

VALIDATION AND APPLICATION OF A THERMODYNAMIC MODEL FOR THE PRETREATMENT OF HANFORD WASTE

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ABSTRACT

Results are presented which document part of the effort required for validation of a thermodynamic model applicable to the tank wastes stored at Hanford. The Environmental Simulation Program (ESP) is undergoing evaluation in these laboratories using a variety of methods including assessment of the base data called by the code, direct comparison with experimental results, and the performance of companion calculations using other theoretical models. The work presented focuses on application of ESP to the dissolution of saltcake. Simulations were carried out for four different compositions and compared with previously reported data. The results indicate that ESP correctly describes the dissolution of nitrate, nitrite, carbonate, oxalate, and chlorine containing species. Predictions for sulfate and phosphate containing compounds were observed to qualitatively agree with experimental measurement when fluoride was absent in the composition. The presence of fluoride, however, resulted in the prediction of phosphate and sulfate in the solid phase as the double salts, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ and Na_3FSO_4 . Both of these molecules have been observed in the waste. Differences in the calculated dissolution behavior for these systems were found and have been traced to the quality of the fundamental data associated with the double salts. A number of factors pertinent to successful operations of the code are discussed.

INTRODUCTION

Pretreatment and delivery of the Hanford wastes to the private contractor is the responsibility of the Office of River Protection (OR), formally the Tank Waste Remediation System. The wastes, contained in single and double-shell tanks, consist of sludges, saltcakes, and high ionic strength supernates. Waste compositions vary from tank to tank and reflect chemistries from a number of nuclear activities.

Knowledge of the compositions within the tanks is largely from documentation of process operations and laboratory analysis. The large amount of material and the complexity of the waste, in terms of the variety of species present, increase the number of analytical experiments needed to assure compatibility with pretreatment, transfer, and vitrification. Additionally, since the waste can be in different relative compositions, some questions remain as to the ability to maintain operational effectiveness, i.e., to ensure that solids do not precipitate and plug transfer lines. The chemical variance in the waste represents a formidable challenge to infrastructure requirements, and to the total remediation cost.

As an alternative to the extensive suite of laboratory experiments that may be needed, workers at Hanford have selected, and are using an aqueous thermodynamic electrolyte model, the Environmental Simulation Program (ESP). A main goal in the use of this code is the assessment of the solid-liquid intra-phase and inter-phase equilibria (SLE) [1,2]. The use of an engineering tool that has the ability to routinely identify tanks with compositions of various species that

could result in difficulties during pretreatment and retrieval offers a vehicle that can result in significant cost-savings. Validation of the code will provide assurance that selected processing conditions will allow waste operations to be performed in the most efficient and economic manner possible. The total number of experimental samples and thus the cost of supporting clean-up should be reduced.

Through a program sponsored by the Tanks Focus Area with co-funding from DOE University Programs, workers at DIAL have been evaluating ESP [3-7]. This effort is in collaboration with workers at Oak Ridge National Laboratory (ORNL) and at Numatec Hanford Corporation (NHC). The team is in regular contact with customers at OR.

ESP is a large code containing extensive thermodynamic databases and many computational modules. The code can be used for corrosion calculations, for water analysis, and for flowsheet development. A number of process blocks, consistent with unit operations for aqueous electrolyte solution, are available. The sheer size of the code precludes line-by-line evaluation and model predictions are only as good as the quality of the selected fundamental data. Validation of the software must center on an indirect approach comprising direct comparison to experimental results, critical evaluation of data quality, and comparisons with prediction of other thermodynamic models. Experimental data is subject to error and alternate thermodynamic models are limited to the applicability of the comparison code. A main problem is development of a proper description of all of the interactions between all of the components in the waste streams. For this reason the code will never be completed validated. Illustrating that the code predicts the SLE for the vast majority of waste constituents will, however, be sufficient for process operation goals.

In what follows we focus on the application of ESP to the dissolution of actual saltcake samples obtained from tank cores. Previous work has been centered on the use of the model to characterization studies involving sludge and supernate phases [1,2]. The work described here provides the opportunity to evaluate various factors that must be taken into account when using the code and also allows for the isolation of some of the potential deficiencies. The contribution described is based upon a comparison of experimental results to model predictions. Information on the results of other methods used for code validation, such as an evaluation of the fundamental data used, and comparisons to other thermodynamic calculations can be found in references 3 and 7.

CALCULATIONS AND RESULTS

Data Pre-Processing and Charge Reconciliation

Experimental measurements to determine the total composition of the saltcake composite samples retrieved from 4 tanks were performed by Herting [8,9]. The analytical data consisted of the weight % of the various cations and anions in the composite as well as a weight % of water contained in the sample. The data were converted to concentrations (using an estimated density) and then input to the Water Analyzer (WA) program within ESP (version 6.0). The WA component is a front-end processor for laboratory analytical data and performs charge reconciliation and adjusts the water content in the mixture such that experimental cation and

anion loadings are achieved in the output molecular stream. The input concentration data may exhibit a slight charge imbalance due to analytical uncertainties.

Data were subjected to charge reconciliation and the molecular streams generated within the WA module were used in subsequent ESP Process simulations. Table 1 provides a summary of species present in the four tanks examined in this work.

Table I. Major Constituents in Saltcakes (Weight % of Sample)^a

	Tank			
	BY-102	BY-106	A-101	S-102
H ₂ O	16.7	14.7	31.2	~5
Al ⁺³	1.65	1.59	2.39	.67
Cr ⁺³	.2	.11	.17	
Fe ⁺³	.05	.02	.014	
K ⁺	.09	.24	.31	.07
Na ⁺	27.77	25.06	21.20	22.99
TIC [*]	4.13	1.43	1.81	.59
C ₂ O ₄ ⁻²	.53	1.26	1.35	.17
Cl ⁻¹	.13	.16	.41	.16
F ⁻¹	1.17	.62	.07	
NO ₂ ⁻¹	1.85	2.72	7.43	2.04
NO ₃ ⁻¹	10.92	40.68	12.6	53.72
OH ⁻¹	1.09	1.14	2.1	.42
PO ₄ ⁻³	.6	.34	.38	.52
SO ₄ ⁻²	5.12	1.17	2.44	.32

^a - Data from Reference [8,9].

*Total Inorganic Carbon (CO₃⁻²÷5)

The charge imbalance present in the analytical data can be rectified in the WA module through the addition of a dominant ion or by the user selecting a specific ion or through a proration process. In the later calculation the make up charge is equally distributed over all of the anions or cations.

The reconciliation method was determined to have a significant impact on subsequent process simulations. Typically the charge imbalance found in the initial data was on the order of 1 to 8% and all four tanks examined, prior to reconciliation, had a net negative charge. Use of the dominant ion reconciliation method resulted in the addition of sodium to balance the charge. Since the majority of solid species that will undergo dissolution as diluent (water) is added to a saltcake sample are sodium salts, the addition of sodium can adversely impact ESP predictions of saltcake dissolution through overestimation of the amount of the various salts present in the solid phase.

The make-up ion or user choice method allows the adjustment of an individual cation or anion to achieve neutrality. Depending on the magnitude of the net charge in the input data, the amount

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of selected ion is increased or decreased. Again, addition/subtraction of a single species to adjust the charge can result in overestimation/underestimation of salts containing this species in the solid phase.

Proration adds an equal percentage of each cation to the sample composition if a net negative charge is computed from the analytic data (or of each anion, if a net positive charge is computed). This method allows the net charge imbalance to be distributed among the various cations (or anions) present.

The impact of selecting a specific mode of charge reconciliation on the adjusted cation and anion concentrations for tank BY-106 is provided in Table 2. As anticipated, the use of the dominant ion or the make-up ion methods leads to a significant change in one ion concentration compared to the others. The proration method, however, leads to electro-neutrality with the impact more uniformly spread over either all cation concentrations or all anion concentrations. For this example, all cation concentrations were increased to balance the original negative charge of the laboratory data. Consideration of the impact of this adjustment on the generated molecular stream and examination of the subsequent saltcake dissolution experiment simulation output (see below) confirmed that the proration method of charge reconciliation provided a more uniform mechanism for adjusting the net charge imbalance.

Ideally, one could reconcile the charge imbalance using both cation and anion concentrations. For example, tank BY-106 exhibits a net negative charge of approximately 6.7 %. An increase of the overall cation equivalence by 3.35 % along with a decrease of the total anion equivalence by 3.35% would result in a net-zero charge. This method of charge reconciliation is not available in the current release of ESP but can be accomplished manually and was evaluated. Anion concentrations from the subsequent dissolution experiment simulation were not significantly impacted; however, the availability of proration within the WA module appears to be equally effective and was employed for the saltcake dissolution simulations.

Table II. Impact of Charge Reconciliation Method on Adjusted Ion Concentrations - Tank BY-106

Species	Original Input (mg/L)	Dominant Ion (Na ⁻)(mg/L)	Make-up Ion (NO ₃ ⁻)(mg/L)	Proration (mg/L)
Al ³⁺	24682	24226	26003	25889
Cr ³⁺	1760	1727.5	1854.2	1846.1
Fe ³⁺	298	292.49	313.95	312.58
K ⁺	3776	3706.2	3978.1	3960.7
Na ⁺	3.8847e+05	4.1133e+05	4.0926e+05	4.0747e+05
OH ⁻	82209	80689	86608	80812
Cl ⁻	2536	2489.1	2671.7	2492.9
CO ₃ ²⁻	1.1111e+05	1.0906e+05	1.1706e+05	1.0922e+05
F ⁻	9580	9402.9	9580	9417.2
NO ₂ ⁻	42166	41387	42166	41450
NO ₃ ⁻	6.3051e+05	6.1886e+05	5.773e+05	6.1980e+05
C ₂ O ₄ ²⁻	19569	19207	19569	19237
PO ₄ ³⁻	5301	5203	5301	5210.9
SO ₄ ²⁻	18105	17770	18105	17797

Table 3 provides a summary of the molecular streams generated by WA for tank BY-106 using the different charge reconciliation methods. The ESP software initially partitions the anions and cations into simple salts, acids and bases within the module. Re-distribution of these species, many of which will not be observed at the pH and ionic strengths of the waste, is accomplished in the ESP Process module. Fractionating the input stream in this manner allows for a simplified tracking of all of the input species. The differences in the composition of the streams are quite noticeable; yet, these compositions provide equilibrated streams for the ESP process module that have the appropriate loading of the various cations and anions and approximately the same % water. The primary reason for the large differences in molalities for the molecular species between the dominant ion/proration methods and those for the make-up ion method is the significant reduction in nitrate concentration for the make-up ion method.

Table III. Impact of Charge Reconciliation Method on Generated Molecular Stream - Tank BY-106

Species	Dominant Ion (Na ⁻) (molality)	Make-up Ion (NO ₃ ⁻) (molality)	Proration (molality)
H ₂ O	55.509	55.509	55.509
Al(OH) ₃	228.056	32.6802	242.527
Cr(OH) ₃	8.43866	1.20924	8.97419
Fe(OH) ₃	1.33026	.190628	1.41472
H ₂ CO ₃	438.116	62.7815	436.625
H ₆ F ₆	19.7921	2.8363	19.7259
HCl	17.8326	2.55541	17.7730
HNO ₂	228.497	32.7427	227.732
HNO ₃	2535.08	315.720	2526.59
KOH	24.0767	3.4502	25.605
Na ₆ (SO ₄) ₂ CO ₃	23.4910	3.36651	23.4126
Na ₇ F(PO ₄) ₂ .19H ₂ O	6.95755	.997002	6.93426
NaOH	4354.76	576.474	4290.87
H ₂ C ₂ O ₄	55.4249	7.94238	55.2417

In addition to supplying the experimental ionic concentrations the user must enter a density. Adjustment of the density allows tuning of the generated molecular stream to reproduce the experimentally measured % water in the sample. This iterative procedure insures that the stream developed in WA and routed to the process module is representative of the loading of cations and anions in the analyzed sample. The process also reduces the impact of the estimated density used to initially convert the original analytic data in weight % to concentrations (in mg/L) for input to the ESP WA program.

In all studies presented in this paper, the proration method has been used for charge reconciliation and the input density was adjusted to achieve the experimentally measured % water in the original saltcake sample. Experimental % water measurements and the predicted % water from ESP are summarized in Table 4. A detailed listing of the molecular streams generated for each tank by the WA program is not included here, but is available [7].

The composite sample for Tank S-102 was extremely dry and the % water was determined experimentally to be 5%. However, Herting [10] indicated that the % water was more likely to be closer to 11% based on mass balance calculations. The low water content prevented tuning of the input density in WA to allow the experimental % water to be achieved; convergence problems arose as the input density was reduced in an attempt to achieve the 5% by weight water value. The lowest predicted % water which could be achieved in the generated molecular stream for S-102 was ~ 16% by weight. This much higher % water impacted the predictions for the saltcake dissolution experiments for tank S-102. Examination of the water loadings in the three other tanks investigated indicated absolute errors of less than 0.6%.

Table IV. Comparison of Predicted % Water with Experimental Measurements

Tank	Experimental Weight % H₂O (from Herting [1,2])	ESP Prediction of Weight % H₂O
BY-102	26.53	26.4
BY-106	14.75	14.9
S-102	5	16.2
A-101	31.2	31.8

Saltcake Dissolution Experiments

Herting has reported the experimental results for dissolution of the four saltcakes [8,9]. The dissolution experiments were conducted at 25°C and 50°C. Detailed experimental procedures are provided in the references and only a summary of the procedure is given here. Known amounts of saltcake from a given tank core sample and diluent water were combined and mixed thoroughly to promote dissolution. The samples were then allowed to equilibrate and centrifuged and the liquid was decanted. The weights of the solid constituents and supernate were obtained. The liquid samples were then analyzed for specific gravity, weight % water, and select anion concentrations (chloride, fluoride, hydroxide nitrate, nitrite, oxalate, phosphate, sulfate, TIC and TOC). The liquid samples were diluted during the analytical procedure; consequently, all species were fully ionized (i.e., aqueous NaNO₃, present at higher ionic strengths, is converted to Na⁺ and NO₃⁻). The % dilution by weight ranged from 50 % to 300% (100% dilution by weight was defined as 100 g of saltcake mixed with 100 g of diluent). For the 50°C experiments, the saltcake and diluent were mixed, and the solution was heated and allowed to equilibrate. The samples were then centrifuged and analyzed as described above.

Simulation of Saltcake Dissolution Experiments

The ESP process model for this experiment consisted of three unit operations, a MIX block, a HEATER block; and a SEPARATE block. In the MIX block, the molecular stream describing the overall saltcake composition for a particular tank (generated within the WA module) was combined with the appropriate amount of water and mixing was accomplished at 25°C and 1 atm. The outlet stream from the MIX block flowed into the HEATER block, where the temperature was adjusted to the laboratory equilibration point (25°C or 50°C). The effluent from the HEATER block was then routed to a SEPARATE block where the stream was partitioned into the relevant (solid and liquid) phases.

The unit operations for the process simulation required the development of a Chemistry Model that described the relationships controlling the intra-phase and inter-phase equilibria between the ionic, aqueous, and solid species present. The number of equations needed to account for the various species is directly related to the number of species defined in the WA (data pre-processing) module. ESP has limitations on the number of aqueous and solid species that can be described and exceeding these limits results in an error. The model must then be refined to exclude molecules and ions that are not expected to form. In the case of the wastes at Hanford, and the ionic strengths and pH values encountered in this work those species that nominally contain one or more hydrogen atoms (aside for input stream composition requirements) can be

omitted. In all simulations described here the models automatically generated by ESP were, however, used with only a single modification. Dawsonite, $\text{NaAlCO}_3(\text{OH})_2$, was excluded as a possible solid species on the basis of discussions with Hanford personnel [11]. In addition to the Public database available within ESP, two private databases denoted NaNO_3 and Trona were used. The NaNO_3 database contained the correct sodium nitrate data from an earlier release of ESP (version 5.4); predictions of NaNO_3 chemistry in version 6.0 were found to be substantially different than that observed in version 5.4 and OLI Inc. supplied a patch database to correct the problem [6]. The Trona database was invoked following the realization that the Public database did not properly describe the behavior of sodium carbonate hydrate(s) at high ionic strengths (see below).

Saltcake dissolution was simulated over the range of 0% to 500 % by weight addition of water, thereby encompassing the experimental measurements. Comparison of the simulation predictions with the experimental data required a significant amount of post-processing. In the ESP prediction of the aqueous stream, nitrate ion will be found in various forms including the dominant species NO_3^- and $\text{NaNO}_{3(\text{aq})}$. The contributions of each constituent containing nitrate ion in the liquid phase were summed after appropriate weighting. For example, the contribution of nitrate from $\text{NaNO}_{3(\text{aq})}$ was found by multiplying the weight of $\text{NaNO}_{3(\text{aq})}$ by the ratio of the molecular weight of nitrate ion to that of sodium nitrate. Calculations for other nitrate containing components were performed and then the total nitrate concentration was obtained from the sum of all of the nitrate fractions over the volume of the aqueous stream. This provides a prediction for the nitrate concentration that is functionally equivalent to that obtained from the decanted liquid in the actual experiments. The predictions for the other anion components were determined in the same way.

Comparison of ESP Predictions with the Experimental Results of Herting [8,9]

The data in Figure-1 compares the predicted (ESP) and experimental nitrate concentrations for all four tanks as a function of % dilution by weight. Solid sodium nitrate was initially present in all saltcake compositions. As water was added, the solid underwent dissolution resulting in an increase in the nitrate anion concentration. Once all of the solid sodium nitrate has dissolved, the total amount of nitrate anion in the supernate liquid will remain constant. As water was added, the concentration decreased reflecting increased dilution.

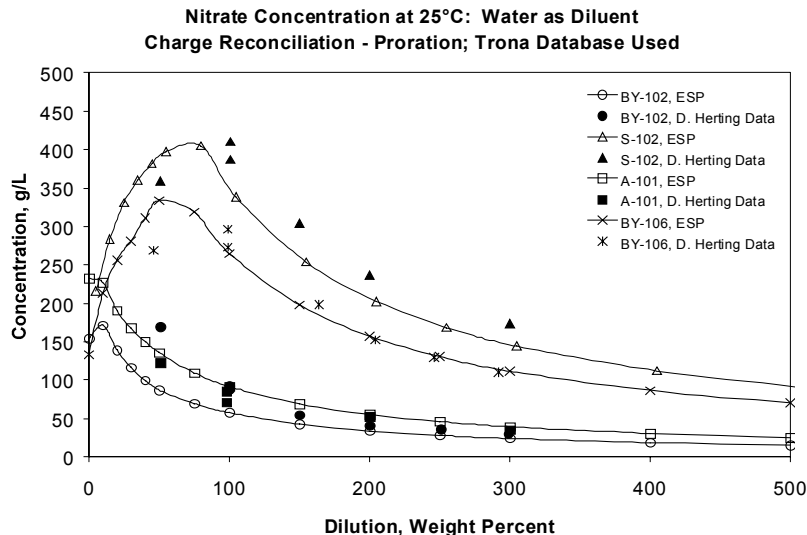


Fig. 1. Comparison of the ESP Predictions of Nitrate Concentration with Experimental Data of Herting [8,9]

The agreement between the experimental measurements and predictions is quantitative at higher dilution levels (> 100%). For both tanks BY-106 and S-102, the weight % of nitrate in the undiluted saltcake (Table-1) was much higher (40.68% and 53.7%) than for tanks A-101 (12.6%) and BY-102 (10.92%). These differences are reflected in the much higher concentrations realized for nitrate in the liquid supernate. For tanks BY-102, BY-106, and A-101, the model predictions of nitrate concentration are within the experimental error of the measurements at the dilution levels > 100%.

Differences between prediction and experiment were found for the S-102 saltcake even at high dilution levels. It is important to note that the maximum concentration of nitrate predicted by ESP is 405 g/L and that at 100% dilution by weight the experimental measurements of nitrate concentration were 387 g/L and 410 g/L. The agreement in the maximum concentrations confirms that the generated molecular stream used as input to ESP contains the appropriate loading of nitrate. If the generated molecular stream had significantly higher nitrate loading, the predicted maximum concentration of nitrate would also be elevated. The trend evident in the experimental nitrate concentration data is reflected in the ESP predictions; however, there is a systematic shift of the predicted concentrations relative to the experimental concentrations. The experimental concentrations were found to be slightly higher than the predicted concentrations at any given level of dilution (for % dilution by weight $\geq 100\%$). Since the generated molecular stream contained larger % water by weight than the experimental data (16% versus 5%), the difference in concentrations could, in fact, be accounted for by the failure of the program to allow convergence at the lower water loading. A rough estimate of the predicted concentration that might be realized if it were possible to achieve the 5% water is $338 \text{ g/L}/(.89) = 382 \text{ g/L}$ at 100% dilution. This compares more favorably to the reported experimental concentrations of 387 g/L and 410 g/L at this level of dilution.

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In the low dilution region (< 100% dilution by weight), only a single experimental measurement at 50% dilution by weight was available. Here, considerable amounts of solids were predicted to remain in the saltcake sample. The largest fraction of these solids arose from the sodium salts, and in addition to sodium nitrate, sodium carbonate monohydrate and sodium oxalate were predicted to be present along with the double sodium salts, natrophosphate [$\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$] and sodium-fluoride-sulfate [Na_3FSO_4].

The dissolution behavior of the double salts has been found to significantly impact the dissolution of the single salts that are present. The predictions for phosphate, fluoride and sulfate for those tanks where fluoride is present (all but S-102) all deviate from experimental data. Figure 2 provides a comparison of predicted sulfate concentrations and the experimental data of Herting [8,9]. Tank BY-102 contained the largest weight % of both sulfate and fluoride of the four tanks examined (ratio of $\text{F}^-/\text{SO}_4^{2-} \sim .228$, total weight % of these two components $\sim 6.3\%$). Thus, the sodium fluoride sulfate double salt is predicted to be present in the solid phase until dilutions of greater than 100%. The general behavior of the dissolving double salt in BY-102 is mirrored by the predicted concentrations. For tank BY-106, which also contains moderate amounts of sulfate and fluoride (ratio of $\text{F}^-/\text{SO}_4^{2-} \sim .53$, total weight % of these two components $\sim 1.8\%$ by weight), this same behavior is reflected for the sulfate concentrations. However, for tank A-101, which contains only a small amount of fluoride (ratio of $\text{F}^-/\text{SO}_4^{2-} \sim .028$, total weight % of these two components $\sim 2.5\%$), only a small amount of the sodium fluoride sulfate double salt is predicted to be present in the solid phase (2.3% by weight of the solid phase). The prediction of sulfate concentration by ESP is in agreement with the trend displayed by the experimental data for tank A-101. For tank S-102, for which the composite saltcake sample contained no fluoride (at detectable levels during total composition by sequential dissolution tests), the agreement between ESP predictions of the sulfate concentration and the experimental sulfate concentration data is within experimental error for the sulfate concentration. Similar behavior is exhibited by the phosphate concentrations predicted by ESP as well. ESP predicts that the phosphate in the tanks containing fluoride is found in the solid phase as the sodium-phosphate-fluoride double salt.

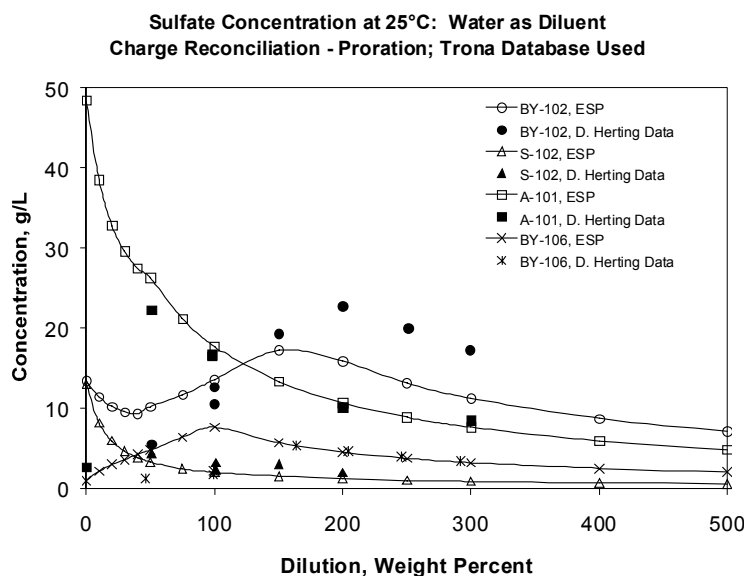


Fig. 2. Comparison of ESP Predictions of Sulfate Concentration with Experimental Data of Herting [8,9]

It is hypothesized that these discrepancies arise from inadequacies in the thermodynamic data contained within the ESP Public database, i.e. the source database for the double salt thermodynamic data. Errors in the thermodynamic data for the sodium double salts will also impact the predicted equilibrium behavior of the single sodium salts such as sodium nitrate and sodium carbonate monohydrate. For tank S-102, the absence of fluoride in the saltcake, compared to the other 3 tanks where fluoride was present, resulted in improved predictions of all anion concentrations in the low dilution region (< 100%). When fluoride is present in the saltcake, ESP predicts that the phosphate and sulfate in the solid phase are found in the double salts, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ and Na_3FSO_4 . It was initially unclear whether the deviations in predicted phosphate and sulfate concentrations were due to ESP incorrectly predicting the solid phase species or due to the quality of thermodynamic data for the double salts in the ESP Public database.

As part of an effort to confirm ESP predictions of the presence of double salts in the dissolving saltcake, Herting carried out crystal identification on the species present in the solid phase for BY-102 saltcake [9]. Sodium carbonate monohydrate, sodium nitrate, sodium fluoride-sulfate, natrophosphate and sodium oxalate were all identified in the solid phase using Polarized Light Microscopy and other techniques [9]. The solid phase predicted by ESP also contained all of these species. This confirms that ESP is properly predicting the species present in the solid phase. Any discrepancies between experiment and prediction are due to the quality of thermodynamic data for these double salt systems. Laboratory efforts are underway to measure the solid-liquid equilibria for these double salts as a function of temperature and ionic strength [7]. These measurements can then be used to improve the quality of the thermodynamic data included in the ESP database.

Figure-3 compares the predicted concentrations for TIC (total inorganic carbon) with the experimental data of Herting [8,9]. Inclusion of the Trona database to provide thermodynamic data for $\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$ was necessary to correctly predict the behavior of carbonate under the high ionic strength conditions realized in these Hanford tanks. Use of the ESP Public database incorrectly predicted that sodium carbonate monohydrate would not, initially, be present. In fact the Public database did not predict that this molecule would be present in the solid phase resulting from dilution levels less than 100%. For tank BY-102, which contained significantly more TIC than the other tanks examined, experimental characterization of the solid phase indicated the presence of the monohydrate of sodium carbonate [9]. In order to predict its existence in the solid phase, the Trona database must be used to provide the relevant thermodynamic data for this monohydrate that allows the prediction of the solid phase forming at lower temperatures due to the higher ionic strength present in the system. As evidenced in Figure 3, the solid phase for BY-102 is predicted to be predominantly composed of this monohydrate of sodium carbonate. At a dilution level of ~50% by weight, the monohydrate is predicted to be completely dissolved and further addition of water results in behavior typical of dilution. Predictions of TIC concentration in the low dilution region (< 100%) do show some discrepancy with experimental measurements except for the prediction of TIC in tank S-102. An examination of the hydrate transition temperature as a function of ionic strength for the sodium carbonate system being initiated will attempt to provide an improved understanding of this behavior under conditions relevant to the Hanford tanks [12]. Data obtained through this effort can then be used to improve the predictive capability of ESP.

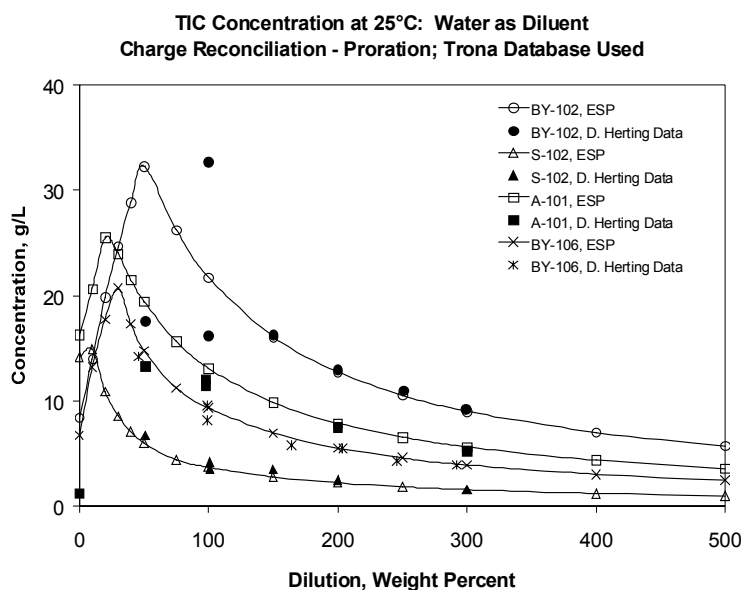


Fig. 3. Comparison of ESP Predictions for carbonate with the experimental predictions of Herting [8.9].

CONCLUSIONS

Evaluation of the application of ESP as a modeling tool for predicting the dissolution behavior of saltcakes present in the Hanford tank is in progress. An iterative approach to balance charge for the experimental analytic data supplied to Water Analyzer has been developed which allows the generated molecular stream used in subsequent ESP calculations to properly reflect the cation and anion loadings as well as the % water in the experimental data. Saltcake dissolution has been modeled using ESP. General trends exhibited by the experimental data are also exhibited by the ESP predictions. These predictions and their comparison to experimental data also indicate a need for improved thermodynamic data for the sodium double salts present in the waste and a need for improved understanding of the relationship between hydrate transition temperature and ionic strength.

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