**A Simplified Gibbsite Solubility Equation for
Modeling the Caustic Leaching of Aluminum-Bearing Sludge**

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ABSTRACT

The Hanford Waste Treatment Plant (WTP) flowsheet includes an optional caustic leach step to remove gibbsite ($Al(OH)_3$) from high-level waste sludge prior to vitrification. Aluminum leaching minimizes the mass that must be vitrified as high-level waste. The steady-state (time averaged) WTP flowsheet uses thermodynamic models that minimize Gibbs free energy to predict aluminum dissolution in the caustic leaching process, but these models are too computationally intensive to be solved in dynamic flowsheets. A gibbsite solubility model that is both accurate and rapidly solved by the computer was needed and developed for a dynamic flowsheet. Available literature data on the solubility of gibbsite in aqueous sodium hydroxide solutions was compiled and the apparent equilibrium constant (Q) was calculated from the experimental data for each data point. The Q value is defined as the true equilibrium constant times the activity coefficients for the aluminate ($Al(OH)_4^-$) and hydroxide (OH^-) ions in the reaction:

$$Al(OH)_4^- \longleftrightarrow Al(OH)_{3(s)} + OH^-$$
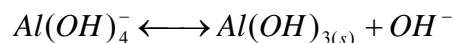
The WTP dynamic flowsheet uses Q to determine the concentration of dissolved aluminate at equilibrium with gibbsite for a given hydroxide concentration. An empirical model to predict Q was developed by multi-linear regression of the experimentally determined Q values from the literature. Four statistically significant model coefficients (all P statistics were less than 10^{-25}) were identified: temperature, solution ionic strength, ionic strength squared, and a regression constant. This model was found to fit a large database of aluminum solubility data with an R^2 of 0.98, which is comparable to the accuracy of more computationally intensive thermodynamic models for this data set.

INTRODUCTION

The solubility of aluminum in nuclear waste may be controlled by the aluminum hydroxide mineral gibbsite (γ-$Al(OH)_3$). The solubility of gibbsite in caustic aqueous solutions has been intensively studied, and review of the experimental data has been compiled by various researchers [1-4]. The solubility of gibbsite in caustic is important to the Hanford Waste Treatment Plant (WTP) because sodium hydroxide can be used within the waste treatment plant to dissolve gibbsite from high-level radioactive waste sludge prior to vitrification [5]. Gibbsite is a major non-radioactive component of the sludge. Removing gibbsite minimizes the mass that must be vitrified as high-level waste.

Sophisticated thermodynamic solubility models have been developed that accurately predicts gibbsite solubility under high pH and high ionic strength conditions such as those found in the WTP [4, 6]. These thermodynamic models usually solve component solubility equations in complex mixtures by numerically minimizing Gibbs free energy [7]. These models, however, are not practical for dynamic process flowsheets because they are too computationally intensive. For instance, within a couple of days of model run time, the WTP dynamic process models are required to simulate many years of plant operation with a 6-minute time interval resolution. The time required to numerically solve Gibbs free energy

minimization routines hundreds of thousands of times over in the process models is prohibitively long, even for modern desktop computers. Nonetheless, a reasonably accurate estimate of gibbsite solubility is needed for the WTP Dynamic Flowsheet so that the impacts of aluminum on tank utilization can be evaluated. The purpose of this paper is to develop a practical aluminum solubility equation for the caustic leaching process in the WTP dynamic flowsheet. Polynomial models are solved much faster numerically than the classic solubility equations, and can be nearly as accurate as the solubility equations for restricted composition ranges. The polynomial models can be thought of as a Taylor Series Expansion solution to the differential equation describing the change in gibbsite solubility with the change in composition. This work was performed for the United States Department of Energy under contract DE-AC27-01RV14136, to support the Hanford Waste Treatment Pant Project.

GIBBSITE EQUILIBRIUM

The reaction of aluminum hydroxide (Gibbsite) with dissolved hydroxide is [1]:

$$Al(OH)_4^- \longleftrightarrow Al(OH)_{3(s)} + OH^- \qquad \text{(Reaction 1)}$$

Besides the aluminate ion [$Al(OH)_4^-$], polymerized forms of soluble aluminum are found at high pH under very high ionic strength conditions [8]. The equilibrium expression for Reaction 1 is:

$$K = \frac{(Al(OH)_4^-)}{(OH^-) * 1} \qquad \text{(Eq. 1)}$$

The variable K is the equilibrium constant. A one appears in the bottom of Equation 1 because the activity of solids is defined as one [9]. The parenthesis denotes the "activity" of the ion that is of interest, where the activity is a function of the concentration:

$$(Al(OH)4\text{-}) = \lambda Al * CAl \qquad \text{(Eq. 2)}$$

In Equation 2, C_{Al} = the aluminate concentration and λ_{Al} = the activity coefficient [9]. The activity coefficient is a calculated value that depends on the concentration of dissolved salts (ionic strength), the charge on the ion, and the size of the ion. The commercially available chemical solubility models estimate the activity coefficients using numerical models that are scaled to experimental data [7]. Equation 1 can be written in terms of concentration of dissolved species instead of activity if the variable K is replaced with Q. The variable Q is K times the activity coefficient for hydroxide divided by the activity coefficient for aluminate. Q is also the measured aluminum to free hydroxide concentration ratio in the liquid phase. Equation 3 is equivalent to Equation 1, but is written in terms of concentrations and Q instead of activities and K.

$$K * \frac{\lambda_{OH}}{\lambda_{Al}} = Q = \frac{C_{Al}}{C_{OH}} \qquad \text{(Eq. 3)}$$

For the WTP dynamic flowsheet, the experimental determined log Q data will be fit directly to the chosen polynomial equation to simplify calculations. Apps et al. [1] found that the activity coefficients are impacted by ionic strength, and these ionic strength effects will manifest themselves in the Q value.

Therefore, Q will be a function of ionic strength. Units of molality (moles/1000 Kg of water) rather than molarity will be used in this paper because molality is independent of solution density.

TEMPERATURE AND IONIC STRENGTH DEPENDENT GIBBSITE SOLUBILITY MODEL

Log Q data compiled by Apps et al. [1] was fit to an equation describing gibbsite solubility as a function of ionic strength and temperature. Apps et al. [1] compiled all of the gibbsite solubility data in the literature for caustic aqueous systems they were able to locate. This data has been screened by both Apps et al. [1] as well as Wesolowski [4]. Only the data recommended by these authors was used to derive the gibbsite solubility relationship. The ionic strength of the feed streams in the WTP is generally between 2 and 8 molal in concentration, so only the data in this range was used to increase model accuracy within the range. The temperature range used was between 25 and 100°C. The model may be extrapolated outside of this temperature and ionic strength range but the accuracy is expected to be greatest within this range. Fig. 1 plots the experimentally determined Log Q values as a function of ionic strength at several selected temperatures. The entire ionic strength range (including ionic strengths outside of the 2 to 8 molal range) is included so that the reader can see that the consequences of extrapolating are small.
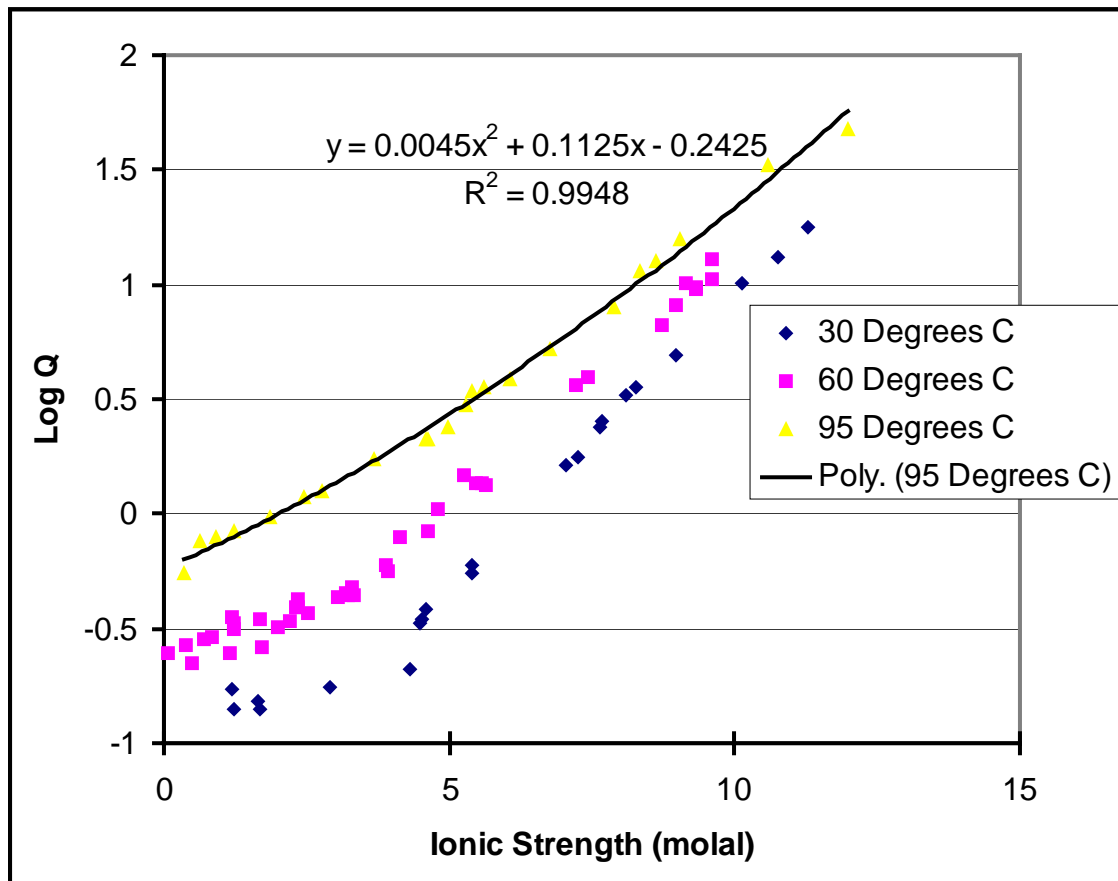

Fig. 1. Log Q as a function of Ionic strength at several illustrative temperatures

From inspecting Fig. 1, it is clear that isothermal Log Q is a polynomial function of ionic strength with a gentle slope. Therefore, the Log Q data was fit to the Temperature (T) in Celsius, the ionic strength (IS), and the IS^2 using multi-linear regression. This equation is shown in Equation 4, below.

$$Log\ Q = a*T + b*IS + c*IS^2 + d \hspace{3cm} \text{(Eq. 4)}$$

In (Eq. 4), "a" is a coefficient for the temperature dependence, "b" is a coefficient for the ionic strength dependence, "c" is a coefficient for the ionic strength squared and "d" is the intercept. The coefficients a, b, c and d are shown in Table I along with the P statistic for each coefficient determined by multi-linear regression. The P statistic indicates if the coefficient is significant or not, and the coefficient increases in statistical significance as P decreases [10]. Commonly, a P statistic of less than 0.01 is considered significant [10]. The highest P statistic in Table I is 2.14×10^{-25}, which achieves the 0.01 criteria by more than 22 orders of magnitude. Therefore, all of the coefficients are statistically significant. The R^2 value for the regression is 0.98 (Table II), which is remarkably accurate considering that the temperature range investigated was large and that the data is a compilation from many different investigators using many different experimental techniques. To put this in perspective, Wesolowski [4] fit this same data set with a much more sophisticated model and obtained a R^2 value of only 0.98.

Table I. Coefficients for Equation 4

Coefficients	Value (log Q units)	P Statistic	Lower 95 % Confidence Interval	Upper 95 % Confidence Interval
a	0.0119	1.31E-106	0.0114	0.0124
b	0.1001	1.90E-31	0.0863	0.1139
c	0.0084	2.14E-25	0.0070	0.0097
d	-1.4050	7.79E-137	-1.4424	-1.3676

Table II. Regression Statistics for Equation 4

Regression Statistics	Value
R^2	0.9819
R^2 Adj	0.9816
Standard Error	0.0802
Observations	184.0000
Degrees of Freedom	3.0000
Ionic Strength Range (molal)	2 to 8
Temperature Range (˚C)	25 to 100

The equilibrium constant embedded in Q (Equation 3) is known to be a function of the change of Gibbs energy from the reaction [9]. The T dependence of Gibbs energy is a function of the heat capacity of both gibbsite and the solution phase. Heat capacity is frequently modeled as a function of T with a polynomial equation [9]. When a T^2 term was included in Equation 4, however, the R^2 did not improve and the P value for the T^2 coefficient was 0.89. Therefore, the T^2 term was dropped from Equation 4 because it was not statistically significant.

Fig. 2 shows the predicted versus measured Log Q results, and indicates that the model works well to reproduce the data. Fig. 3 plots the "measured minus predicted" values (frequently called the "residuals" by statisticians) against ionic strength, and indicates that the equation predicts the ionic strength dependence equally well over the entire ionic strength range. Fig. 3 also indicates that the predicted value is usually within 0.1 Log units of the measured value; an accomplishment equal to Wesolowski [4] despite the fact that he used a much more rigorous model.
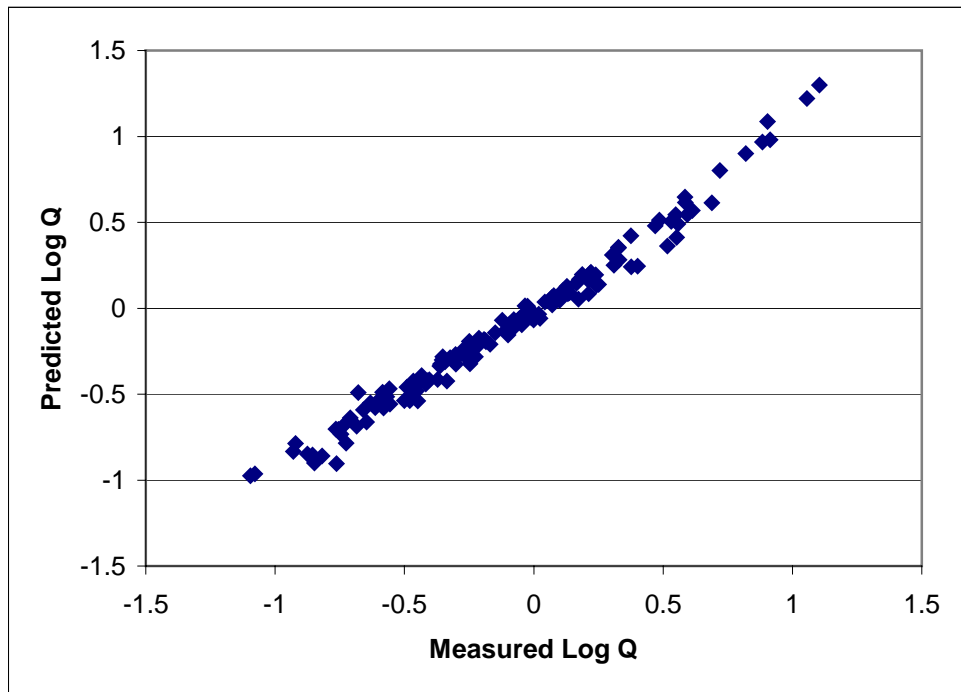
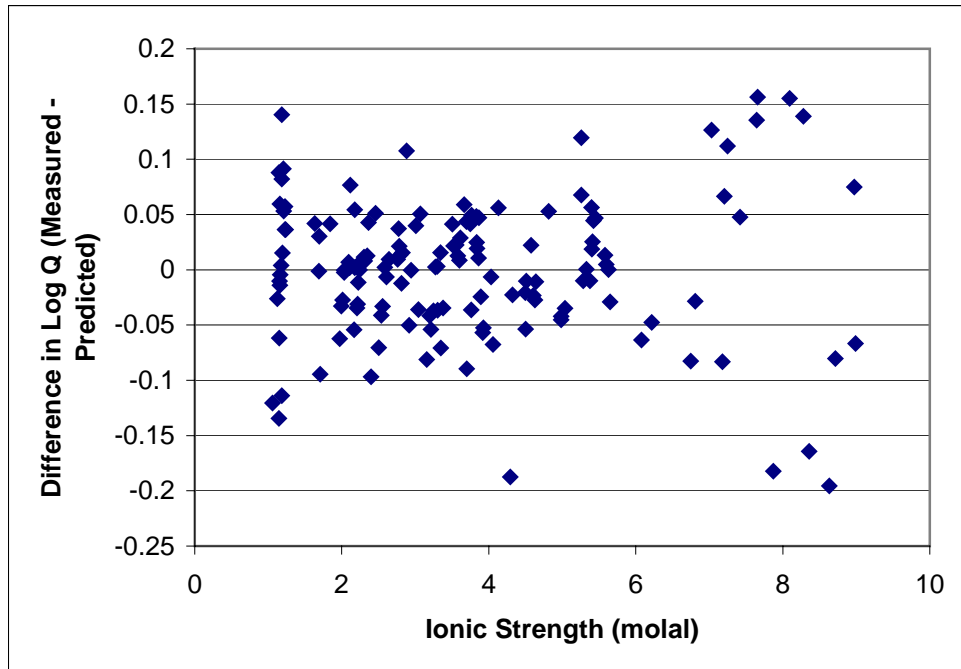Fig. 2. Measured versus predicted (using Eq. 4) log Q values

Fig. 3. Difference between measured and predicted log Q values as a function of Ionic strength

MASS BALANCE EQUATIONS

The Q value provides the ratio of aluminum to hydroxide at equilibrium but it does not provide the number of moles of aluminate, hydroxide, and aluminum hydroxide that must react to achieve equilibrium. The number of moles reacting (per kilogram of water in the supernatant) to achieve equilibrium will be given the variable name "A". The variable A can be either positive or negative depending on the direction that is needed to achieve equilibrium.

If the beginning concentration is not at equilibrium, then A moles of aluminum must react to achieve equilibrium, so A moles of aluminum must be subtracted from the beginning aluminum concentration ($C_{Al,beg}$) to achieve the equilibrium concentration described in Equation 3 ($C_{Al}=C_{Al,beg}-A$). Likewise, A moles of hydroxide must be added to the beginning hydroxide concentration ($C_{OH,beg}$) to achieve the equilibrium hydroxide concentration ($C_{OH}=C_{OH,beg}+A$). These mass balance relationships result in Equation 5 below when they are plugged into Equation 3.

$$\frac{C_{Al,beg} - A}{C_{OH,beg} + A} = Q \qquad \text{(Eq. 5)}$$

Solving Equation 5 for A results in Equation 6.

$$\frac{C_{Al,beg} - Q * C_{OH,beg}}{Q + 1} = A \qquad \text{(Eq. 6)}$$

When A is a positive number, A moles of aluminate precipitate to form A moles of gibbsite and A moles of dissolved free hydroxide. When A is a negative number, A moles free hydroxide are consumed by dissolving A moles of gibbsite to create A moles of aluminate. The system is at equilibrium when A = zero, or if one of the reactants goes to zero.

CONCLUSIONS

A model of gibbsite solubility in sodium hydroxide was developed (Equation 4). Model development determined that the solubility of gibbsite in sodium hydroxide was a function of the ionic strength, as expected from current theory of the activity coefficients of electrolytes in water. The solubility was also found to increase with increasing temperature.

ACKNOWLEDGMENTS

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