Modeling of Unsaturated Saltcake Dissolution for S-109 Simulant - 8294

R.K. Toghiani[1,2], J.S. Lindner[1]
[1]Institute for Clean Energy Technology
[2]Dave C. Swalm School of Chemical Engineering
Mississippi State University
205 Research Boulevard, Starkville, MS 39759

ABSTRACT

The Environmental Simulation Program (V7.0, OLI Systems, Inc.) with V7DBLSLT, the latest version of the double salt database developed by the Institute of Clean Energy Technology (ICET), was used to predict effluent stream compositions and densities, residual saltcake composition, and saltcake heights for an unsaturated saltcake dissolution test with a simulant representative of waste contained in Hanford tank 241-S-109. Predictions for major cation and anion concentrations were in excellent agreement with the experimental data obtained at the Applied Research Center (ARC) at Florida International University (FIU). The utility of ESP as a means to predict effluent stream compositions and effluent stream properties, such as density and column saltcake height, is demonstrated through the agreement between experimental and predicted values. These, and previous calculations, validate the use of thermodynamic models (with proper chemistry representations) for HLW pretreatment and retrievals. A powerful and useful tool is the result. Cost reductions are possible as the amount of sampling and subsequent laboratory analysis can be reduced. Additionally, overall processing risk is reduced through the ability to rapidly evaluate different processing and retrieval scenarios. The application of appropriate models can thus lead to more efficient operations and campaign cost savings while also evaluating parameters pertinent to safety.

INTRODUCTION

The ability to predict the composition of waste streams arising from saltcake dissolution during retrieval operations is valuable in that simulations of the dissolution process allow for examination of various retrieval strategies prior to their use in the field. In addition, accurate composition predictions have implications on safety (activity, corrosion, waste blending) and on assessing whether particular feeds meet waste acceptance criterions. At the Hanford site, examination of retrieval strategies through such predictions is a formidable task, with 53 million gallons of waste contained in 177 single shell and double shell tanks to consider. The underground waste tanks have capacity up to 10^6 gallons. Waste was placed into the tanks over decades of production and process demonstration runs at the Hanford site, and the bulk composition of waste varies from tank to tank, as does the composition at differing locations within a single tank.

Herting [1] performed laboratory scale experiments examining the dissolution of saltcake, using core samples from eight tanks. His selection of tanks was judicious, in that core samples were chosen for testing such that extremes in anion composition were examined. For example, saltcake from tank TX-113 was rich in nitrate (29 % by weight), carbonate (14 % by weight), and sulfate (13 % by weight) while saltcake from tank S-102 was essentially pure sodium nitrate

(53.7 % nitrate by weight). These saltcake dissolution experiments were modeled by researchers at ICET [2] using the Environmental Simulation Program (ESP, OLI Systems, Inc.). Deviations observed between the experimental concentrations for various ions in the equilibrated liquid stream (nitrate, phosphate, fluoride, carbonate, and sulfate) led to the subsequent measurement of solubility of various binary combinations of these sodium salts in aqueous solution and in sodium hydroxide solutions. These solubility measurements have been used to improve the predictive capabilities of ESP with respect to process modeling of alkaline brines [3-5].

As a means to assess applicability of ESP modeling to waste retrieval from pilot scale dissolution experiments, simulation of the S-109 Unsaturated Tall Column Dissolution Test was conducted. The experimental dissolution test was performed at ARC (Applied Research Center) [6], and experimental results were provided to ICET for comparison with ESP model predictions. The term 'unsaturated' is used to define the hydrology of the column dissolution test; in this case, the pores in the saltcake are not entirely filled with interstitial brine.

BACKGROUND AND MODELING APPROACH

In the experiment, a recipe for S-109 simulant was prepared in multiple batches and charged into the 12-inch diameter, 10-foot tall column. The preparation of the simulant was performed in such a manner as to ensure consistency across the batches. The requisite amount of each chemical was added to water at elevated temperature, and the resulting mixture was then evaporated to remove a portion of the water and induce precipitation of various solid species. Table I provides a summary of the simulant recipe employed.

Table I. S-109 Simulant Recipe for Unsaturated Tall Column Dissolution Test

Chemical Species	Mass (kg)
H_2O	359.936
$NaNO_3$	290.890
$Na_3PO_4. 0.25NaOH.12H_2O$	16.814
Na_2CO_3	14.621
$NaAlO_2. 0.22H_2O$	10.019
Na_2SO_4	4.113
$NaNO_2$	3.886
$Na_2C_2O_4$	1.393
NaOH	0.735
NaCl	0.363
NaF	0.202

Previously, the composition of the technical grade sodium aluminate employed in the experiments at ARC had been determined at ICET using TGA and ICP measurements to be $0.5785NaAlO_2 \cdot 0.0484Al(OH)_3 \cdot 0.2171NaOH \cdot 0.17H_2O$. This chemical formula was employed in developing the input composition for ESP. The simulant was prepared in three batches of similar size. Evaporation of each batch was conducted at 100 °C with approximately 34% of the batch mass removed during the process. Each batch was allowed to cool to 25 °C before transfer into the tall column. The evaporation removed a total of 244.353 kg of water from the slurry.

Predictions of the S-109 unsaturated dissolution test were carried out using ESP V7.0, with V7DBLSLT. Input to ESP is provided in Table II. For the sodium aluminate and trisodium phosphate, the amounts of each individual compound were input separately. For example, the mass of technical grade sodium aluminate was input as masses of $NaAlO_2$, $NaOH$, $Al(OH)_3$ and H_2O, calculated from the chemical formula. Trisodium phosphate was handled in the same manner. The mass of water input to ESP reflects the water from the original recipe, plus the water contributed by the technical grade sodium aluminate and trisodium phosphate, minus the 244.353 kg of water removed during the evaporation process.

Table II. ESP V7.0 Input for S-109 Unsaturated Dissolution Test

Chemical Species	Mass (kg)
H_2O	125.388
$NaNO_3$	290.890
Na_3PO_4	7.066
Na_2CO_3	14.621
$NaAlO_2$	7.548
Na_2SO_4	4.113
$NaNO_2$	3.886
$Na_2C_2O_4$	1.393
$NaOH$	2.548
$NaCl$	0.363
NaF	0.202
$Al(OH)_3$	0.601
TOTAL	458.619

After charging of the slurry batches to the tall column at ARC, the brine was recirculated so as to ensure equilibration of the tall column contents. A net 156.12 kg of brine were removed after recirculation, leaving an initial charge in the tall column of 55.42 kg saturated brine and 247.08 kg solids, for a total of 302.50 kg. The solids species predicted to be present in the column at the start of diluent addition are shown in Table III. Sodium nitrate represented the largest fraction of the solid phase.

Table III. Predicted Solids Speciation at Start of Diluent Addition

Chemical Species	Mass (kg)
$NaNO_3$	219.484
$Na_3PO4. 0.25 NaOH. 12H_2O$	13.255
$Al(OH)_3$	6.010
$Na_2CO_3.1H_2O$	3.773
$Na_7F(PO_4)_2.19H_2O$	3.246
$Na_2C_2O_4$	1.308
TOTAL	247.076

The dissolution test was divided into 74 intervals. For each interval, the given mass of diluent was combined with the solids and the retained brine from the previous interval using a MIX block. A SEPARATE block was used to partition the brine and solids into individual streams. The brine stream was then partitioned using a SPLIT block into two streams: a retained portion

and a removed portion, based on the mass of brine drained from the column during the experimental interval.

Approximately 318 hours into the dissolution test, the experiment was halted due to channeling. The column was subjected to vibration and brine was recirculated in an attempt to repack the column. This occurred at interval 14 in the simulation. To mimic the process, the amount of brine removed during the vibration/recirculation process was removed in the simulation using a SPLIT block. The experiment then continued for an additional 61 intervals.

DISCUSSION OF RESULTS

For each interval, the predicted brine composition was used to calculate cation and anion concentrations, which were then compared to the experimental data. Additionally, the volume of solids in each interval was estimated using the predicted mass of each solid species divided by the density of that species. The total volume of solids was combined with the volume of brine to yield a total volume of the column contents. Division by the cross sectional area of the column allowed an estimate of the saltcake height. Brine density was also predicted within ESP V7.0 for each interval and the predictions compared with the experimentally reported values.

Figure 1 compares the experimental column height with the model predictions. Initial predictions of the column height were significantly lower than the experimental values, particularly during the early portion of the experiment. Approximately 1200 hours into the experiment, predicted and experimental column heights are in good agreement. During modeling of the S-109 Saturated Test conducted previously [7], this approach to estimation yielded excellent agreement between predicted and experimental column heights. However, in a saturated test, the solids in the column are completely wetted with saturated brine and a small amount of saturated brine is maintained above the height of the solid saltcake. Thus, the pores within the solid saltcake structure are completely filled with saturated brine. In the unsaturated test, a large portion of the solid saltcake structure is not fully wetted by the saturated brine. Only a small portion of the saltcake located near the bottom of the column is fully wetted. Near the end of the experiment, a larger fraction of the solid saltcake structure would be wetted by the retained brine, compared to the initial stages of the dissolution test. A porosity of the solid saltcake of 30 % was assumed to adjust for the unfilled pores (incompletely filled pores) within the saltcake. Saltcake height was then recalculated using this porosity and the results are also depicted in Figure 1. The use of an assumed porosity of 30 % provided for a better estimate of the height of contents within the tall column.

The predicted brine specific gravity is compared to the experimental specific gravity of the effluent brine in Figure 2. The density of a saturated sodium nitrate solution at 25 °C is predicted to be 1.35 kg/L by ESP. The experimental specific gravities are stable about a value of approximately 1.38 kg/L for the bulk of the experiment during the first 1200 hours. The marked drop in the specific gravity in the first 200 hours of the experiment is a result of the channeling that occurred early in the experimental run. The diluent added did not have sufficient residence time in the column to fully saturate before being drained. The drop in specific gravity after approximately 1200 hours reflects the complete dissolution of the sodium nitrate in the column. Once the sodium nitrate has been completely dissolved, other sodium salts begin to dissolve, first

natrophosphate (fluoride-phosphate double salt), followed by sodium oxalate and trisodium phosphate. The predicted specific gravity is in excellent agreement with the experimental measurements, until the later portion of the experiment.
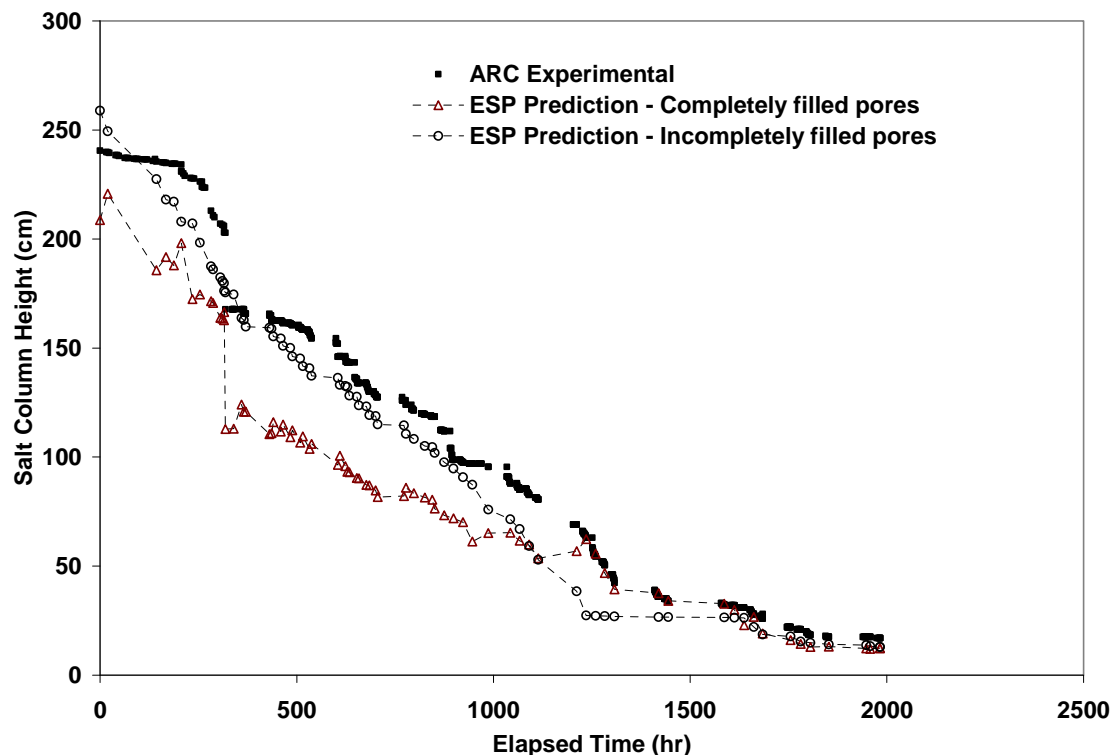

Figure 1. Comparison of Experimental and Estimated Saltcake Height for S-109 Unsaturated Tall Column Dissolution Test

Experimental data for sodium and nitrate cations are compared to the ESP predictions in Figure 3. It is evident from the experimental data as well as the predictions that the effluent brine is saturated in sodium for the initial 800 hours of the experiment. During the latter portion of the experiment, the predicted values are markedly lower that the experimental data for the period 800 hours to approximately 1200 hours (when sodium nitrate is predicted to be completely dissolved). During the last portion of the experiment (later than 1200 hours), the ESP predictions are much lower than the experimental values. One possible explanation for these differences is that the ESP predictions are based on equilibrium. At 800 hours, approximately two thirds of the sodium nitrate originally present in the solid phase has been predicted to be dissolved, and over the next 400 hours, the remaining portion of the sodium nitrate is predicted to undergo dissolution. The ESP predictions were conducted assuming that the entire column contents are contacted by the added diluent. In reality, this is not the physical situation that will occur in the column. Thus, it is not surprising that ESP overestimates the sodium concentration between 800 and 1200 hours, nor is it surprising the ESP underestimates this concentration in the interval past 1200 hours.
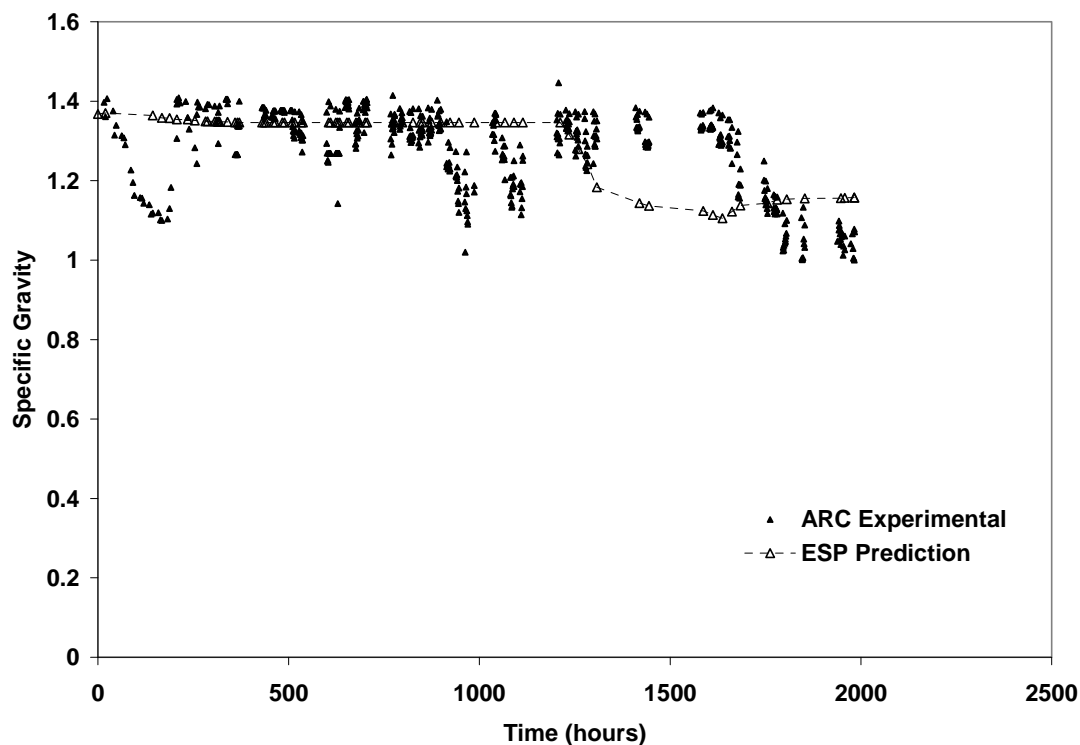
Figure 2. Comparison of Predicted and Experimental Specific Gravity of the Effluent Brine

Also shown in Figure 3 is a comparison of experimental and predicted nitrate concentrations. There is a great deal of scatter in the experimental nitrate concentration data. The period when channeling occurred in the saltcake column is readily evident in the experimental data, when nitrate concentration dropped to < 100 g/L. Similar to sodium concentrations, predicted nitrate concentrations are greater than experimental concentrations during the last 400 hours of the experiment. Again, the explanation for this difference is the assumption of equilibrium being achieved in the ESP model.

Only a small amount of carbonate is present in the solid phase initially and is present as sodium carbonate monohydrate. This approximately 4 kg are predicted to dissolve during the first two diluent additions; thus, an increase in carbonate concentration is observed initially. Once the sodium carbonate monohydrate has been dissolved, the carbonate concentration profile follows a pattern typical of dilution. A comparison of experimental and predicted carbonate concentrations is provided in Figure 4.

The aluminum concentration profiles depicted the much lower levels of aluminum present in the system. The predicted profile was typical of a dilution. Aluminum present in the solid phase is in the form of gibbsite. The total amount of gibbsite present in the solid phase was fairly constant at 6 kg over the entire course of the simulation, indicating that essentially no dissolution of aluminum-bearing species occurred. This is reflected by the low concentrations of aluminum in the liquid phase.
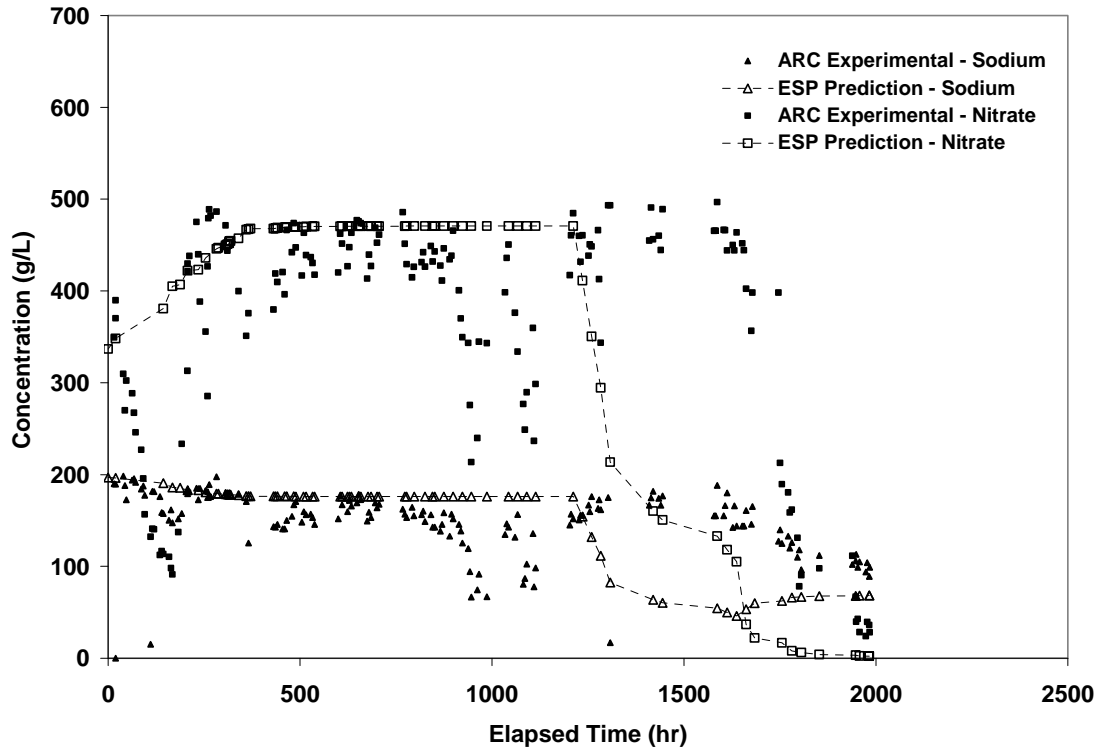
Figure 3. Comparison of Predicted and Experimental Sodium and Nitrate Concentrations in Effluent Brine
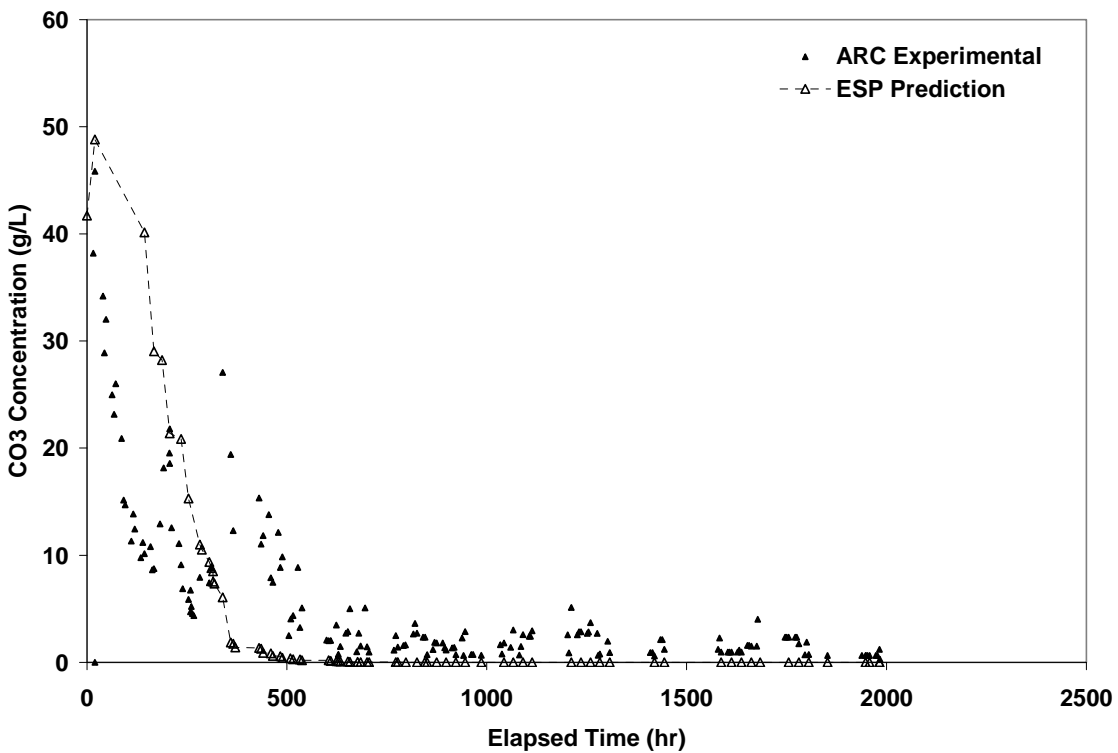

Figure 4. Comparison of Predicted and Experimental Carbonate Concentrations in Effluent Brine.

The remaining anions tracked during the experiment for which concentrations were estimated using ESP could be classified into two categories. The first category is comprised of chloride, nitrite and sulfate. Present in the initial simulant recipe in fairly small quantities, these anions were only predicted to be in the liquid phase; no solid species containing these anions were predicted at start of diluent addition. As a result, their profiles were typical of a dilution profile, rather than a dissolution profile. The second category is comprised of phosphate, fluoride, and oxalate. These species are also present in the initial simulant recipe in fairly small quantities; however, in contrast to the other category, these were found to be predicted to be present predominately in the solid phase, as natrophosphate [$Na_7F(PO_4)_2 \cdot 19H_2O$], sodium orthophosphate dodecahydrate [$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$] and sodium oxalate [$Na_2C_2O_4$]. Dissolution profiles for these were predicted to be essentially flat, with little or no dissolution occurring until the dissolution of sodium nitrate was essentially complete.

CONCLUSIONS

Predictions for major cation and anion concentrations were in excellent agreement with the experimental data obtained at the Applied Research Center at Florida International University. The utility of ESP as a means to predict effluent stream compositions and effluent stream properties such as density and column saltcake height is demonstrated through the agreement between experimental and predicted values. These, and previous calculations, validate the use of thermodynamic models (with proper chemistry representations) for HLW pretreatment and retrievals. A powerful and useful tool is the result. Cost reductions are possible as the amount of sampling and subsequent laboratory analysis can be reduced. Additionally, overall processing risk is reduced through the ability to rapidly evaluate different processing scenarios. The application of appropriate models can thus lead to more efficient operations and campaign cost savings while also evaluating parameters pertinent to safety.

ACKNOWLEDGEMENT

REFERENCES

[1]   Herting, D. L., (2000), *Saltcake Dissolution FY 2000 Status Report*, HNF-7031, Fluor Hanford, Richland, WA.
[2]   Toghiani, R. K, Lindner, J. S., (1999), *Saltcake Dissolution Modeling, FY 2000 Status Report*, DIAL-40395-TR00-1, Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, Mississippi State, MS.
[3]   Toghiani, R.K., Phillips, V.A., Lindner, J.S., "Solubility of Na-F-SO4 in Water and in Sodium Hydroxide Solutions", *J. Chem. Eng. Data*, 50, 1616-1619, (2005).
[4]   Toghiani, R.K., Lindner, J.S., Selvaraj, D., "Solubility in the Na-F-NO3 and Na-PO4-NO3 Systems in Water and in Sodium Hydroxide Solutions", submitted for publication, 2007.

[5]   Toghiani, R.K., Phillips, V.A., Smith, L.T., Lindner, J.S., "Solubility in the Na-SO$_4$-NO$_3$ and Na-SO$_4$-NO$_2$ Systems in Water and in Sodium Hydroxide Solutions", *J. Chem. Eng. Data*, accepted for publication, December 2007.
[6]   Tachiev, G.L., personal communication, 2006.
[7]   Toghiani, R.K., Smith, L.T., Lindner, J.S., Tachiev, G.I., Yaari, G., "Modeling of Pilot-Scale Saltcake Dissolution", *WM'06 Conference Proceedings*, Tucson, AZ, February 26-March 2, 2006.