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Studies on the Gibbsite to Boehmite Transition

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Abstract: The transition of gibbsite to boehmite is of interest with regard to high level waste processing associated with the Hanford and Savannah River sites. Both materials have been observed in core samples. From the temperature histories of the waste, it is possible that some fraction of gibbsite has been converted to boehmite. This paper describes thermal gravimetric analysis studies of products resulting from controlled temperature measurements of pure gibbsite in NaOH. Results indicate that the gibbsite to boehmite transformation can take place at temperatures as low as 100°C. This information, along with available data on waste inventories and temperature histories, may be used to estimate the fractions of gibbsite and of boehmite in a given waste tank. Site engineers can then tailor the sludge leaching process for a particular tank to account for the delayed dissolution of boehmite, allowing separation of the aluminum and processing as a low activity waste.

Keywords: Boehmite, gibbsite

INTRODUCTION

Currently, there are approximately 400 million liters of high level nuclear waste (HLW) stored in underground carbon steel tanks at the Hanford and Savannah River Sites (1). A large percentage of the waste consists of non-radioactive insoluble sludge components such as metal oxides or hydrated metal oxides and high ionic strength, high pH salt solutions (2). SRS/Hanford site engineers have developed and continue to improve processes for permanent disposal of these sludges, blended with the radionuclides, into borosilicate glass waste forms produced by vitrification.

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Aluminum is of significance to the vitrification process. For the Hanford wastes, aluminum is the largest inventoried element, excepting sodium (3). A high concentration of aluminum in a melter feed stream results in higher viscosities during the glass forming process, thereby slowing production. Additionally, the ability to remove aluminum from the waste destined for vitrification has ramifications on the number of canisters that must ultimately be produced. In practice, if the aluminum can be separated from the less-soluble constituents of the feed, the separated stream containing aluminum can be processed as a low activity waste (cementacious waste forms such as grout or saltstone or as bulk vitrification); thereby allowing the more expensive high level waste vitrification process to focus on the insoluble and associated radionuclides. For these reasons, site engineers and scientists have focused on the pretreatment of sludge.

One such pretreatment process includes a caustic leaching step. The major aluminum phase within the sludge waste was thought to be gibbsite (α-Al(OH)$_3$) which is moderately soluble in caustic. Recent studies have suggested that another aluminum phase, boehmite (γ-Al(O)OH), which is much more insoluble, may be the more predominant species in the tanks as a result of variations in tank waste storage conditions over time. Numerous dissolution studies have been performed on both gibbsite and boehmite (4–6) in caustic solutions at selected temperatures. Results indicate a much slower dissolution rate, almost 600–700 times less for boehmite, as compared to gibbsite. Thus, proper identification of the aluminum phases present within the sludge will provide information that can be used to tailor the caustic leach process, resulting in increased efficiency in waste processing.

It is well established that the direct heating of 1 mole of gibbsite [Al(OH)$_3$] will liberate 1 mole of water and 1 mole of boehmite [AlOOH]. From thermal gravimetric analysis experiments, this transition occurs at temperatures between 200 and 400°C (7,8). Workers at the Savannah River National Laboratory believed that the transition could occur at lower temperatures at slower rates (9). Thus, Gong et al. studied the conversion of gibbsite to boehmite at 150°C using X-ray diffraction (XRD) (9). Complete conversion of gibbsite to boehmite was observed in as little as 3.5 hours. The present work extends the efforts of Gong et al. to lower temperatures. The determination of kinetic parameters (rate constant, activation energy) would allow site engineers to estimate the fractions of gibbsite and boehmite present within the various waste tanks when historical records on tank waste temperatures and waste composition estimates were available. Fortunately, waste temperatures have been compiled by Flanagan (10). Considerable efforts have been directed at waste characterization and inventory estimation (from historical records of process transfers) of the compositions within the single and double shell tanks. Chemical as well as physical data are available through the

Best Basis Inventory (11). This includes the total mass loadings of aluminum in all 177 tanks. This information, along with the results of the present work, may then be used to determine the mass fractions of gibbsite and boehmite. In turn, leaching conditions can be tailored for waste retrieval from specific tanks.

EXPERIMENTAL

Materials and Instrumentation

Crystalline gibbsite (product number C-333) was kindly provided by Almatis. The $Al(OH)_3$ was reported as 99.6% pure with average particle size on the order of 1–10 microns (12). Aqueous hydroxide solutions of 1.5 and 3 m concentrations were prepared using ACS reagent grade sodium hydroxide (Fisher Scientific) with degassed, deionized water (Barnstead Nanopure Infinity, 18 $m\Omega/cm^2$). All mass determinations were obtained using a Mettler Toledo analytical balance (Model AB304-S; ±0.1 mg).

Solutions of 0.128 m gibbsite and 1.5, 3, or 5 m NaOH were placed in either Nalgene Teflon PFA ($T > 135°C$), LDPE ($T \leq 135°C$) vials, or in Parr stainless steel, general purpose pressure vessels with TFE gaskets (22 mL). The latter containers have typically been used for the product consistency test (PCT). The plastic bottles allowed for total evaporation of the water from the aqueous phase and resulted in completely dried solids. The solids resulting from the "dry" conversion required pulverization in order to be properly washed, sampled and analyzed. Use of the PCT vials resulted in increased pressures, but no evaporation of water. For those solutions examined in the PCT vials under these "wet" conditions, the caustic was first placed in the vessel and brought to temperature prior to the addition of the gibbsite. Solutions were placed in either a Precision Thelco Laboratory Oven (±1.0°C) or Thermolyne model 48000 Furnace (stability of ±0.2°C at a maximum temperature of 1000°C with a uniformity of ±3.6°C). The gibbsite to boehmite reaction was investigated at temperatures of 80°C, 100°C, 120°C, 135°C, and 150°C. Following the completion of the desired reaction time at temperature in the oven, the sample was cooled to room temperature, filtered (Fisherbrand® Glass Fiber circles, 55 mm × 0.28 mm thick, particle retention size of 1.2 microns) and washed with copious amounts of deionized water. The solids were then dried at ambient temperature.

During the high temperature, high pressure experiments, some corrosion of the interior of the stainless steel vessel occurred. The trace impurities ($\leq 0.02\%$ by weight) were analyzed using a Perkin Elmer Optima 4300 DV inductively coupled plasma optical emission spectrometer. The impurities were identified as Fe, Cr, Si, Mo, and Ni, all components of stainless steel and also nominally present in tank wastes. The results given below (c. f. sequence) do not indicate that corrosion products from the steel vials had any significant effect on the rate of the gibbsite reaction.

Thermal gravimetric analysis was conducted on solid samples using a Perkin Elmer Pyris Diamond TG/DTA 6300. X-ray diffraction (XRD) provided confirmatory information on selected samples and was conducted by the Evans Analytical Group, Round Rock, TX. For all experiments, TGA was used as the primary means of determining the gibbsite and boehmite weight percent of samples. Previous studies (8,9) using TGA/DTA methods have reported thermal analysis patterns for both crystalline and coarse grained gibbsite (α-Al(OH)$_3$) and boehmite (γ-Al(O)OH). These studies suggest many variables, such as heating rate, water vapor pressure, and/or particle size, may influence the results.

The TGA temperature program consisted of heating the sample to 150°C at 10°C per minute and holding it at 150°C for 30 minutes. Any interstitial water remaining after filtration and drying evaporated at the hold temperature of 150°C. Next, the sample was heated to 600°C at 10°C per minute. A sample TGA output scan of pure gibbsite subjected to this temperature program is shown in Fig. 1. As evident in the scan, gibbsite undergoes two transition steps when heated sufficiently. The first transition step is dehydration of gibbsite to form boehmite, then a second dehydration from boehmite to form alumina (Al_2O_3). Upon further analysis of, it was concluded that there was no one identifiable maximum temperature at which complete conversion of boehmite could be achieved without the transition of some of the boehmite to alumina occurring.

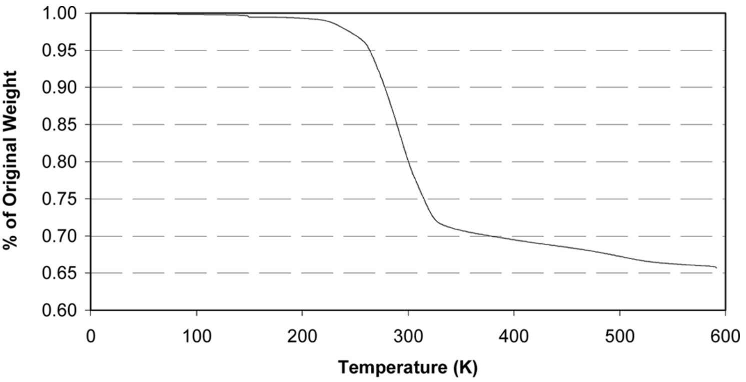

Figure 1. Weight loss as a function of temperature for the Almatis gibbsite.

Thus, the approach taken in these studies was to utilize a TGA program that heats the sample to 600°C to ensure complete conversion to alumina.

During TGA analysis, the assumption was made that the starting solid sample consists of only gibbsite and/or boehmite. Thus, the removal of residual caustic from the sample was important so that any weight loss occurring at temperatures above 200°C could be attributed to the dehydration of gibbsite to boehmite. A sample composed of 100% gibbsite will yield a maximum weight loss of 23.1% when completely converted to boehmite. A sample of pure boehmite would result in a maximum weight loss of 15% when undergoing the transition to alumina. Taken together, and accounting for the stoichiometry of the reactions:

$$2Al(OH)_3 \rightarrow 2AlOOH + 2H_2O \tag{1a}$$

$$2AlOOH \rightarrow Al_2O_3 + H_2O \tag{1b}$$

The total weight loss from 2 moles of gibbsite being completely converted to alumina through reactions (1a) and (1b) totals 3 moles of water, roughly 34.64% of the initial weight. The trace shown in Fig. 1 for the Almatis gibbsite yield a loss of 34.6% of the initial weight; which corresponds to 99.88% of the theoretical value.

The weight loss data, obtained using TGA, can be used to estimate the weight fraction of gibbsite and of boehmite in the original sample. Equation (2) is used to calculate the mass fraction of boehmite in a sample from weight loss data, where w_i denotes the initial sample mass, w_f denotes the final sample mass, and MW_i is the molecular weight of species i.

$$x_{boehmite} = \frac{w_i - \left[\frac{(w_f - w_i)MW_{gibb}}{MW_{H_2O}}\right]}{w_i} \tag{2}$$

First, it is known that the original sample is composed of only gibbsite and/or boehmite. Second, the final product contains only alumina. Using these two assumptions, the mass fraction of Al(OH)$_3$ ($x_{Al(OH)3}$) in a sample analyzed by TGA may be calculated by equation (3). Again, w_i and w_f are the initial and final weights of the sample, respectively.

$$x_{Al(OH)_3} = \frac{\left[\frac{w_i - w_f}{w_i} - \frac{1}{2}\frac{MW_{H_2O}}{MW_{boeh}}\right]}{\left[\frac{3}{2}\frac{MW_{H_2O}}{MW_{gibb}} - \frac{1}{2}\frac{MW_{H_2O}}{MW_{boeh}}\right]} \tag{3}$$

Differential thermal analysis (DTA) output was collected for most samples during TGA analysis. DTA displays peaks at temperatures when

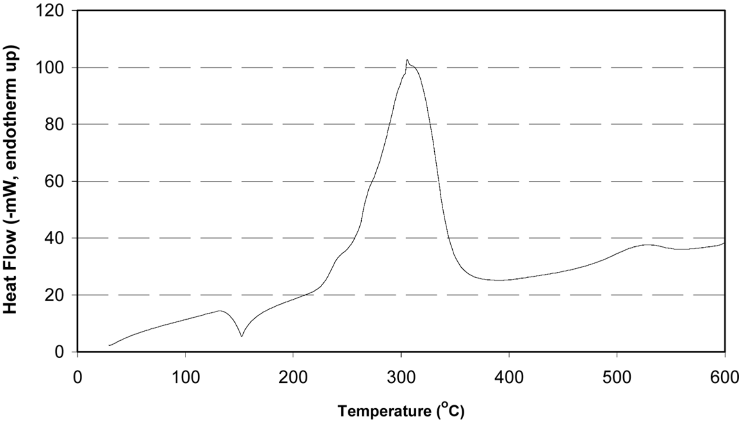

Figure 2. DTA plot of the Almatis gibbsite.

reactions are initiated. All samples contained gibbsite and/or boehmite so that at least two DTA peaks appeared for all samples at very similar temperatures. These data were useful for comparison with previously cited literature results to confirm that the expected transitions were taking place during TGA/DTA analysis (13,14). The DTA data plot obtained for pure gibbsite is shown in Fig. 2. XRD of the starting materials was performed and results established the Almatis product to be pure crystalline gibbsite as shown in Fig. 3 (15).

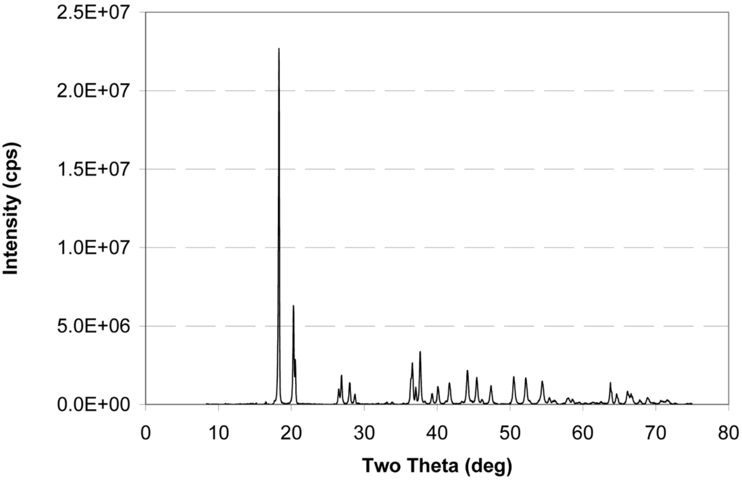

Figure 3. XRD trace for the Almatis C-333 crystalline gibbsite.

The accuracy of the balance within the TGA was determined through the use of known mass standards. A 5 mg standard was found to weigh 4.95 mg and a mass of 19.7 mg was found for a 20 mg standard. These results translate into 1 and 1.4% errors. The larger value was used to estimate the potential errors in the calculation of the activation energy. Obtained masses from the 100 and 150°C sample tests were subjected to uncertainty by the addition or subtraction of 1.4% of the measured mass. In one case, the addition was performed on the starting weight, and in the second instance, the addition was performed on the final weight with mass taken away from the starting sample. These data were then converted into rate constants and plotted against 1/T. Corresponding slopes were indicative of the activation energy.

Aside from errors in mass determination, a possibility does exist that sodium aluminate, $NaAlO_2$, may form during the reaction. Simulations using the Environmental Simulation Program (ESP, OLI Systems Inc.) predicted increased formation of sodium aluminate when higher caustic loadings were employed. Sodium aluminate is a recalcitrant impurity; in this case, because it will remain unchanged and undergo no reactions while undergoing TGA analysis. ESP estimates the solubility of sodium aluminate at 70 g per 100 g of water at 25°C. Such a high solubility leads one to believe that sodium aluminate would be sufficiently removed during washing of the solids prior to analysis by TGA/DTA, a step that was performed for all solid samples. The lack of appreciable amounts of sodium aluminate detected by XRD confirms that this impurity was not present in the prepared samples and thus, did not need to be considered during the composition calculations for these experiments. Any sodium aluminate formed must have, indeed, been effectively washed from solid samples during sample preparation.

Initial experiments were performed in order to duplicate results obtained by Gong et al. (9) and validate the experimental procedure and analysis methods employed in the present effort. Subsequent experiments were performed at lower temperatures and at higher caustic loadings. The validation of the TGA method allowed for an accurate determination of the weight fraction of gibbsite present at various times. Knowledge of the change in mass with time permits the determination of a reaction rate. These data were subsequently fit to the Arrhenius expression, allowing determination of the activation energy.

RESULTS

The weight fraction of gibbsite obtained from the TGA measurements and calculated according to equation (3) is plotted in Fig. 4 as a function

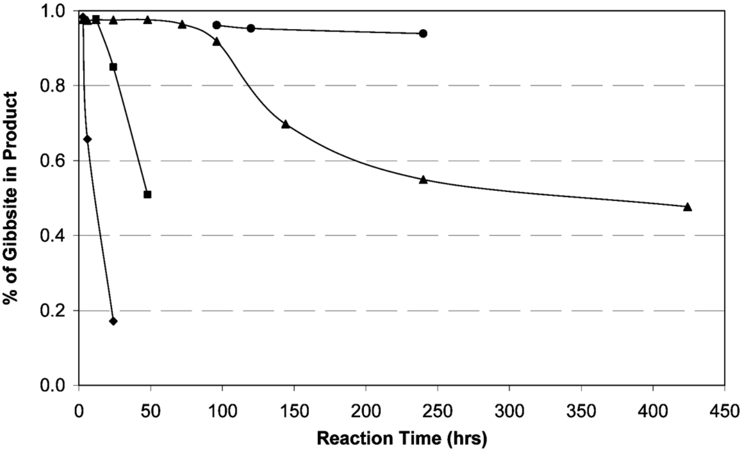

Figure 4. Plot of weight percent of gibbsite as a function of time for the "dry" experiments conducted in 1.5 m NaOH. Symbols are as follows: diamonds 150°C; squares, 35°C; triangles, 120°C; and circles, 100°C.

of reaction time for the 100, 120, 135, and 150°C "dry" experiments. The transition from gibbsite to boehmite occurred rapidly at both 135 and 150°C. A lag, or induction period, was observed for the run at 120°C, which corresponds to the evaporation of the aqueous phase. No similar lag, attributed to evaporation, was observed at 100°C. At this temperature, the reaction rate was considerably less than at the elevated temperatures. Data employed for the determination of rates and the activation energy omitted the regions in the transitions where evaporation was occurring and where little change in mass was observed (at longer reaction times). The rate of the reaction was calculated from the linear portions of the curves. For 150°C, the rate of change from gibbsite to boehmite was $\sim 4.4 \times 10^{-3}$ mol hr^{-1}. Values of 1.82×10^{-3} and 3.1×10^{-4} mol hr^{-1} were obtained for the 135 and 120°C temperatures, respectively. At 100°C, the rate of change was significantly slower, and was determined as 1.87×10^{-5} mol hr^{-1}.

Validation of the TGA method was accomplished through XRD analysis of selected samples. Figure 6 is a trace corresponding to the solids obtained after 240 hours at 120°C. The product ratio was approximately 50% gibbsite and 50% boehmite (16). The characteristic trace of boehmite, shown in Fig. 7, indicates the peak around a 2θ value of 15°. The 50% value is in good agreement with the experimental result of 55%.

Different concentrations of NaOH in the solutions did not give rise to significantly different weight loss as a function of time, as shown in Fig. 5. The induction period was extended for the sample in 3 m NaOH

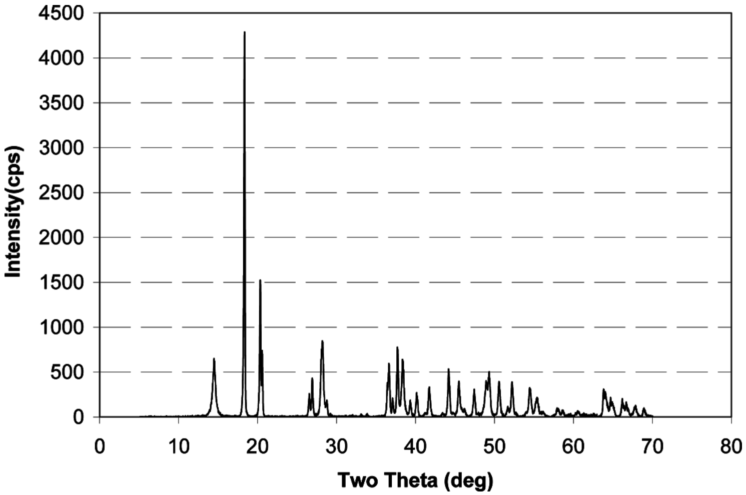

Figure 5. Weight fractions of gibbsite measured as a function of time in 1.5 and 3 m NaOH. Solid symbols are for samples originally made in 1.5 m NaOH; hollow symbols are for samples originally prepared in 3 m NaOH. Diamonds correspond to 150°C; squares to 135°C.

at 135°C, indicating delayed evaporation (boiling point elevation). The rate constants for the solutions starting with 3 m NaOH were found to be 3.77×10^{-3} and 1.55×10^{-3} mol hr^{-1} at 150 and at 135°C, respectively.

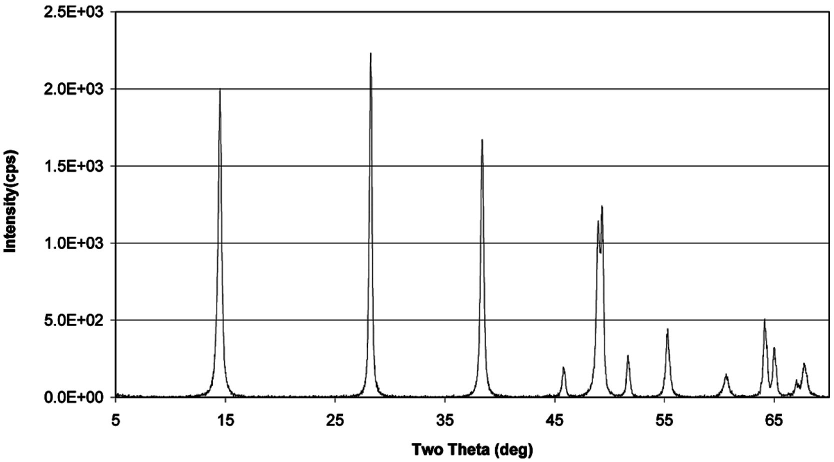

Figure 6. XRD trace of the solids recovered from an experiment at 120°C after 240 hours.

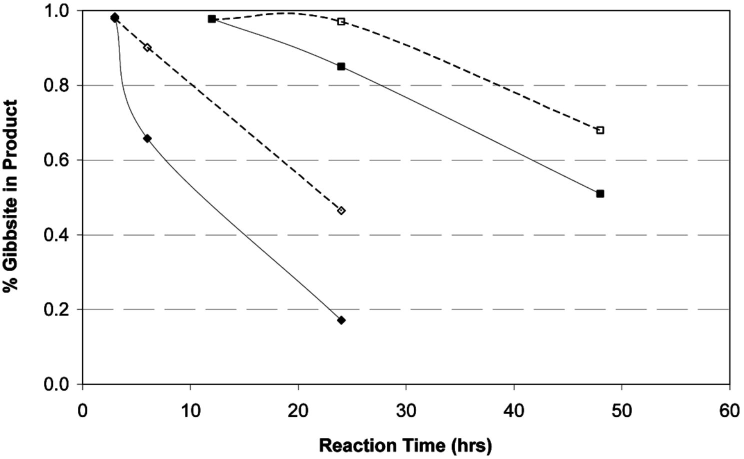

Figure 7. XRD trace of boehmite obtained after complete reaction.

Whereas these values are somewhat smaller than those obtained from the 1.5 m NaOH runs, the limited data precludes the direct establishment of specific solvent effects.

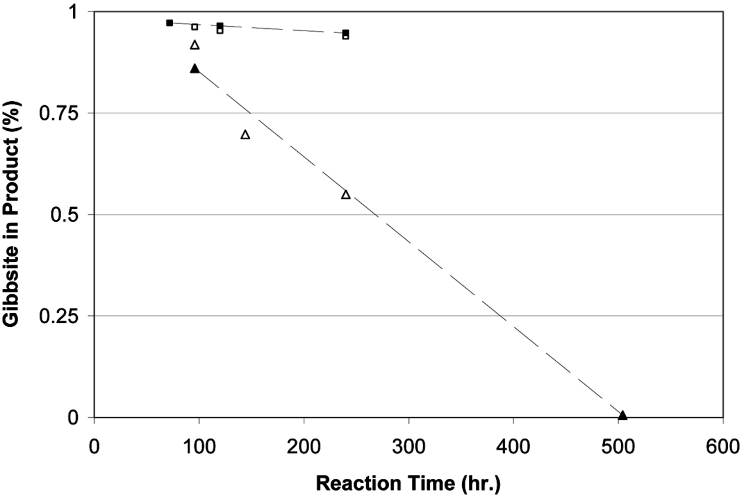

Figure 8. Conversion of gibbsite to boehmite under both "dry" and "wet" conditions. The square symbols are from the 100°C measurements and the triangles are from the 120°C experiments. Solid symbols correspond to "wet" conditions. Hollow symbols are from the "dry" experiments. Lines are linear fits to the data meant to guide the eye.

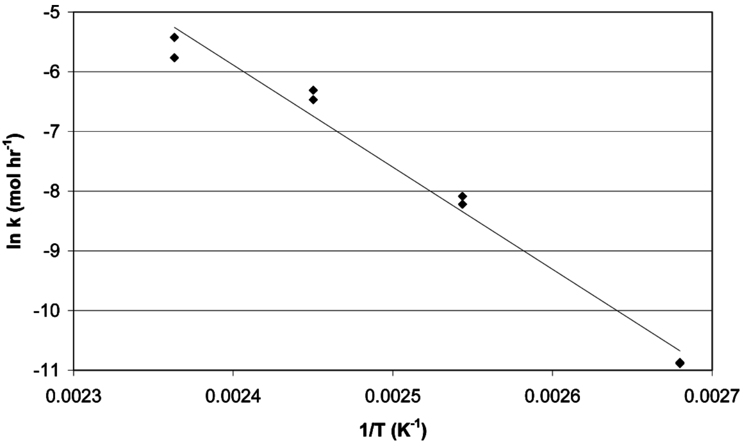

Figure 9. Arrhenius plot of the rate constant for all of the experiments.

A comparison of the conversion of gibbsite to boehmite under both "dry" and "wet" conditions is presented in Fig. 6. Little change in the rate of reaction was observed at 120°C. Under the higher pressure "wet" conditions, the reaction rate was determined as 2.7×10^{-4} mol hr^{-1}. This value is slightly reduced from that obtained under the conditions where complete evaporation occurred (3.1×10^{-4} mol hr^{-1}). The rate obtained under "wet" conditions in 1.5 m NaOH at 100°C was calculated as 1.9×10^{-5} mol hr^{-1}. The corresponding result for the "dry" conditions was 1.87×10^{-5} mol hr^{-1}. Little to no evaporation took place at 100°C. These results support the assumption that the corrosion products from the steel vials did not affect the reaction and, in addition, these results also confirm the experimental procedure.

A number of attempts were made to determine the conversion rates at even lower temperatures of 50 and 80°C. No significant weight loss was noted during incubation times of up to 504 hours.

The natural logarithm for the rate constants obtained under the "dry" and the "wet" conditions are plotted against 1/T in Fig. 7. The data can be approximated as $\ln k = 35.17 - 17108/T$, yielding an activation energy of $142+/-2.2$.kJ mol^{-1}.

CONCLUSIONS

Evaluation of the gibbsite to boehmite transition indicates that conversion can take place at temperatures as low as 100°C. Measurements in 1 and 3 m caustic resulted in similar rate constants. No differences were observed in performing the experiments in sealed or unsealed containers, corresponding to "wet" and "dry" conditions, indicating that vapor pressure of water did not significantly impact the results. Additional experiments using more complex simulants are planned. The rate constants and the activation energy reported here can be used, along with available information on tank temperature histories and inventories, to determine the mass fractions of the predominant forms of aluminum in the waste. From an assessment of that information, site engineers will be able to tailor sludge leaching conditions to account for the widely varying dissolution kinetics of gibbsite and boehmite.

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