

Kinetics of Aluminum Formation in the Caustic Side Solvent Extraction (CSSX) Process - 11046

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ABSTRACT

The Caustic Side Solvent Extraction Process (CSSX) process is used for cesium separation at the Savannah River Site (SRS). The CSSX process is comprised of 4 steps: 1) extracting cesium into the solvent; 2) scrubbed of the loaded solvent to remove co-extracted sodium and potassium; 3) stripping to transfer the cesium out of the solvent; and 4) washing of the stripped solvent to remove solvent degradation products if present. During the scrubbing process, aluminum precipitation has been observed. This is a concern as solids formation may have undesirable consequences during operation. The work reported was undertaken to identify conditions under which solids formation may occur and to identify an operating region where solids formation is avoided or minimized.

Room temperature experiments on the CSSX scrubbing process were conducted using simulants based on various dissolution fractions of SRS Tank 25F contents. Simulants representing dissolution fractions of 10, 40 and 50 % by weight were prepared in the laboratory. A small fraction of this stream may be transferred into the 0.05 M nitric acid scrub solution. Thus, experiments were performed as a function of the % carryover of the dissolved stream in the nitric acid scrub solution. Carryover percentages of 0.5 % to 10 % by volume were examined, where x mL of the Tank 25F simulant stream were combined with (100-x) mL of the nitric acid stream. The aluminum concentration and solution pH were measured for the resulting solutions. Simulation of the experiments was also carried out using the Environmental Simulation Program (ESP) and comparisons made.

For a select subset of carryover percentages, solids formation was identified. This subset of carryover percentages was different for each of the transfer streams, ranging from 2 to 5 % for the dissolution fraction of 10%, and from 4 to 6% for the dissolutions fractions of 40 and 50 %. The common feature for these ranges was that the resulting mixed stream (dissolution fraction plus nitric acid) possessed a pH in the range of 4 to 10. ESP calculations predicted the formation of dawsonite in this range of pH.

For these mixtures, a second set of solutions were prepared in the laboratory. The aluminum concentration in each sample was monitored as a function of time, until solids formation was visually observed. For the majority of these solutions, solids formation occurred within two weeks, and equilibrium was established by the stabilization of aluminum concentration over time. After solids had formed, the solutions were filtered. Recovered solids were dried and

examined using an Olympus Polarized Light Microscope (PLM) and in select cases, using x-ray diffraction (XRD). The resulting temporal aluminum concentration data were fit to a first order reversible rate expression, and forward and backward reaction rate constants determined. Forward rate constants were in the range of 0.007 to 0.32 hr⁻¹, while reverse rate constants were in the range of 0.001 to 0.009 hr⁻¹.

INTRODUCTION AND BACKGROUND

The Caustic Side Solvent Extraction (CSSX) process is comprised of a number of sequenced steps that recover cesium ion from a waste stream to reduce the waste stream's activity. The first step is the extraction of cesium from the waste stream into an organic solvent. The organic solvent is composed of an extractive agent, BOBCalixC6, a modifier, Cs-7SB (an alkyl aryl polyether), whose purpose is to keep the BOBCalixC6 in solution, a suppressant, trioctyl amine, whose purpose is to minimize the effects of anionic organic impurities and to improve cesium recovery in later processing steps and a diluent, IsoparL, which is a mixture of branched hydrocarbons [1]. In the CSSX process [2], cesium is extracted from the waste stream into the organic solvent. The cesium-loaded organic solvent is then scrubbed with a dilute nitric acid (0.05 M) stream to recover co-extracted sodium and potassium. The scrubbed solvent is then contacted with a 0.001 M nitric acid stream that results in the transfer of the cesium into the dilute nitric acid stream. This stream is then sent to the DWPF for vitrification. The stripped solvent is washed with a dilute sodium hydroxide (0.01 M) stream so that it can be recycled in the process.

During the scrubbing operation, there is the potential for carryover of the waste stream into the nitric acid scrub solution, which may result in solids reprecipitation. Solids formation on the rotor walls in the centrifugal contactor has been reported; this location is where the waste stream enters the extraction section [3]. Solids reprecipitation is undesirable as it could lead to erosion in the centrifugal contactors or plugging of piping during transfer. Thus, it is desirable to investigate the conditions that may give rise to solids reprecipitation and the kinetics of the reprecipitation process.

Cesteros et al. [4] reported on the influence of temperature, concentration and pH on the formation of gibbsite and indicated that the precipitation of gibbsite was 'very slow'. Benzeth et al. [5] examined the precipitation kinetics of gibbsite at 50 °C and reported that the precipitation followed first order kinetics, with specific reactions rates ranging from 0.0079 to 0.016 min⁻¹.

For a reversible equilibrium reaction, temporal data on the concentration may be used to determine both forward and reverse specific reaction rate constants, as well as the equilibrium constant for the precipitation process. A typical reversible equilibrium reaction will result in a measurable species concentration at equilibrium, C_{Ae} . With an initial concentration of C_{A0} , the temporal data may be used in the integral method of analysis to determine the kinetic parameters. In the integral method of analysis, a reaction order is proposed, and the corresponding rate law is integrated to yield an equation; this equation is written in linear form, with identification of dependent and independent variables. If the proposed reaction order is correct, then the experimental data, when plotted as dependent and independent variables, will exhibit a linear trend.

EXPERIMENTAL METHODS AND MATERIALS

Materials: All chemicals used were ACS grade or better with assays of > 97% purity. Chemicals were purchased from Fisher Scientific Sigma, Aldrich, Almatris and Advanced Research Chemicals, Inc., and were used without further purification. Standards required for ion chromatography (IC) were purchased from Inorganic Ventures, Inc., and were traceable to NIST. Standards for inductively coupled plasma (ICP) analysis were purchased from Environmental Express. Standards for total inorganic carbon (TIC) and total organic carbon (TOC) analysis were purchased from Fisher Scientific. Deionized water with a resistance of 17.9 to 18.3 M Ω -cm from a Barnstead Nanopure Infinity Still was used in the preparation of all solutions.

Experimental Methods: Two series of experiments were performed. Full details of the experiments are provided in Naik [6]. The first series examined the mixing of a simulant with different amounts of 0.05 M nitric acid; these experiments were designed to identify those combinations that would give rise to precipitation of solids. The second series of experiments examined the kinetics of the solid precipitation in those combinations identified during the first series of experiments.

Simulants were prepared to represent the streams obtained when the contents of Tank 25F were dissolved with different amounts of diluent (10, 40 and 50% by weight). Thus, each stream represented the expected stream composition corresponding to a given point in the retrieval process. Table I summarizes the simulant recipes for these three streams. Each stream was normalized to a total mass of 1000 g and batches in this amount were prepared to provide sufficient material for each set of experiments. Stream 1 is the simulant recipe for a 10 % diluent addition by weight (i.e., 10 g diluent added to 100 g Tank 25F contents) and Stream 4 and Stream 5 are the recipes for 40 % and 50 % diluent addition by weight, respectively.

A given simulant was prepared in the following manner. Appropriate amounts of the required compounds were weighed using a Mettler-Toledo analytical balance with an accuracy of \pm 0.0001 g. Deionized water was weighed and measured into a 1250 ml Nalgene bottle. These polyethylene bottles were used instead of glass beakers to prevent leaching of silicon from the glass into the highly alkaline simulant solution. The required amount of sodium hydroxide was weighed and mixed with 200 g deionized water in a separate beaker, then stirred using a magnetic stirrer until the sodium hydroxide was completely dissolved. After this solution was cooled, sodium nitrate was added and the solution stirred until it was completely dissolved. The remaining compounds, $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, NaNO_2 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$, Na_2SiO_3 , NaF, NaCl and KOH were then added in order, either as a solid or dissolved in a small aliquot of water, and the resulting solution stirred until no solids were visible in the solution. For sodium fluoride (NaF), trisodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$), sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), and sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), the required amount of solid was dissolved in water, and the resulting solution added to the simulant mixture.

Each simulant prepared in this fashion was allowed to equilibrate at room temperature for a period of at least two weeks. A small aliquot of the solution was removed from the simulant sample daily for aluminum and sodium determination by ICP analysis. Once the measured aluminum and sodium concentrations remained relatively constant in samples taken on several

consecutive days, it was assumed that the solution had attained equilibrium. Any solids formed during equilibration were filtered under vacuum. The prepared simulants were then stored in sealed containers until use.

Table I. Simulant Recipe for Tank 25 F Retrieval Streams.

Chemical	Stream 1 Simulant (g)	Stream 4 Simulant (g)	Stream 5 Simulant (g)
Water	590.2794	559.5575	563.9793
Aluminum Hydroxide	18.61409	5.601252	5.541557
Sodium Nitrate	286.5172	350.3725	344.0567
Sodium Nitrite	14.80765	14.86085	15.95906
Sodium Carbonate Monohydrate	30.65944	19.37239	15.88407
Sodium Sulfate	7.845048	21.40353	23.62659
Sodium Fluoride	0.257897	0.147593	0.137729
Sodium Chloride		0.062642	0.061933
Sodium Hydroxide	49.30423	27.92818	29.58702
Potassium Hydroxide		0.120305	0.338786
Sodium Oxalate	0.233476	0.5103	0.461156
Sodium Phosphate Dodecahydrate	0.003227	0.011254	0.012865
Sodium Metasilicate Nonahydrate		0.051886	0.310163
Ferric Nitrate Nonahydrate	1.478305		
Cesium Chloride			0.043084

Mixing Experiments: The objective of the mixing experiments was to determine those combinations of simulant and 0.5 M nitric acid that result in the formation of precipitated solids. In these experiments, a known volume (V_1 mL) of simulant solution was combined with $(100 - V_1)$ mL of 0.05 M HNO_3 . Solutions representing % carryover (by volume) from 2% to 10% were prepared and allowed to equilibrate. For example, a solution of 2 % carryover would contain 2 mL of simulant solution and 98 mL of 0.05 M HNO_3 . The pH of each solution was measured using a VWR Model 8025 pH meter. A small aliquot (1 mL) of liquid solution was removed daily and aluminum concentration determined by ICP. Once the aluminum concentration had remained relatively constant for several (three to four) days, the solution was then filtered and any solids formed recovered. The isolated solid was dried at 50 °C. Once dry, the solid was ground and washed for analysis. Solids were analyzed by XRD and PLM.

Kinetics of Solids Precipitation Experiments: For each of the mixtures prepared for the mixing experiments that resulted in the formation of solids, a second set of experiments were conducted. Samples were prepared in the same fashion as for the Mixing Experiments. A small aliquot of solution was removed each day and aluminum concentration determined by ICP. Sampling was performed daily until solids were visually observed in the remaining solution.

MODELING APPROACH

Initial Efforts: Simulation of the mixing experiments was performed using the Environmental Simulation Program (ESP, V8.0, OLI Systems, Inc.). All simulations were performed using two specialized databases, V7DBLSLT and CORROSION, along with the PUBLIC database. Care was taken to ensure that the modeling approach matched the experimental procedure. Initial modeling efforts were undertaken in the following manner. The simulant recipe was used as input to a MIX block. An isothermal equilibration of the simulant recipe yielded an effluent stream with two phases in equilibrium - a liquid phase plus solid precipitate (primarily gibbsite). This effluent stream was then passed into a SEPARATE block, where the liquid and solid phases were separated. The resulting liquid phase was then SPLIT, with the major fraction discarded and the remainder (minor fraction) was sent to a MIX chamber where it was isothermally mixed with a stream of 0.05 M nitric acid. The block specifications for the split were set to examine % carryover by volume from 0 to 10 %, in increments of 0.5%. A 10 % carryover by volume meant that 10 mL of liquid phase were mixed with 90 mL of 0.05 M nitric acid.

Refined Efforts: Based on preliminary modeling results, the modeling approach was refined based on comparison of the experimental results. While there was good agreement between some of the tracked process variables, discrepancies were noted for the aluminum concentration. Experimental values were much greater than those predicted by ESP. In examining the experimental procedure and comparing it with the modeling approach, it was noted that, although ESP predicted solids formation during the initial simulant preparation, no solid precipitation was ever observed during preparation. As such, the initial simulant contained the entire complement of aluminum present in the original recipe. In the initial modeling effort, the use of the separator block to partition the predicted solids and liquid into two separate streams resulted in the majority of aluminum being removed as solid precipitate. The aluminum that remained in the liquid stream was only a very small percentage of the aluminum in the simulant recipe. ESP predicted that gibbsite $[\text{Al}(\text{OH})_3]$ formed for the majority of solutions. The precipitation kinetics of gibbsite are known to be slow [5] and thus, since the prepared simulant was not allowed to equilibrate for a sufficiently long time, the aluminum predicted to be in solid form as gibbsite by ESP was actually still present in the solution as $\text{Al}(\text{OH})_4^-$. Thus, the modeling approach was refined in the following manner. The simulant recipe was used as input to a MIX block, where isothermal equilibration was performed. The resulting mixed stream was then passed to a SPLIT block, where the required volume of stream was separated from the remainder of the stream. The larger remainder of the stream was discarded. The smaller portion, the required volume of simulant stream for a designated % carryover, was then sent to a second MIX block, where it was combined with the appropriate volume of 0.05 M nitric acid. The process flow diagram is shown in Figure 1.

RESULTS AND DISCUSSION

Mixing Studies: For each of the simulants prepared, aluminum concentration and solution pH in the equilibrated solutions were measured and compared with model predictions from ESP. Shown in Figure 2 is a comparison of predicted and experimental results for the Stream 1 Simulant. The ESP results are based on minimization of the Gibbs energy (i.e., establishment of thermodynamic equilibrium). With the addition of 0.05 M nitric acid, the pH of the solution was

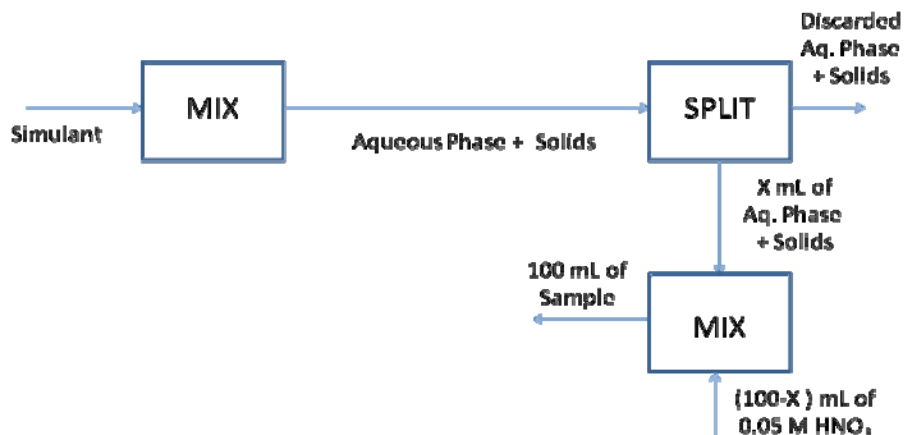


Fig. 1. Refined Modeling Approach for Mixing Experiments

observed to rise quickly, with a pH of 12 achieved at approximately 3 % carryover by volume. The predictions for pH by the model are in agreement with the experimental data.

In the region where the pH rapidly increases, solids formation is predicted by ESP, with the appearance of gibbsite $[Al(OH)_3]$ at a % carryover of 1.5. At a % carryover of 2.5 %, ESP predicted the formation of dawsonite $[NaAlCO_3(OH)_2]$ as well as gibbsite. The experimentally measured aluminum concentrations were very low in samples for this same region from 1 to 3% carryover. In the ESP results for carryover percentages greater than 3 %, the equilibrium solid predicted was gibbsite. No solids formation was observed in experimental solutions for % carryover less than 2 % or greater than 4 % by volume over the time interval of the experiment; this was not unexpected, as the kinetics of gibbsite precipitation are known to be slow. For stream 1, a small amount of solids were observed to form experimentally in the samples for 2 to 4 % carryover by volume. Examination of these solids using PLM indicated crystal structure similar to that of dawsonite.

The experimental concentrations at % carryovers greater than 4 % by volume were significantly larger than those predicted by ESP. These larger concentrations are also explained by the slow kinetics associated with gibbsite precipitation from solution.

In initial modeling efforts, the predicted ESP concentrations were at least an order of magnitude smaller than those using the refining modeling approach. It was this discrepancy between prediction and experiment that resulted in refinement of the modeling approach. The experimental concentrations were much greater, greater than could be accounted for by aluminum in the X mL of solids-free brine mixed with the (100-X) mL of 0.05 M nitric acid. In addition to examination of the modeling approach, all steps in the analytical procedures used for aluminum concentration determination were critically examined and analysis was repeated for a number of the samples to confirm the reported measurement.

Shown in Figure 3 is the comparison between experimental measurements and model predictions for Stream 4. This stream is less concentrated compared to Stream 1, and as a result, the shift

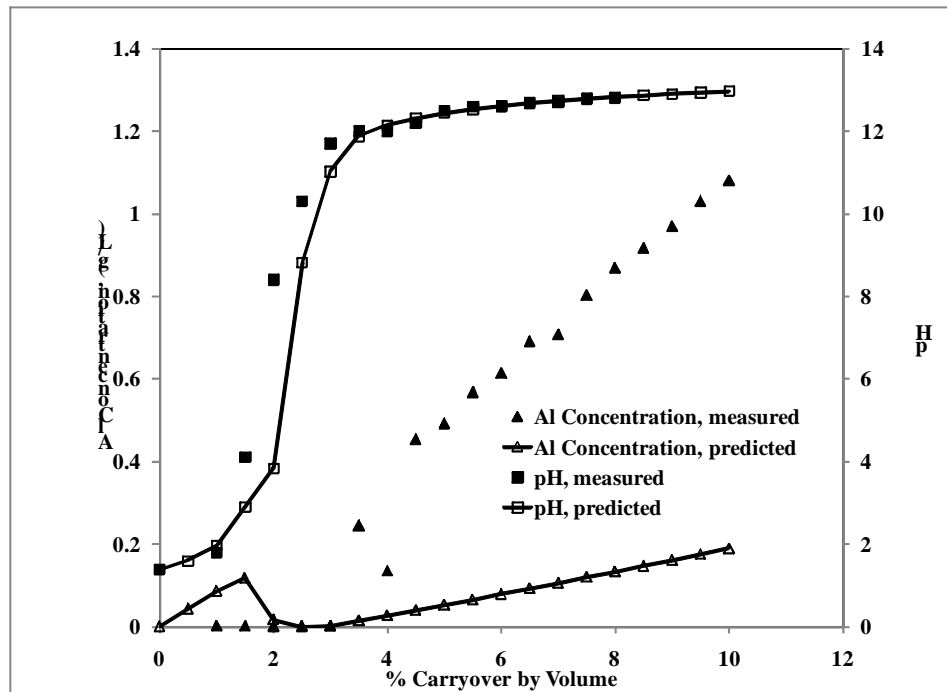


Fig. 2. Comparison of Experimental Results with ESP Predictions for Stream 1.

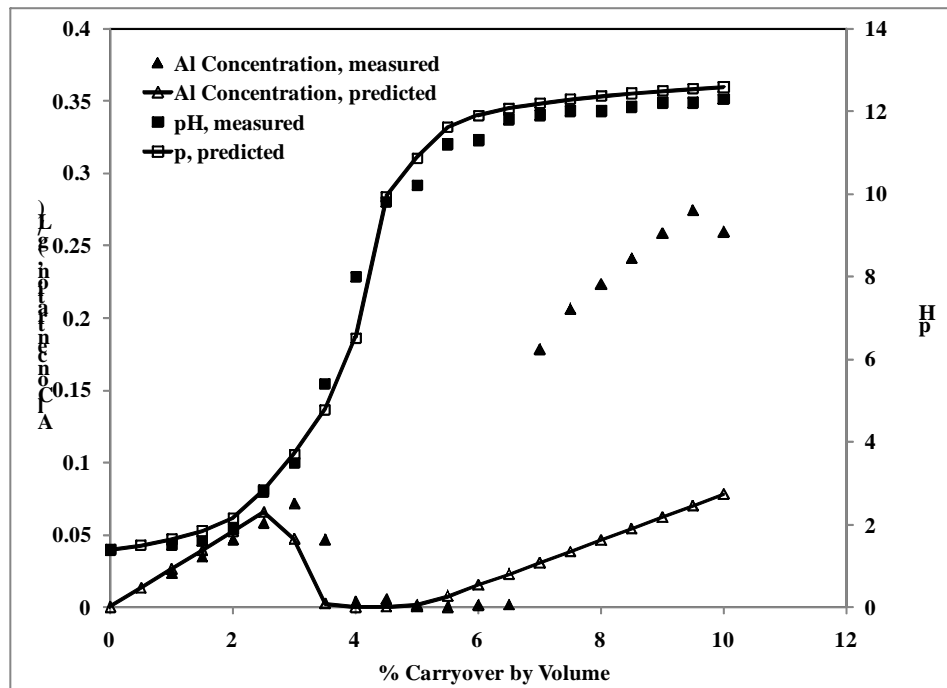


Fig. 3. Comparison of Experimental Result with ESP Predictions for Stream 4.

(significant increase) in solution pH upon addition of 0.05 M nitric acid is shifted to higher % carryover compared to Stream 1. The experimental solution pH rose from 3.5 at 3 % carryover by volume to 11.3 at 6 % carryover by volume. Again, the experimental solution pH values are in excellent agreement with the ESP predictions.

Also shown in Figure 3 is the comparison between experimental and predicted aluminum concentrations. At low % carryover (< 3 % carryover by volume), no solids are predicted to form by ESP, and the experimental and predicted aluminum concentrations in the liquid phase are in agreement. As the pH begins to rise, both experimental and predicted aluminum concentrations were observed to decrease significantly. In the range of 4 to 6.5 % carryover by volume, experimental aluminum concentrations were on the order of 0.004 g/L. Predicted concentrations in this range were an order of magnitude smaller. Over the 4-6 % carryover by volume range, solids begin to be predicted by ESP; initially only gibbsite is predicted to form, but at 4.0 and 4.5 % carryover, dawsonite is also predicted to form. For carryover % by volume greater than or equal to 5 %, the only solid predicted is again gibbsite. In the prepared samples, no solids formation was observed for solutions with % carryover greater than 6.5 %. In the range of 4 to 6 %, a small amount of solids was observed to form as the solutions equilibrated.

Again, the predicted ESP aluminum concentrations are significantly lower than those observed experimentally, and this is attributed to the kinetics of gibbsite precipitation. The concentrations, however, do exhibit the same general trend.

Shown in Figure 4 is the comparison for Stream 5. The experimental and predicted pH was very similar to that exhibited by Stream 4. The pH rise occurred between 3 % and 6 % carryover by volume. However, one significant difference observed for Stream 5 was with respect to prediction of solids formation. Only at 4 % carryover by volume was dawsonite predicted to form (the noticeable dip in the predicted Al concentration curve). Very small amounts, on the order of 0.01 to 0.05 g of gibbsite (out of a total solution mass of approximately 100 g) were predicted to form in the other solutions. The improved agreement between predicted and experimental concentrations reflects the small amount of aluminum contained in the predicted solids. These results lend greater credibility to the hypothesis that the differences between experimental and predicted aluminum concentrations for Streams 1 and 4 is due to the slow kinetics of gibbsite precipitation.

Kinetic Studies: For those samples in which solids were observed to form during mixing studies, a second set of samples was prepared. X mL of simulant were combined with (100 - X) mL of 0.05 M nitric acid. Shown in Table II are the samples for which kinetic studies were undertaken.

A representative set of the obtained temporal concentration data is shown in Figure 5. These data were obtained for Stream 5 with 6 % carryover by volume. The last four data points were used to estimate the equilibrium aluminum concentration. Shown in Figure 6 are the integral method results, assuming a first order reversible reaction. The data are well represented by this

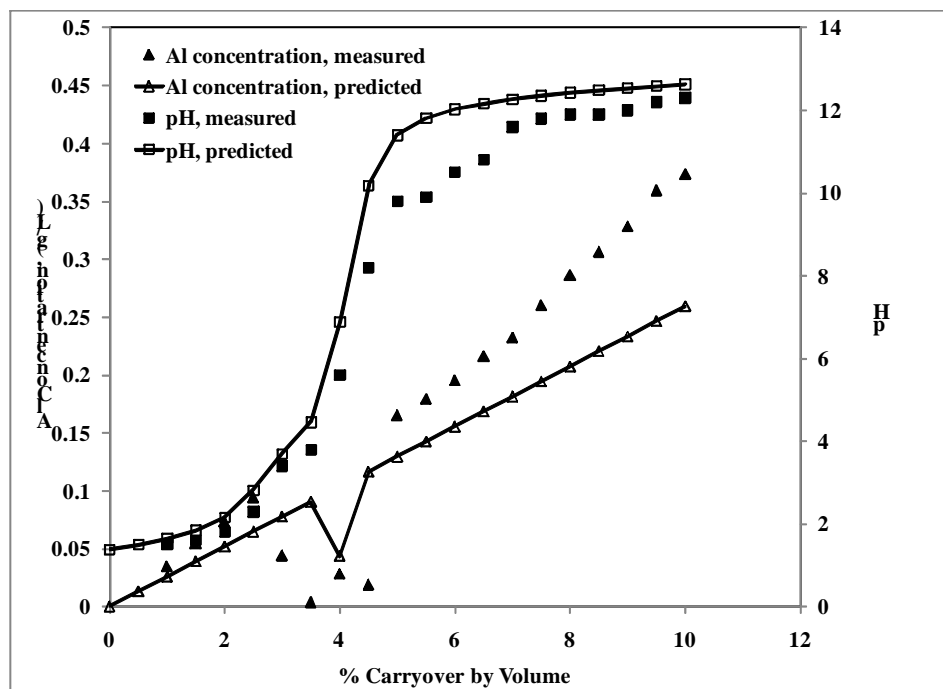


Fig. 4. Comparison of Predicted and Experimental Results for Stream 5.

Table II. Experimental Matrix for Kinetic Studies

Tank	Transfer Stream	Simulant (ml)	0.05M HNO ₃ (ml)	Carryover (Volume)
25F	1	2.0	98.0	2.0
		3.0	97.0	3.0
		4.0	96.0	4.0
25F	4	4.0	96.0	4.0
		5.0	95.0	5.0
		5.5	94.5	5.5
		6.0	94.0	6.0
25F	5	4.0	96.0	4.0
		5.0	95.0	5.0
		5.5	94.5	5.5
		6.0	94.0	6.0

first order model. Both forward and reverse specific reaction rates were obtained through the regression analysis. All of the samples listed in Table II were prepared, aluminum concentration measured as a function of time, and the resulting data fit to a first order reversible kinetic rate law. Shown in Table III are the obtained forward and reverse specific reaction rate constants. The obtained forward specific reaction rates ranged from 0.007 to 0.032 hr⁻¹, while the reverse specific reaction rates were an order of magnitude smaller, ranging from 0.0015 to 0.0095 hr⁻¹.

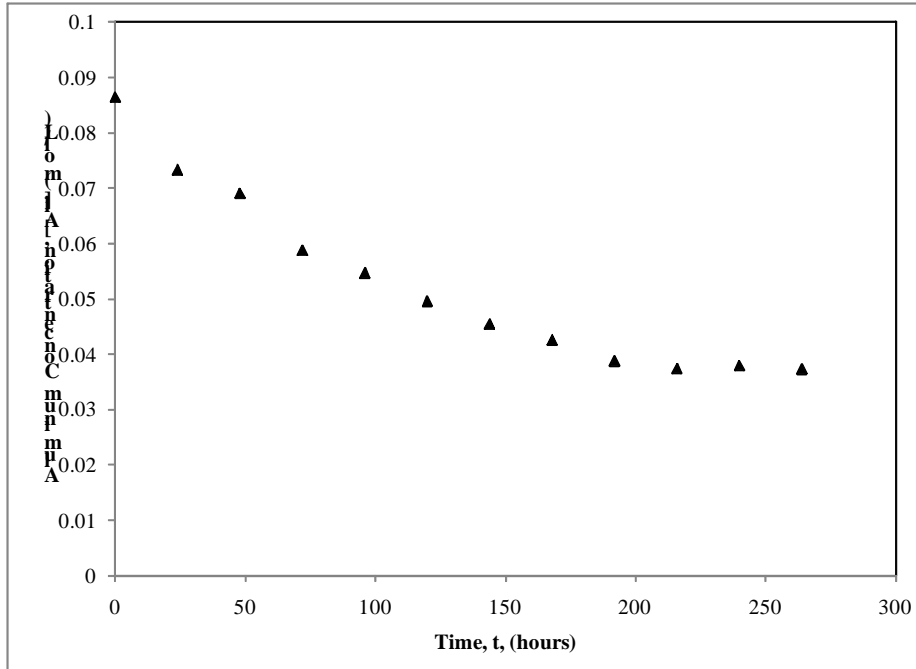


Fig. 5. Temporal Aluminum Concentration Data for Stream 5, 6 % Carryover by Volume.

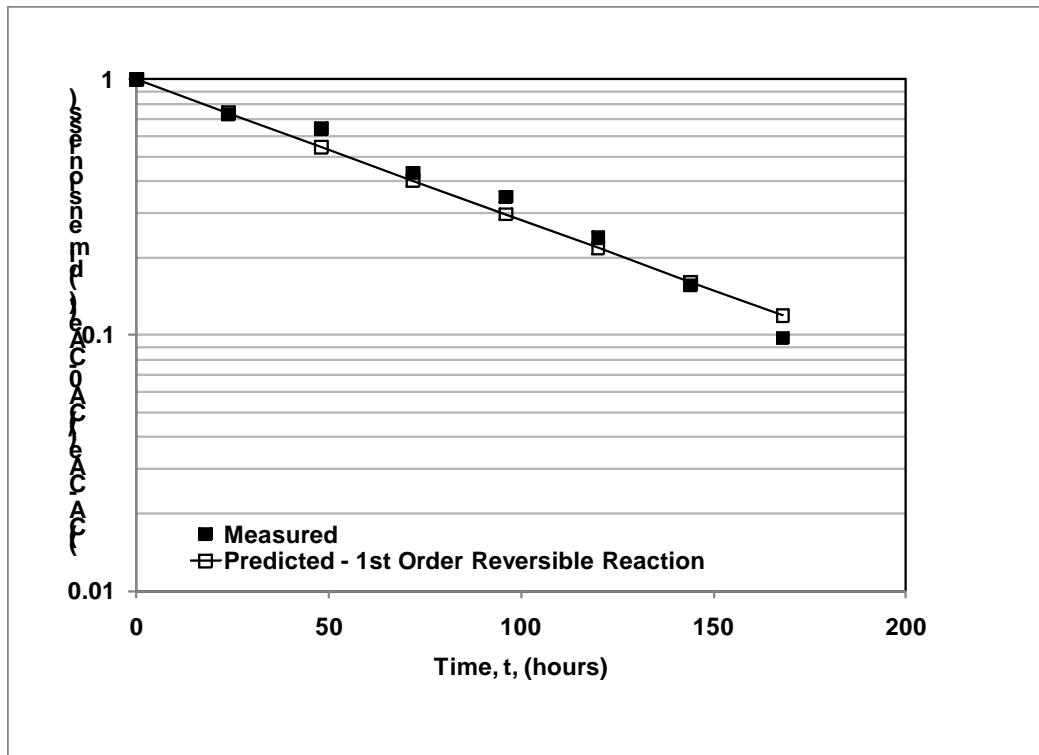


Fig. 6. Integral Method - First Order Reversible Rate Law - Stream 5, 6% Carryover by Volume

Table III. Specific Reaction Rates for Gibbsite Precipitation

Stream	% Carryover By Volume	Forward Specific Reaction Rate k_f (Hour ⁻¹)	Reverse Specific Reaction Rate k_r (Hour ⁻¹)	[Al] _e (mol/L)	R ²
Stream 1	2	0.0265	0.0024	0.0254	0.9874
	3	0.0194	0.0047	0.0612	0.9302
	4	0.0114	0.0064	0.1120	0.9827
Stream 4	4	0.0316	0.0015	0.0041	0.9959
	5	0.0167	0.0035	0.0154	0.9853
	5.5	0.0180	0.0023	0.0100	0.9859
	6	0.0208	0.0022	0.0086	0.9953
Stream 5	4	0.0162	0.0042	0.0179	0.9917
	5	0.0144	0.0068	0.0278	0.9054
	5.5	0.0165	0.0095	0.0320	0.9840
	6	0.0071	0.0055	0.0379	0.9762

CONCLUSIONS

Mixing experiments examining the potential for solid formation during the CSSX scrubbing process were performed, with a companion modeling effort. Predictions for Streams 1 and 4 were in good agreement with experimental results, while there was some deviation noted in the comparison between predictions and measurements for Stream 5. Kinetic studies, undertaken on solutions that gave rise to visually observed solids during the mixing experiments, provided data that were used to determine specific reaction rate constants, for the forward and reverse reactions. A first order reversible rate law was used, and all data sets were well represented by this model, as evidenced by the correlation coefficients > 0.90.

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