tables I and II). The highly radioactive nature of the wastes means that specific studies with the waste materials are both difficult to conduct and extremely costly. As a result, obtaining insight into the chemical behavior of these complex wastes without the necessity for expensive sampling and characterization is of significant value to site engineers. One means for obtaining such insight is in the area of chemical equilibrium modeling which offers the potential for predicting the behavior of the wastes, or at least providing ideas on how such wastes might behave, in response to different proposed remediation or processing strategies. As a result of this need, chemical equilibrium models have been used for over twenty years by engineers at the Hanford site. However, the accuracy of these models depends upon the input data used in the calculations. This area of database development, which requires the inclusion of accurate thermodynamic data, is an example of how fundamental scientific information is used to directly impact practical engineering decision making.

In this manuscript, examples are presented of the scientific studies used to develop and enhance the database for chemical equilibrium models that can be used in applications by site engineers. The specific applications chosen as examples include: Sr⁹⁰ and TRU separations and waste leaching to remove specific components of tank sludges.

Table I Waste tank AN-107 diluted feed composition [1].

Major Compounds	Concentration (m)	Minor Components	Concentration (m)	Organic Ligands	Concentration (m)
Na ⁺	8.9	Al	1.7x10 ⁻¹	Glycolate	.30
NO ₃ ⁻	3.1	Ba	3.4x10 ⁻⁵	Gluconate	.022
NO ₂ ⁻	1.3	Ca	1.3x10 ⁻²	Citrate	.055
CO ₃ ²⁻	1.6	Ce	2.3x10 ⁻⁴	EDTA	.024
OH ⁻	0.84	Cd	4.9x10 ⁻⁴	HEDTA	.0094
SO ₄ ²⁻	0.1	Cr	3.3x10 ⁻³	NTA	.037
PO ₄ ³⁻	0.037	Cs	1.1x10 ⁻⁴	IDA	.056
*F ⁻	0.39	Cu	3.9x10 ⁻⁴		
Cl ⁻	0.046	Fe	2.4x10 ⁻²		
		K	3.8x10 ⁻²		
		La	1.9x10 ⁻⁴		
		Mn	2.3x10 ⁻³		
		Nd	5.8x10 ⁻⁴		
		Ni	7.9x10 ⁻³		
		Pb	1.45x10 ⁻³		
		Sr	3.5x10 ⁻⁵		
		U	3.6x10 ⁻⁴		
		Zn	3.4x10 ⁻⁴		
		Zr	5.6x10 ⁻⁴		

* IC analysis probably includes formate and acetate

Table II Radionuclide concentrations in Hanford waste tank AN-102 [2].

Analyte	Supernatant (μCi/ml)	Wet Centrifuged Solids (μCi/g)
⁶⁰ Co	8.49E-02	5.71E-02
⁹⁰ Sr	5.72E+01	1.44E+02
⁹⁹ Tc	1.48E-01	9.88E-02
¹²⁵ Sb	NM	2.E-01
¹³⁷ Cs	3.69E+02	2.16E+02
¹⁵² Eu	NM	1.E-02
¹⁵⁴ Eu	2.31E-01	5.12E-01
¹⁵⁵ Eu	1.00E-01	3.20E-01
²³⁸ U	NM	2.18E-05
²³⁷ Np	1.20E-04	9.21E-04
²³⁸ Pu	1.65E-03	1.19E-02
²³⁹ Pu	6.47E-03	5.56E-02
²⁴⁰ Pu	2.01E-03	1.50E-02
^{239/240} Pu	5.90E-03	4.17E-02
²⁴¹ Am	1.65E-01	4.21E-01
²⁴² Cm	6.29E-04	2.E-03
^{243/244} Cm	6.71E-03	1.72E-02

NM – not measured

MODEL DEVELOPMENT

The development of the thermodynamic data for use in chemical models and other applications has been the subject of fundamental science investigations for over fifty years (see reviews by Martell and Smith [3], Grenthe et al., [4], LeMire et al., [5], Silva et al., [6], and Rard et al., [7])

to name just a few). During this time the methods and techniques have evolved from relatively simple solubility and potentiometric studies to NMR determinations of solution phase structures, X-Ray absorption spectroscopy of solution species and very recently molecular simulations of the structures and energetics of different complexes. This section gives examples of some of these recent efforts and how each resulted in new data for use in chemical modeling.

Molecular Simulation

With recent rapid advances in the development of computational capabilities, molecular simulations (for example ab initio or density functional theory and/or molecular dynamics) have advanced to the point where such methods can provide unique insight into the species present in solution and potentially the dynamics of such complexes. This information is especially important in cases where the species are present in very low (but environmentally significant) concentrations and are therefore difficult to measure directly.

Two areas in which molecular simulation can contribute to the development of thermodynamic models are in defining the nature of the solvated ions in solution and in calculating or estimating the stability constants for different possible species that could occur in solution. The latter case can be particularly valuable since many different possible chemical structures can be evaluated in a relatively rapid time greatly decreasing the number of structures to target for experimental studies.

Solvation reactions

All of the chemical models that we have discussed are based upon aqueous phase reactions. As such, the interactions of the metal ions and radionuclides with the solvent are of central importance. The nature of these reactions is usually described by hypothesizing the formation of different monomeric or polymeric hydrolysis species in solution (see the early review of Baes and Mesmer [8]). Unfortunately, such models often do not fully describe the entire excess Gibbs free energy for solutions, especially at high ionic strengths or if the interactions of the metal ion or radionuclide with the solvent are relatively weak.

In the case of Sr^{90} (an important radionuclide in the Hanford waste tanks) complexation by hydroxide, classical thermodynamic approaches utilized the specific formation of hydrolysis species in solution (i.e., SrOH^+ ...) [3,8] as a means of accounting for the changes in thermodynamics that occur in solution with the changes in base concentration. However, our initial density functional theory (DFT) calculations of gas phase clusters involving Sr^{2+} ion and hydroxyl and water molecules brought doubt into the use of such approaches. For example, when the hydration number for the Sr^{2+} cation exceeded seven water molecules the hydroxyl detached from the central metal and formed hydrogen bonds with the solvated water molecules in an outer sphere like complex indicating relatively weak attachment of hydroxyl with the large Sr^{2+} cation (Fig. 1). This fact, combined with solubility data on Sr hydroxide compounds at high base concentration, which showed associations even weaker than predicted by Debye-Hückel theory indicated that the hydrolysis of Sr^{2+} was fairly weak and that the entire range of NaOH concentrations extending to 6M NaOH could be described using Pitzer ion-interaction parameters [10] for Sr^{2+} - OH^- interactions along with a Na^+ - Sr^{2+} mixing term. No clear evidence was found for the formation of SrOH^+ or other hydrolysis species.

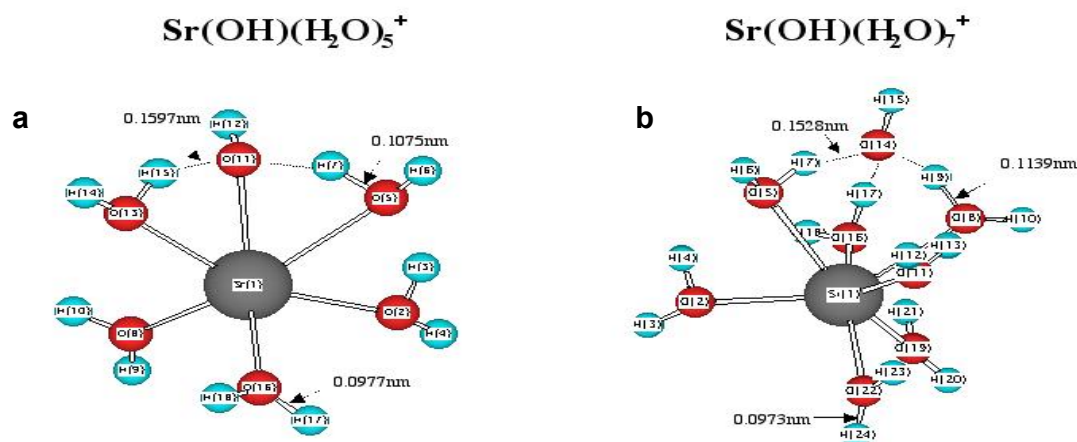


Fig. 1 Structures of a) gaseous $\text{Sr}(\text{H}_2\text{O})_7\text{OH}^+$, and b) gaseous $\text{Sr}(\text{H}_2\text{O})_5\text{OH}^+$ calculated by density functional theory (DFT) [9].

Estimating aqueous phase stability constants

In the presence of strongly complexing inorganic or organic ligands, metal ions or radionuclides can form many different species or structures in solution. Often several of these species can be present simultaneously in solution making it difficult or impossible to uniquely quantify their presence solely by experimental approaches. In such cases the use of molecular level simulation can be especially valuable. However, in order to effectively utilize such approaches, either the absolute free energy for the species must be calculated with high precision or correlations must be developed between measured solution phase free energies and molecular level binding energies. One method correlation establishes a linear free energy relationship between gas phase structures which can readily be calculated by such methods as DFT and solution phase equilibrium constants.

The examples of the development of linear free energy relationships for estimating solution phase binding constants are shown in Fig. 2. The calculated density functional theory (DFT) binding energies for gas phase clusters (see Felmy et al., [9] for details) are shown to correlate well with known stability constants for Ca and Sr complexes (Fig. 2a) as well as for aqueous chelate complexes of La(III) with organic chelates (EDTA, HEDTA, and NTA) (Fig. 2b) [11] which contain variable numbers of associated hydroxyl groups. Such calculations not only demonstrated the reasonableness of the experimentally determined equilibrium constants for such species but also allowed eliminating numerous other possible species from consideration in the interpretation of the original experimental data.

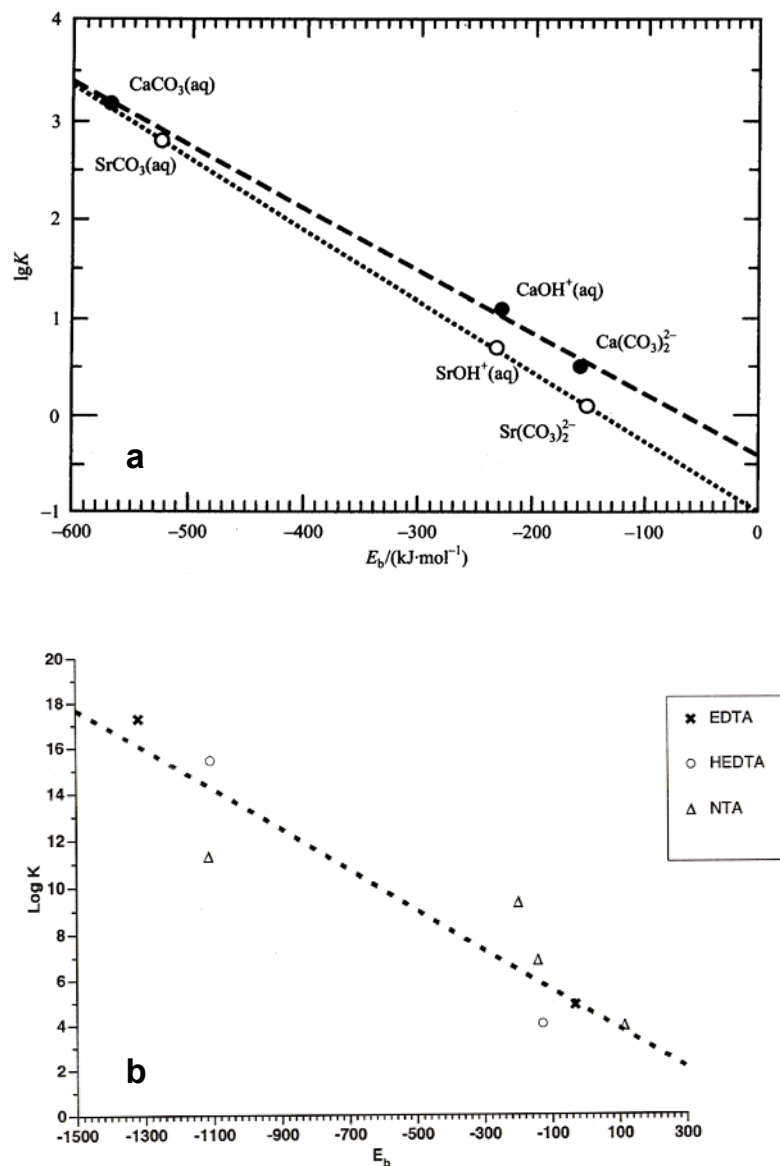


Fig. 2 Relationship between gas-phase binding energies (E_b) and solution phase equilibrium constants. a) Sr/Ca hydroxide and carbonate species [9]; b) La (III) organic chelate complexes [11].

Spectroscopic Studies

In a similar fashion to the advances in computational capabilities, advances in analytical and spectroscopic techniques have been enormous over the past twenty years. These advances have occurred in a wide range of areas including mass spectrometry, nuclear magnetic resonance (NMR), synchrotron based spectroscopies, and laser based spectroscopies. In the case of developing accurate thermodynamic models, the major contributions of these molecular based methods is the more precise identification of species present in solution or the structure and composition of solid phases involved in the thermodynamic reactions. It must be emphasized

that each of these methods has its strengths and limitations and that no one technique is capable of providing unique species characterizations for all elements and compounds of interest in chemical modeling. Two examples of the types of molecular level information that can be obtained by these methods are described below.

Synchrotron based spectroscopies

Beginning in the late 1960's and early 1970's synchrotron facilities came under construction in the United States and elsewhere, primarily with the objective of conducting fundamental research in high energy and nuclear particle physics. The fact that such facilities generated X-Rays was incidental to their original development. As a result, these first generation facilities were often referred to as "parasitic" sources since the operations often had to be altered to generate the X-Rays that the chemists wanted. Second generation sources, developed for dedicated operations, began in 1976 with the construction of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Construction of these second generation facilities, along with the development of *ab initio* electronic structure models for calculating parameters needed to interpret the X-ray absorption spectrum by J.J. Rehr and others in the early 1990's [12] allowed the use of X-Ray based techniques for analyzing samples of chemical interest to really develop. Use of such methods has become almost standard practice for chemists in a wide range of disciplines (see Brown et al., [13] and associated references for theory and details).

One example of the use of X-Ray based techniques (such as X-Ray Absorption Fine Structure XAFS) with relevance to our thermodynamic model development is shown in Fig. 3 for solution phase species of Th with the strong complexing ligand carbonate [14]. The XAFS spectrum can be used to obtain the phase and amplitude for the individual scattering paths to the equatorial oxygen, the carbon, and the distal oxygens (denoted Th-O, Th-C, and Th-O_d in Fig. 3). This information can then be used to determine the coordination number and structure of the species in solution. In this specific example, the results allowed the unique identification of a thorium pentacarbonate species in solution (i.e., Th(CO₃)₅⁶⁻) which then allowed the accurate modeling of the influence of carbonate (which is in high concentration in tank waste) on the solubility of Th and other tetravalent actinides.

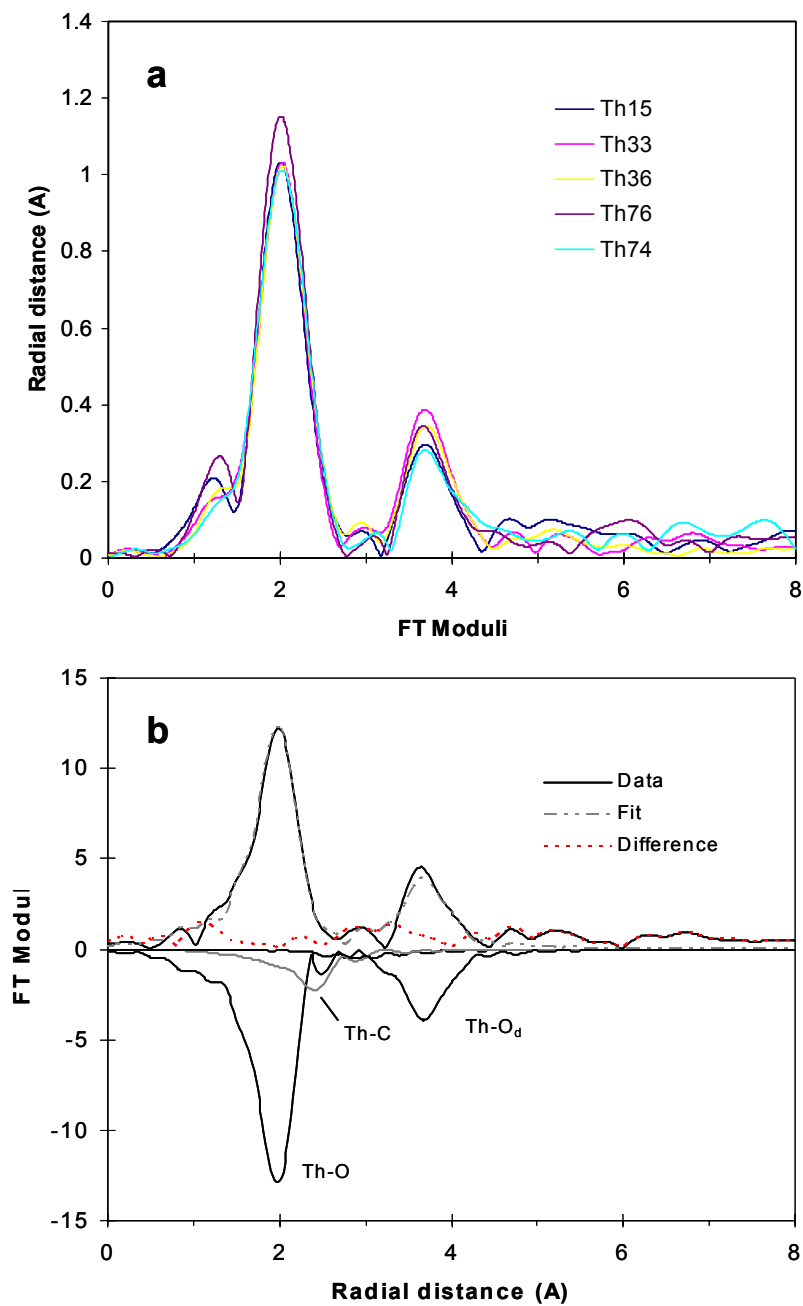


Fig. 3 a) Fourier transforms of Th containing solutions (Th15 - 2M Na₂CO₃, 0.1M NaOH; Th33 - 2M Na₂CO₃, 0.5M NaOH; Th36 - 2M Na₂CO₃, 1.0M NaOH; Th76 - 0.25M NaHCO₃, pH 9.3; Th74 - 0.1M NaHCO₃, pH 9.36; and Th71 - 0.1M NaHCO₃, pH 9.39); b) Comparisons of fits and experimental data for sample Th33 from Hess et al., [14].

Laser based spectroscopies (fluorescence)

Due to the limitations of the excitation light sources and detection systems, earlier studies of lanthanides and actinides using fluorescence spectroscopy were primarily associated with mineral solids and concentrated solutions. Broad applications of fluorescence spectroscopy in the speciation and quantitative analysis of lanthanides and actinides in solutions and complicated solid matrices started only when high power lasers, especially nanosecond pulsed lasers, and sophisticated electronics and photon detection systems became available in the past three decades [15-18].

Such methods are of use not only for identifying species in solution, but also for determining the presence of particulate or nanoparticulate particles in solution. The latter effect is especially important since a significant amount of solubility data in the literature are based upon total or filtered concentrations. Passage of small or nanosized particles through the filtration system can therefore result in erroneous assumptions as to the species present in solution and resulting inaccurate thermodynamic data.

Cm(III), a trivalent actinide of considerable importance in waste tanks, not only because of its direct presence (see Table II), but also since it is an analog for other trivalent actinides such as Am(III), has a strong fluorescence signature. In fact, with pulsed laser excitation in the near-UV absorption bands (375 nm and 396 nm), fluorescence spectroscopic characterization of Cm(III) at sub-nanomolar concentration can be achieved.

By analyzing a series of Cm(III) complexes with known hydration numbers, Kimura et al., [19] found that there is a linear relationship between the fluorescence decay constant and the number of water molecules in the inner coordination sphere of Cm(III),

$$N_{H_2O} = 0.65 \cdot k_{obs} - 0.88 \quad (\text{Eq. 1})$$

where, N_{H_2O} is the number of water molecules in the inner sphere of Cm(III) and k_{obs} (in ms^{-1}) is the measured fluorescence decay constant of Cm(III) complex in aqueous solution. Using Eq. (1) the number of inner-sphere water molecules in the Cm(III) species can be calculated and this allows changes in solution speciation to be followed.

One example of how such effects can be used to determine both the species present in solution and trace the importance of nanoparticles was recently given by Wang et al., [20]. In one test, two series of Cm(III) solutions at constant Cm(III) concentration and different HEDTA concentrations from $4 \cdot 10^{-5}$ M to 0.01 M at NaOH concentrations of 1.0 M and 7.5 M, respectively, were prepared and fluorescence spectra were recorded. Part of the spectra is shown in Fig. 4. In 1.0 M NaOH, the decreasing HEDTA concentration causes a drop of the fluorescence intensity at 607.0 nm by about 30% and an increase of the intensity at 616.0 nm with a factor of slightly over 2 (Fig. 4a). However, in 7.5 M NaOH the fluorescence intensities of both the bands at 607.0 nm and 616.0 nm decreased with decreasing HEDTA concentration (Fig. 4b). While in 1.0 M NaOH all of the Cm(III) fluorescence spectra and most of those in 7.5 M NaOH could be reasonably fit by two bands at 607.0 nm and 616.0 nm, those in 7.5 M NaOH at lower HEDTA concentrations required the inclusion of a third peak, at ca. 612 nm. Analysis of the fluorescence decay curves resulted in fluorescence lifetimes between 74 μs to 88 μs with

an average of ca. 82 μs for the species with fluorescence peak at 616.0 nm. Calculation using Eq. (1) would indicate that approximately seven water molecules should be present in the inner coordination sphere of Cm(III) in the species with a fluorescence maximum of 616.0 nm. In 7.5 M NaOH even if the ligand(s) does not fully saturate the Cm(III) coordination sphere, hydroxyl groups would preferentially bind over water molecules, resulting in a much smaller hydration number than seven. It therefore appears, that the species associated with the 616.0 nm peak cannot be an aqueous complex but must have decay modes more consistent with species on the surface of Cm(III) containing particles. Monitoring this peak therefore became an accurate tracer of the presence of Cm(III) containing nanoparticles in solutions.

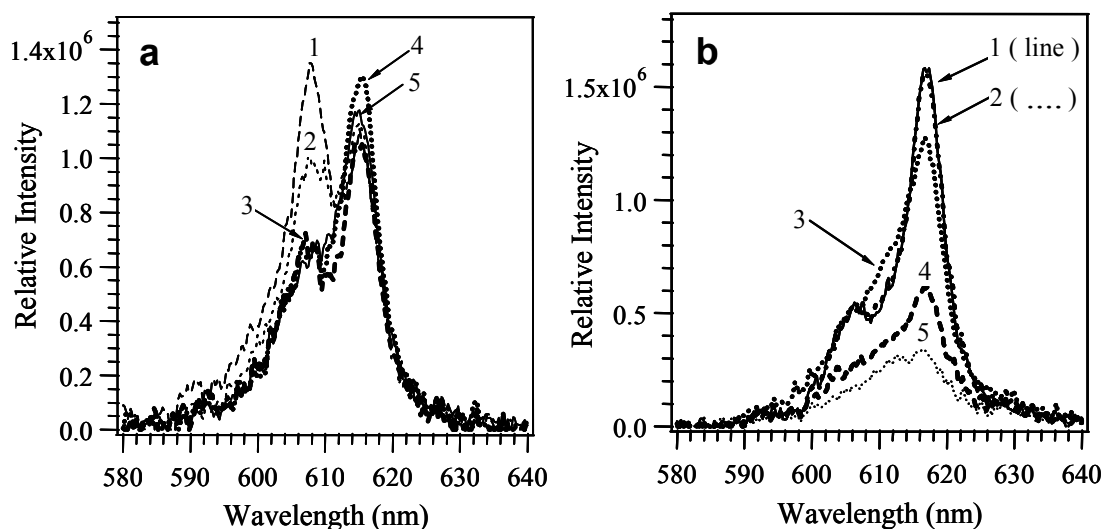


Fig. 4 Fluorescence emission spectra of Cm^{3+} at different HEDTA concentrations in 1.0 M. a) and 7.5 M; b) NaOH solutions. (Cm^{3+}) = 9.6×10^{-9} M. The concentration of HEDTA is 1 – 1×10^{-2} M; 2 – 4×10^{-3} M; 3 – 8×10^{-4} M; 4 – 1×10^{-4} M; 5 – 4×10^{-5} M. $\lambda_{\text{ex}} = 375$ nm [20].

Understanding the presence of nanoparticles rather than aqueous species, resulted in a completely different interpretation of the thermodynamic behavior of trivalent actinides under highly basic conditions. Rather than be present as soluble anionic species (i.e., trivalent actinide (An), $\text{An}(\text{OH})_4^-$) which would be transported with the aqueous solutions, it appears that small nanoparticles are the primary species of concern under highly basic conditions.

Model Applications

This section presents examples of the application of chemical models to issues of interest in tank processing. The objective is to provide examples of how the thermodynamic data can be used in practical engineering applications. Two examples of Hanford specific applications are presented: $\text{Sr}^{90}/\text{TRU}$ removal and sludge leaching to remove selected components. A brief description of each application is given followed by a series of processing questions. The processing questions are used to highlight issues of importance and the practical applications of chemical modeling.

Sr-⁹⁰/TRU Separations

Radioactive wastes stored at Hanford require different levels of pretreatment to meet prespecified limits for low-activity waste or other disposal categories. Wastes currently labeled as Envelope C in the waste treatment process present difficult challenges in this regard as they contain high levels of organic complexants (e.g., EDTA, HEDTA, NTA, ...) and elevated levels of Sr⁹⁰ and transuranics (TRU's), Tables I and II. Current strategies for removal of these radionuclides from the supernatants call for Sr⁹⁰ and Am²⁴¹ removal (Sr/TRU) via solid phase precipitation induced by the addition of stable Sr and KMnO₄.

Processing Question: *Why do the waste supernatants initially consume added Sr with little or no Sr⁹⁰ removal then remove amounts of Sr⁹⁰ at higher additions?*

The chemical modeling results show that the initial feed solution is undersaturated with respect to SrCO₃(c), despite the very high dissolved carbonate concentration, as a result of strong complexation with the organic chelate EDTA. In addition, the calculations show that there is some "excess" EDTA present. The first additions of stable Sr thus go to saturating the chelates without precipitation of SrCO₃. Once the chelates are saturated, precipitation of SrCO₃ proceeds and the Sr⁹⁰ is removed by isotopic substitution into the precipitated SrCO₃. These simulations agree with the experimental observations of the diluted feed, which shows increases in total dissolved Sr concentration (i.e., negative decontamination factors for total Sr) followed by significant Sr⁹⁰ removal.

Processing Question: *Does the removal of Sr⁹⁰ by the addition of stable Sr effect the removal of the transuranic components specifically Am(III)?*

As previously described, the modeling calculations indicate that the Sr is tied up with the organic complexants. Further calculations show that the TRU components are also tied up with organic complexants. Thus the possibility exists that the addition of Sr could displace the TRU components (specifically Am²⁴¹, see Table II) and impact TRU separations. However, the added Sr is not predicted to be effective in displacing the TRU components from the chelate complexes since the high carbonate concentration keeps the total Sr concentration in solution low as a result of precipitation of insoluble as SrCO₃(c). The low final Sr concentration means that ligand displacement of other complexant bound ion by added Sr will be minimal.

The TRU removal appears to be related to the addition of the permanganate. The added MnO₄⁻ is predicted to be reduced and precipitate as Mn(IV) oxides. If the model is "correct" the removal of TRU components upon treatment is the result of an adsorption or occlusion of the TRU's in the precipitated manganese oxides. This latter conclusion is also partially supported by the experimental data for the actinides themselves (i.e., Am²⁴¹, Cm²⁴², and Cm²⁴³ and Cm²⁴⁴). These radionuclides are present at quite low concentrations (i.e., 10⁻⁷ to 10⁻¹² m). These concentrations are far below any predicted solubility equilibrium with respect to the hydroxide phases, yet they all show significant decontamination factors (30 – 66). Hence the removal of the trivalent actinides and actinide analogs (Eu(III)) is occurring at concentrations well below the solubility limits strongly indicating that adsorption reactions with the bulk precipitated

manganese oxides is a likely mechanism. Adsorption of Am^{241} on precipitated manganese oxides has been previously hypothesized as a removal mechanism from AN-107 simulants [21].

Leaching of waste tank slurries

Sludge washing is used at Hanford and other sites to remove components from the waste sludges that can limit or negatively impact the formation of waste glasses. Briefly the process consisted of a series of wash, leach, and rinse steps. The wash steps are designed to remove easily soluble salts (i.e., NaNO_3 , NaNO_2 , ...) that are relatively non-hazardous but would contribute to the total volume of waste glass if they remained in the process. The two wash steps use dilute 0.01M NaOH. The single leach step was conducted using 3M NaOH and at a temperature of 85°C . The leach step is designed to remove significant amounts of Al and other constituents from the sludges that also could contribute to the waste glass loading. There are three rinse steps. All rinse steps use 0.01M NaOH. The entire process is described in detail by Geeting et al., [22]. A complete description of the thermodynamic modeling is given in Felmy and MacLean [23].

Processing Question: *Are two wash steps required to remove the soluble precipitates?*

The modeling results indicate that as a minimum the second wash step can be eliminated. The first wash does dissolve small amounts of precipitates (i.e., $\text{Na}_2\text{C}_2\text{O}_4$, $\text{NaF}\cdot\text{Na}_2\text{SO}_4$) and therefore should be retained. The second wash step really does nothing except dilute already soluble constituents (Na, NO_3 , NO_2 , ..).

Processing Question: *Should the reaction time in the caustic leach step be increased?*

The models predict that the initially present gibbsite ($\text{Al}(\text{OH})_3$) should be completely soluble in the leach step, yet Buck et al., [24] found gibbsite present in the solids following the final rinse. This gibbsite could have been re-precipitated in the rinse steps or may not have had time to completely dissolve in the leach solution. Therefore increasing the leach time should be tested.

Processing Question: *Should a higher NaOH concentration be used in the caustic leach step?*

The analytical data on the initial slurries indicates that the Al is present initially as a mixture of gibbsite and boehmite (AlOOH). The models indicate that boehmite is more insoluble than gibbsite in the leach step. If this is the case, the only way to remove the insoluble boehmite is to increase the NaOH concentration. Our models indicate that the NaOH concentration would need to be increased to 5M NaOH (from 3M) at 85°C to dissolve the boehmite.

Processing Question: *Should the rinse steps be retained?*

The modeling calculations show that the rinse steps perform the valuable function of removing the high dissolved Al generated in the caustic leach step. The dissolved aluminum has the potential to re-precipitate later in the process stream if it is not removed. Therefore, the rinse steps are critical and should be retained. Use of a higher NaOH concentration in the rinse steps should also be considered since this would reduce the tendency for precipitation of aluminum hydroxide phases and thereby avoid potential Al re-precipitation problems in the low activity waste (LAW) stream.

SUMMARY

Chemical modeling has been used at the DOE Hanford site for over twenty years to assist process engineers in making decisions on the processing of many different waste streams. The use of fundamental thermodynamic data in these models is a key to their successful use and application. Recent advances in both computational technology and molecular level spectroscopy have allowed the characterization of solutions and solid phases in unprecedented detail. These advances have directly contributed to the improvement of the thermodynamic models and contributed to the solution of waste processing issues at Hanford.

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FOOTNOTES

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