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Modeling and Validation of Hanford Low Activity Waste Evaporation System

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Abstract

The aqueous electrolyte chemistry of the low activity waste (LAW) evaporation process was modeled using the Environmental Simulation Program (ESP) licensed by the OLI Systems, Inc. The model was used to predict the operating vacuum required to reach the target endpoint of 80% saturation in the bottom product during the bench-scale evaporation of a LAW supernate simulant at 55 ^{o}C. The bench-scale data showed that the model not only predicted correctly the sodium double salt, $Na_7F(PO_4)_2.19H_2O$, to be the first major salt species to precipitate out during storage at 25 ^{o}C but accurately determined its solubility limit as well.

The thermodynamic database of the ESP software was revised by re-fitting the equilibrium constant parameters for gibbsite, $Al(OH)_3$, and sodium carbonate monohydrate, $Na_2CO_3.H_2O$ to match the solubility data obtained during this study. The revised database was used to construct the solubility curve of Hanford Tank 241-AZ-101 supernate between 15 and 85 ^{o}C. The resulting solubility curve clearly showed that at T ³ 55 ^{o}C the bulk solubility of Tank 241-AZ-101 supernate is controlled by the formation of $Na_2CO_3.H_2O$, while at T < 55 ^{o}C it is controlled by the formation of $Na_7F(PO_4)_2.19H_2O$.

Introduction

With the advent of high-powered personal computers, process models dealing with aqueous electrolyte chemistry have become increasingly rigorous and thus found increased application in many environmental and industrial processes such as wastewater treatment, gas scrubbing, bio-separations, and corrosion, just to name a few. This study is concerned with a particular aqueous electrolyte system involving the LAW supernate currently stored in dozens of underground tanks at the Department of Energy's Hanford Site. The supernate in each waste tank is strongly alkaline

and composed mainly of sodium salts of nitrate, nitrite, carbonate and sulfate, and some even contain high levels of organic complexant.

The baseline flowsheet for the Hanford's River Protection Project (RPP) Waste Treatment Plant includes pretreatment of the LAW supernate by removing cesium, technetium, strontium and transuranics (TRU) via a series of ion exchange and precipitation operations. The radionuclides thus removed are immobilized in a high level waste (HLW) glass melter along with the sludge portion of each waste tank that contains most of the radioactivity. The decontaminated LAW liquid is next concentrated in a forced-circulation evaporator and sent to an interim storage tank, before being fed to a LAW glass melter. In order to preclude the formation of solids during storage, the maximum concentration of dissolved solids in the evaporator bottom is limited to 80% saturation at 25 ° C. In a multi-electrolyte solution, 100% saturation is defined here as the point where one of the major salt species starts to precipitate out.

The LAW evaporator is designed to operate at 55 ^{o}C under vacuum to protect the integrity of the vessel. A bench-scale process demonstration of the LAW evaporator was conducted recently using a simulated Tank 241-AZ-101 (AZ-101) supernate. This paper describes a process model built to support the bench-scale demonstration by pre-determining the steady state evaporation rate as well as the operating vacuum required at 55 ^{o}C in order to reach the target endpoint of 80% saturation in the bottom product. This paper also shows how the thermodynamic database of the ESP software was fine tuned using the data taken during the small-scale solubility tests that were conducted in a constant-temperature shaker-bath.

The chemical constituents and crystal phases of the solids samples taken during these tests were determined by the X-ray diffraction (XRD). The XRD results were then used along with the revised database to construct the solubility curve of Tank AZ-101 supernate between 15 and 85 ^{o}C. A detailed description of both experimental and modeling tasks performed during this study is given in the campaign report.[1]

Aqueous Electrolyte Model

Process modeling of aqueous electrolyte systems consists of two parts. The first part is to develop a predictive thermodynamic model that describes the aqueous electrolyte chemistry of the given input species. Compared to the processes involving non-electrolytes only, the formulation of such a model is much more complicated. This is mainly because the number of species to be included is increased dramatically due to the formation of ions by dissociation reactions and complexes by association reactions. As a result, electrolyte chemistry models must consider the interactions not only between molecule-molecule pairs but ion-ion and ion-molecule pairs as well. The second part is to actually develop unit operation models that are unique to each process and is essentially the same for both electrolyte and non-electrolyte processes.

To illustrate how a predictive electrolyte chemistry model is formulated,[2] we use as an example a simple 2-component system containing water and nitric acid only. Suppose we are given inflow rates of H_2O and HNO_3 to a tank, which is kept at a constant temperature (T) and pressure (P). The problem is then to determine the outflow rates and concentrations of the liquid and vapor phases that are in equilibrium. The relevant equilibrium reactions are:

$$H_2O\,(aq) = H^+ + OH^- \quad (1)$$

$$H_2O\,(v) = H_2O\,(aq) \quad (2)$$

$$HNO_3\,(aq) = H^+ + NO_3^- \quad (3)$$

$$HNO_3\,(v) = HNO_3\,(aq) \quad (4)$$

There are eight unknowns in this problem: molar flow rates of H_2O (aq) and vapor, $\dot{n}_{H_2O}$ and $\dot{n}_{vap}$, vapor-phase partial pressures of H_2O and HNO_3, P_{H_2O} and P_{HNO_3}, and liquid-phase concentrations of HNO_3 (aq), NO_3^-, H^+ and OH^-.

So, a set of eight equations is required to solve for these eight unknowns. First, we have four equilibrium relationships, one for each of the reactions (1) to (4):

$$K_{H_2O(aq)} = \frac{\gamma_{H^+}\, m_{H^+}\, \gamma_{OH^-}\, m_{OH^-}}{a_{H_2O(aq)}} \quad (5)$$

$$K_{H_2O(v)} = \frac{a_{H_2O(aq)}}{\phi^v_{H_2O}\, P_{H_2O}} \quad (6)$$

$$K_{HNO_3(aq)} = \frac{\gamma_{H^+} m_{H^+} \gamma_{NO_3^-} m_{NO_3^-}}{\gamma_{HNO_3(aq)} m_{HNO_3(aq)}} \quad (7)$$

$$K_{HNO_3(v)} = \frac{\gamma_{HNO_3(aq)} m_{HNO_3(aq)}}{\phi^v_{HNO_3} P_{HNO_3}} \quad (8)$$

where K_i is the equilibrium constant, g_i the activity coefficient, f_i the fugacity coefficient, a_i the activity, P_i the vapor-phase partial pressure, and m_i the liquid-phase concentration of species *i*, usually expressed in molality, i.e., gmoles of solute per 1,000 gm of solvent, H_2O. So, m_i's are independent of *P* and *T*.

Next, the charge balance between cations and anions must be maintained:

$$m_{H^+} = m_{OH^-} + m_{NO_3^-} \quad (9)$$

With no air purge or gas stream defined, the sum of the partial pressures of H_2O (aq) and HNO_3 (aq) must equal the total system pressure:

$$P_{H_2O} + P_{HNO_3} = P \quad (10)$$

The overall mass balance yields:

$$\dot{m}_{H_2O,in} + \dot{m}_{HNO_3,in} = \dot{n}_{vap} \frac{P_{H_2O}(18) + P_{HNO_3}(63)}{P}$$

$$+ \dot{n}_{H_2O}(18) \left\{ 1 + \left[\begin{array}{l} m_{H^+}(1) + m_{OH^-}(17) \\ + m_{NO_3^-}(62) + m_{HNO_3}(63) \end{array} \right] / 1000 \right\}$$

(11)

where $\dot{m}_i$ and $\dot{n}_i$ are the mass and molar flow rates of species i, respectively.

Finally, the nitrogen balance yields the eighth equation:

$$\frac{\dot{m}_{HNO_3}}{63} = \dot{n}_{vap} \frac{P_{HNO_3}}{P}$$

$$+ \frac{\dot{n}_{H_2O}(18)}{1000}(m_{HNO_3} + m_{NO_3^-}) \quad (12)$$

The difficulty of solving Eqs. (5) to (12) essentially lies in the high nonlinearity of the correlations used for *K* and g_i. The equilibrium constant, *K*, is usually expressed in the following form adopted by the ESP software:

$$\log_{10} K(T) = A + B/T + CT + DT^2 \quad (13)$$

where A, B, C and D are the constants that are determined by regressing the equilibrium data. The equilibrium constant can also be calculated directly from the thermodynamic principles:

$$\ln K(T) = -\Delta\overline{G}^o_{rxn}(T)/RT \quad (14)$$

where $\Delta\overline{G}^o_{rxn}$ is the partial molal Gibbs free energy of reaction and is calculated as the stoichiometric sum of the Gibbs free energies of the reactants and products, many of which are tabulated in the literature. R is the gas constant.

The activity coefficient, g_i, can be calculated from the available thermodynamic models such as Pitzer, Bromley, Chen NRTL, etc., and the choice

of a suitable model depends on the characteristics of the solution in consideration. The current ESP software database is based on:[3] (1) the revised Helgeson equation of state for predicting the standard state properties of all species in water, (2) the Bromley-Zemaitis formulation for predicting the excess thermodynamic properties, (3) the Pitzer and Setschenow formulation for predicting the excess thermodynamic properties of molecular species in water, and (4) the enhanced SRK equation of state for predicting the vapor- and nonaqueous liquid-phase proterties.

AZ-101 Chemistry Model

The compositions of the simulated Tank AZ-101 supernate feeds used in the experimental and modeling studies are compared in Table 1. The feed used in the model contained every species included in the bench-scale feed but was more concentrated.

TABLE 1. Tank AZ-101 Supernate Simulant Compositions Used in this Study.

Analyte	Bench Scale Run (mg/L)	Shaker-Bath Study (mg/L)	ESP Model Input (mg/L)
Al	9,314	10,830	10,877
NH_3	273	317	319
CO_3	20,149	23,078	23,521
Cs	33	0	38
Cl	174	203	203
Cr	637	741	744
F	1,583	1,841	1,849
OH	18,188	22,600	21,185
NO_3	66,034	76,758	77,082
NO_2	56,810	66,039	66,319
PO_4	1,312	1,525	1,532
K	4,037	4,693	4,714
Na	95,163	110,625	111,050
SO_4	3,078	0	3,669
Zr	2.68	3.10	6.40
density (g/ml)	1.198	1.246	1.246
total solids (wt%)	24.65	28.38	28.07

The concentrations given in the Model Input column of Table 1 were converted into an input vector of neutral species, which was then entered into the ESP model. A list of species that were included in the resulting AZ-101 chemistry model is shown in Table 2.

TABLE 2. Species Included in Tank AZ-101 Chemistry Model.

Gases	N2 (l)	H2P2O7	ZrF6
N2	NaF	H2PO4	ZrF
O2	NaHCO3	H3P2O7	Zr
CO2	NaNO3	HCO3	Zr(NO3)2
NH3	NH3 (l)	HCrO4	ZrNO3
SO3	NH4NO3	HF2	Zr(OH)2
H2F2 (g)	O2 (l)	H	Zr(OH)3
H2O (g)	SO3 (l)	HP2O7	Zr(OH)5
H2SO4 (g)	ZrCl4	HPO4	ZrOH
HCl (g)	ZrF4	HSO4	ZrSO4
HF (g)	Zr(OH)4	HZrF6	
HNO2 (g)		K	***Solids***
HNO3 (g)	***Ions***	KSO4	Al2(SO4)3 (s)
	AlF2	Na2F	Al(OH)3 (s)
Neutral	AlF4	NaCO3	Na2CO3 (s)
H2O	AlF5	Na	Na2SO4 (s)

AlF3	AlF6	NaSO4	Na2ZrF6 (s)
Al(OH)3	AF	NH2CO2	Na3FSO4 (s)
CO2 (l)	Al	NH4	Na3PO4 (s)
CsCl	Al(OH)2	NH4SO4	NaAlCO3(OH)2 (s)
CsNO3	Al(OH)4	NO2	NANO2 (s)
H2F2	AlOH	NO3	NANO3 (s)
H2SO4	Al(SO4)2	OH	NH4NO3 (s)
H2ZrF6	AlSO4	P2O7	Al2(SO4)3.16H2O
H3PO4	Cl	PO4	Al2(SO4)3.6H2O
H4P2O7	CO3	SO4	Na2CO3.10H2O
HCl	Cr2O7	ZrCl2	Na2CO3.1H2O
HF	CrO4	ZrCl3	Na2CO3.7H2O
HNO2	Cs	ZrCl	Na3PO4.1H2O
HNO3	CsSO4	ZrF2	Na2Al2O4.2.5H2O
KCl	F	ZrF3	Na7F(PO4)2.19H2O
KHSO4		ZrF5	NaZrF5.1H2O

According to Table 2, a total of 120 species, including 60 ionic, 28 neutral, 12 gas and 20 solid species, were required along with 102 equilibrium reactions to describe the electrolyte chemistry of AZ-101 simulant. The model further checked the likelihood of forming 84 additional solid species beside those shown in Table 2. The selection of solids species must be made judiciously in a large system like this, since the computational load increases significantly with each additional solid species added to a model, which could then lead to non-convergence.

Evaporation Model

The bench-scale evaporator unit consisted of a pot with a natural-circulation calandria (thermosiphon reboiler) and a surface condenser. As shown in Figure 1, the evaporation model was built on just five ESP unit operation blocks: a MIX block representing the evaporator pot, a SEPARATE block used to separate the overhead vapor from the liquid, a SPLIT block to split the recycle off the remaining liquid, a SEPARATE block to condense steam and other condensable vapors in the overhead, and a MIX block to cool and store the bottom product. A forced, re-circulation evaporator was simulated by recycling 90% of the liquid in the pot, and the mode of operation was continuous.

The model simulated a full-scale operation producing 60 metric tons of Envelope B glass per day at 10 wt% Na_2O. The evaporator pot and the primary condenser were operated at 50 and 40 ^oC, respectively, under vacuum. The target endpoint of evaporation was 80% of the solubility limit at 15 ^oC of the first-precipitating major salt, which is yet to be determined. Since the actual LAW evaporator has no design air purges, the non-condensable overhead flow will be the air leakage into the system, which was set at the design value of 135 gmole/hr. It was shown earlier that the air inleakage would have a profound effect on the air emission of volatile organics and heavy metals in systems operating under vacuum.[5]

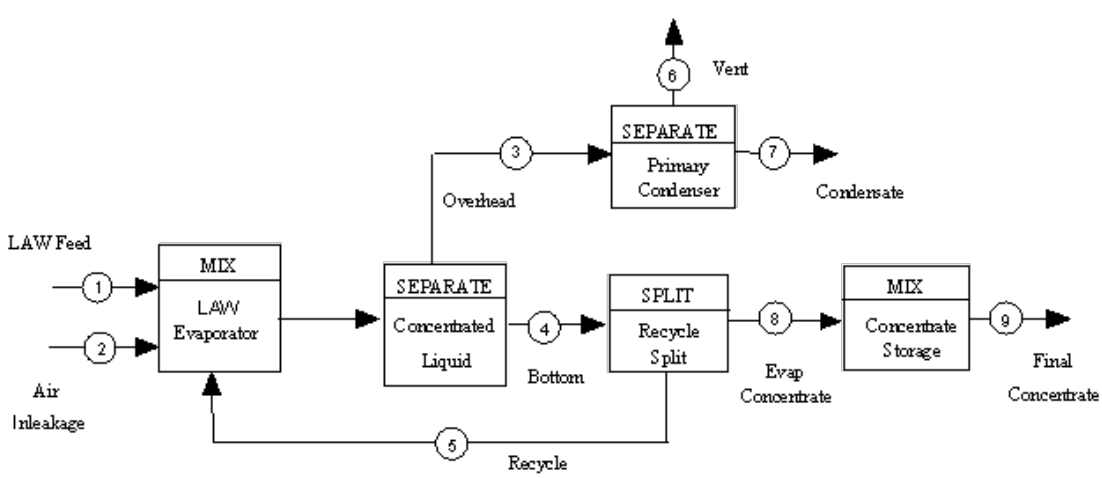

FIGURE 1. Schematic of AZ-101 Evaporator Model.

Solubility Test Results

Unlike the bench-scale runs, the solubility tests did not require any input from the model, and were conducted before any of the model runs were completed. Several flasks containing the AZ-101 simulant were immersed in a constant-temperature shaker-bath, and the detection of the "first" solids was done by visually inspecting the contents of each flask for solids every two hours. Once the "first" solids were detected, the content of each flask was cooled to room temperature and then filtered for the XRD analysis of solids. For more information on the experimental design and procedure, reference should be made to the campaign report.[1]

Ranges of measured solubilities of AZ-101 simulant are reported in Table 3 in terms of total dissolved solids (TDS) per 100 g H_2O. The lower bounds are the values taken just before any solids were detected, and the upper bounds are those taken when the solids were first detected. So, the true solubility limit should lie somewhere within each range. It is shown that the range of measured solubilities increased with increasing temperature, since the monitoring interval was kept constant at every two hours despite sharply higher evaporation rates at higher temperatures. Furthermore, since the amount of "first" solids formed increased with increasing temperature, it can be inferred that the true solubility limit should move farther away from the upper bounds at higher temperatures. This means that at T > ~50 ^oC the AZ-101 simulant has a retrograde solubility behavior, i.e., the solubility decreases with increasing temperature. This conclusion is supported by the XRD results; the major crystal phase identified at all T's was sodium carbonate monohydrate, $Na_2CO_3.H_2O$, which is known to exhibit a retrograde solubility behavior.

TABLE 3. Solubilities of AZ-101 Simulant in g TDS/100 g H_2O and XRD Results.

T (^oC)	measured	model	crystals by XRD
50	88.0 – 89.8	92.5	$Na_2CO_3 \cdot H_2O$, $Na_7F(PO_4)_2 \cdot 19H_2O$
65	84.1 – 87.9	81.2	$Na_2CO_3 \cdot H_2O$
85	78.6 – 88.5	74.3	$Na_2CO_3 \cdot H_2O$

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Initial Model Results

The evaporation model based on the ESP version 6.0 database was run to find out whether the model can predict the measured solubilities during the shaker-bath tests, and the results are shown in Figure 2. The curve connecting those filled circles represents the calculated solubilities when the double salt $Na_7F(PO_4)_2 \cdot 19H_2O$ was predicted to be the first species to precipitate out. On the other hand, the curve connecting those open circles represents the calculated solubilities when the model predicted monohydrated sodium carbonate $Na_2CO_3.H_2O$ to be the first species to precipitate out. It is clearly shown that the latter curve not only predicted the measured data much better than the former but correctly predicted the retrograde solubility behavior exhibited by the shaker-bath data.

Another significant result of the solubility tests was that the double salt $Na_7F(PO_4)_2 \cdot 19H_2O$ was identified as one of the two major solid species formed at 50 ^oC (Table 3). However, the double salt could not have formed by the time the tests were halted at the appearance of the "first" crystals, since the kinetics of the double salt formation is very slow, i.e., on the order of several days. So, it is most likely that the double salt formed long after the tests were completed. Therefore, the true solubility of AZ-101 simulant at 50 ^oC should be determined by the delayed appearance of the double salt, rather than by the instant visual detection made at the time of experiments. In other words , had another sample been taken earlier and analyzed, it would have contained the double salt but not the sodium carbonate monohydrate. This means that the true solubility limit of AZ-101 simulant at 50 ^oC must be less than the measured data in Table 3. The model results appear to support this postulation; the two calculated solubility profiles are shown in Figure 2 to intersect each other at ~55 ^oC, and the curve representing the double salt formation begins to fall below the other curve.

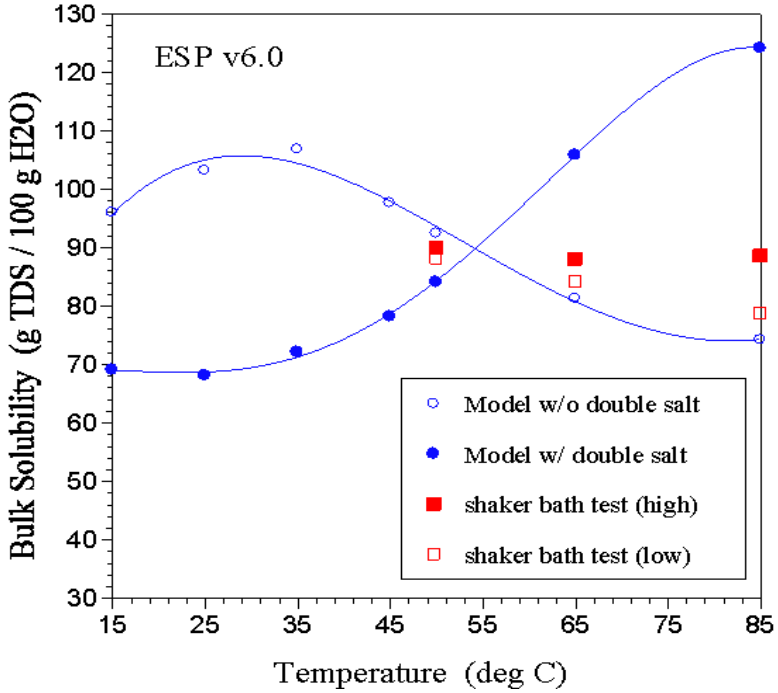

FIGURE 2. Calculated vs. Measured Bulk Solubilities of AZ-101 Simulant.

Final Model Results

During the course of this study, the ESP version 6.2 was received along with its improved PUBLIC database. The model developed earlier with the double salt formation was re-created with the updated version, and the solubilities predicted by the new model are compared in Figure 3 against the earlier model predictions. Also shown are the shaker-bath data discussed earlier and two additional data points from the bench-scale runs just completed. The delayed appearance of the double salt $Na_7F(PO_4)_2.19H_2O$ was accounted for in the bench-scale data taken at 20 ^oC but not at 50 ^oC. Therefore, the bench-scale data at 20 ^oC represented the true solubility limit of AZ-101 simulant, while the data at 50 ^oC represented the apparent solubility limit, just as the shaker-bath data did.

Both new and old models predicted the double salt to be the first salt to precipitate from the AZ-101 simulant at T £ 55 ^oC. However, it is clearly shown in Figure 3 that the new model predicted the measured solubility data much better than the old model. This was mainly because the new PUBLIC database contained revised interaction parameters for the Na^+ and NO_3^- pair, and the equilibrium reactions of any salts containing either ion are influenced by the same change. As shown in Figure 3, the impact would be more intensified, if changes were made to one or more of the major species of the system.

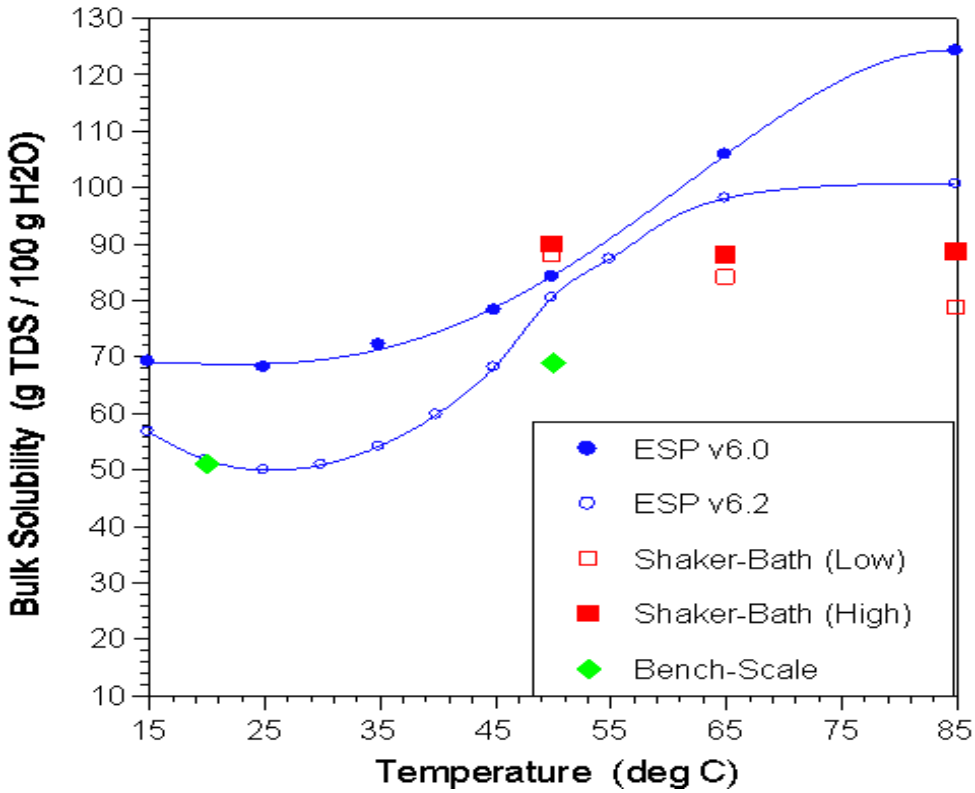

FIGURE 3. Calculated Solubilities of AZ-101 Simulant Using New and Old Models.

In an effort to make the model predictions not only better match the data at T ³ 55 °C but exhibit the retrograde solubility behavior, the regression coefficients used for the equilibrium dissociation constant of $Na_2CO_3.H_2O$ were next fine tuned, and the results are shown in Figure 4. The calculated solubilities are well fitted with the following polynomials:

$$S = -0.0006T^3 + 0.11T^2 - 4.388T + 100.3, \quad 15 \le T \le 55\,^{\circ}C$$
$$= 0.002T^2 - 0.384T + 101.2, \quad 55 \le T \le 85\,^{\circ}C$$

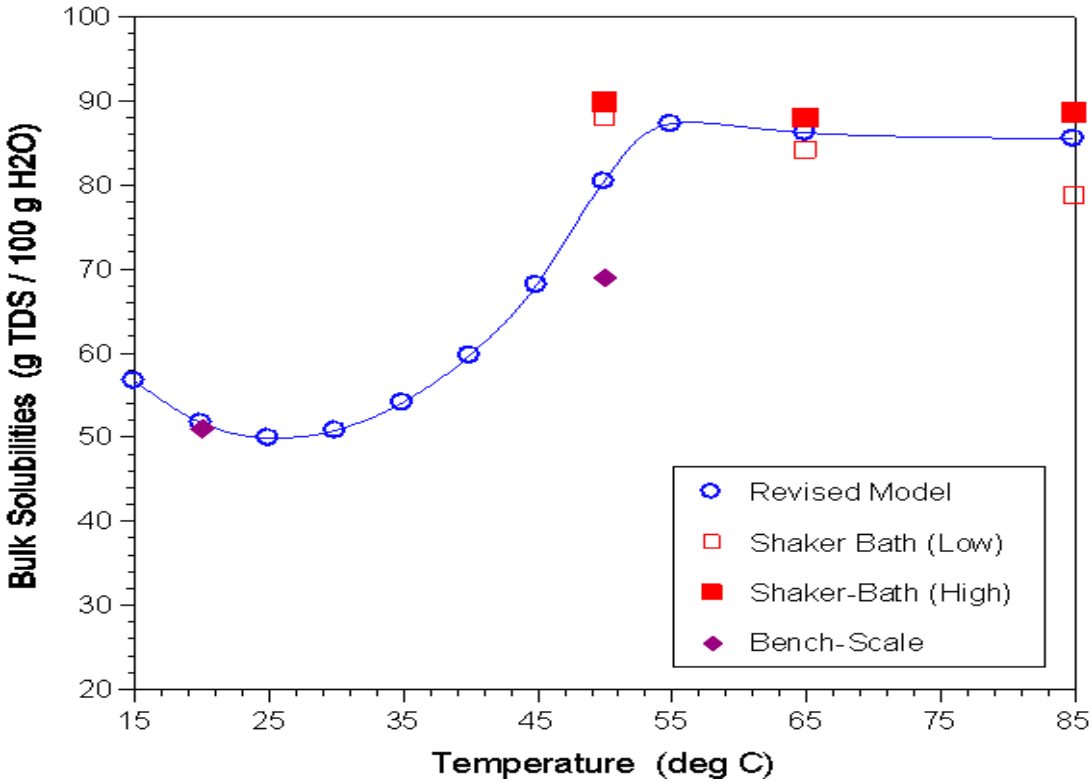

FIGURE 4. Calculated Solubilities of AZ-101 Simulant with Revised Coefficients.

A similar change was made to the gibbsite database, since the model underpredicted the solubility of $Al(OH)_3$ by ~60% compared to the in-house data. The evaporation model was then run with the revised database to determine the operating vacuum required to reach the target endpoint of 80% saturation. However, the model instead determined that the as-prepared AZ-101 simulant feed was already 80% saturated.

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