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Bench-Scale Testing of the Continuous Sludge Leaching Process

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Boehmite has proved to be a difficult aluminum phase to dissolve out of high-level waste (HLW), requiring longer residence times and higher temperatures than the gibbsite phase for more complete dissolution. To provide a simple, compact, effective, and proven method to remove aluminum from HLW sludges, HLW feed can be blended with caustic in a reaction vessel while continuously removing permeate from the reactor. This approach allows for a concurrent addition of fresh caustic and HLW feed while simultaneously removing concentrated reacted slurry. Separation in this manner will keep solids in the reactor for longer periods of time, allowing for higher conversions than could be achieved in a normal batch reactor. The advantages for this continuous sludge leaching process are the reduction of the number of high level waste canisters by one-third to one-half at the Hanford Tank Waste Treatment and Immobilization Plant, resulting in billions of dollars in life-cycle cost savings. Bench-scale continuous reactor tests confirmed that the boehmite removal can be achieved to meet these canister reduction goals.

Keywords boehmite; filtration; high level waste; leaching

INTRODUCTION

After processing waste at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to remove aluminum using the current WTP Pretreatment Facility baseline process, the vitrification of approximately one half of the waste will still be limited by aluminum. The baseline WTP flowsheet is currently designed to target the effective removal of aluminum in the gibbsite form—however, roughly 45% of the water insoluble aluminum in the Hanford Tank farms is in the more intractable boehmite form. Dissolving and separating aluminum in the form of boehmite is essential, both at SRS and the Hanford WTP, in reducing the quantity of high-level waste (HLW) set for disposal.

In SRS and Hanford wastes, aluminum is found as gibbsite ($Al(OH)_3$) and sodium aluminate ($NaAlO_2$) (1). Both of these phases are easily dissolved by heat treating with caustic (2). However, a significant quantity of boehmite (Al(OOH)) is also present, which is more resistant to caustic dissolution and requires higher treatment temperatures, contact times, and hydroxide concentrations. Boehmite is responsible for as much as 50% of all the aluminum in the wastes, with as much as 2,000 metric tons (MT) in the Hanford tanks alone. While gibbsite is the common aluminum precipitate in the waste tanks, it appears that significant quantities of boehmite formed due to storage conditions (3).

The caustic leaching reactions for gibbsite and boehmite are shown below.

$$Al(OH)_3(s) + OH^-(aq) \leftrightarrow Al(OH)_4^-(aq) \qquad (1)$$

$$Al(OOH)(s) + OH^-(aq) + H_2O \leftrightarrow Al(OH)_4^-(aq) \qquad (2)$$

Martino and Fondeur (4) identified a conversion mechanism where the conversion from gibbsite to boehmite is thermodynamically favorable. Gong et al. (5) showed that gibbsite could be converted from gibbsite to boehmite in as little as 4 hours at 150°C. Figure 1 shows that boehmite is the favored aluminum phase at temperatures above about 80°C (6). In several waste tanks at SRS and Hanford, fission product activity was sufficient for decay heat to cause boiling. Scanning electron microscopy (SEM) analyses of these tanks indicate boehmite as the dominant aluminum phase (7).

Scotford and Glastonbury (8,9) measured the dissolution of relatively large (20 to 40 micron) boehmite particles and found the reaction rate at 85°C in 5 M NaOH to be relatively slow—approximately 3% in 3 hours. They also reported apparent activation energy of 123 kJ/gmole. In a subsequent study, Scotford and Glastonbury found that the initial rate appears to be proportional to the hydroxide activity to the $\frac{1}{2}$ power. Packter measured the dissolution rate of much smaller boehmite crystals (0.07 to 0.1 micron) and found the reaction rates to be much higher—approximately 60% in 6 hours at 60°C. Packter (10) proposed a model for the

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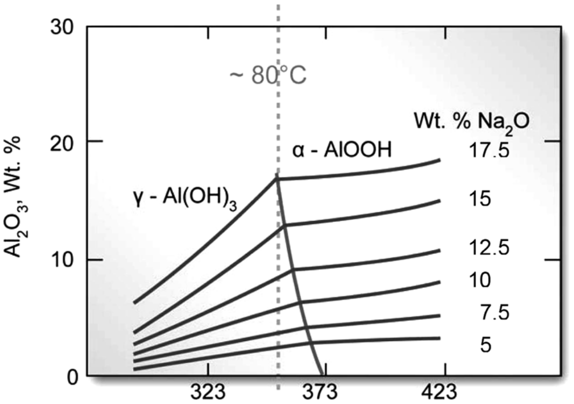


FIG. 1. Phase diagram for gibbsite $(g - Al(OH)_3)$ and boehmite (a - AlOOH) at caustic conditions (3), temperature in K.

dissolution of boehmite as:

Packter Model

$$\frac{d\left(\frac{M}{M_o}\right)}{dt} = -k\left(\frac{M}{M_o}\right)^{4/3} \tag{3}$$

Where (M/Mo) is the mass fraction of the original boehmite solid and k is the rate constant. Packter found that for these small crystals, the reaction rate increased linearly with the hydroxide activity. Packter also found the activation energy to be between 115 and 125 kJ/gmole.

Testing by Lumetta et al. (11) with waste from Hanford Tank S-110 showed 50% dissolution of boehmite in 24 hours at 80°C in 5 M NaOH. These results suggest that the actual waste boehmite appears to behave more like the larger boehmite crystals from the Scotford and Glastonbury study. More recent work by Fiskum et al. (12) confirmed that the actual waste produced similar results as observed by Lumetta. However, these tests also demonstrated significantly lower apparent activation energy of 25.2 kJ/mole. Further testing done by Hay et al. (13) showed 42% dissolution of aluminum at 55°C in Tank 51H (Savannah River) over a 3-week period. The aluminum concentration had not leveled, indicating a continued dissolution of aluminum with more time. The slow dissolution rate in their studies was attributed to the boehmite form of aluminum. Again, these results suggest that the kinetic behavior is similar to the larger crystals from the simulant work. However, the SEM micrographs in Fig. 2 (12) indicate that the primary crystal sizes for the actual waste samples are relatively small.

These crystals do, however, appear to have agglomerated into larger "particles" as evidenced in the particle-size distribution (PSD) plot shown in Fig. 3 (12).

The WTP baseline caustic-leaching process has been developed to operate at relatively low temperatures (approximately 100°C) with a short residence time on the order of 8 hours. Unfortunately, the time required to drive the boehmite leaching reaction is much higher than the gibbsite reaction. As it stands, the current WTP leaching process does not efficiently remove aluminum in the form of boehmite.

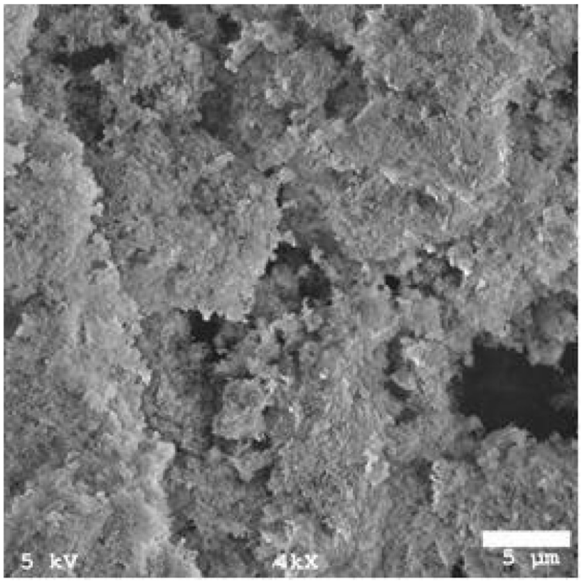


FIG. 2. SEM of actual tank waste.

The proposed continuous sludge leaching (CSL) process will target the leaching of boehmite under more aggressive conditions. Under these conditions, both gibbsite and boehmite will be effectively removed with an overall target conversion of 90%.

The CSL process will use a continually stirred reactor operating at 90 to 100°C and residence times of 300 hours to remove Al from HLW sludge such as those at Hanford and at SRS. CSL will effectively dissolve the recalcitrant boehmite phase of Al which, as of yet, has not been fully tested and is inconclusive as to whether it can be

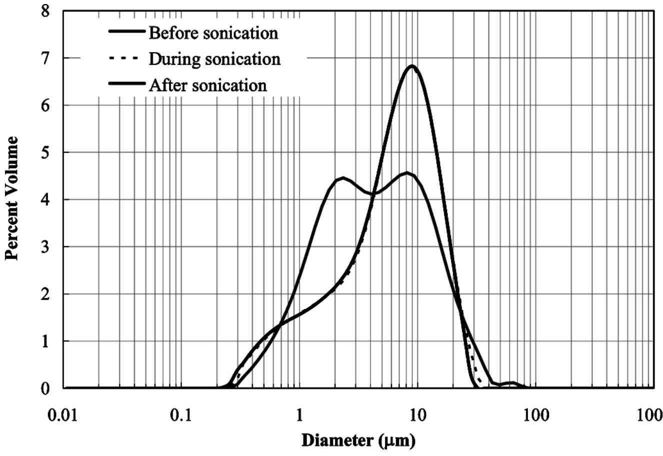


FIG. 3. PSD measurement.

accomplished by any existing or planned facilities at either site. Cross-flow filtration will be used to separate the reduced volume of HLW sludge from the Al-laden liquid stream. Following the cesium (Cs) separation using a separate process (where required), the Al-laden stream can be disposed at onsite facilities as low activity waste (LAW). The reduced volume of sludge can be vitrified as HLW.

The following equations were developed and will be used to predict the impact of residence time and hydroxide concentration on reaction kinetics. This equation was developed based on simulant data obtained with a large crystal size (4).

Simulant developed model #1

$$\frac{d\left(\frac{AlOOH}{AlOOH_i}\right)}{dt} = -A_o e^{-\frac{121,000}{RT}} \left(\frac{AlOOH}{AlOOH_i}\right)^{2/3} (OH)^{-}(1-\sigma)(1-\sigma_i) \tag{4}$$

where:

$$\sigma = \frac{Al(OH)_4^-}{Al(OH)_{4,s}^-} \tag{5}$$

And $(-A_o e^{-\frac{121,000}{RT}})$ is the rate constant with the activation energy.

However, these tests were not intended to assess the impact of the hydroxide ion, and therefore the 1/2 order observed by Packter for larger crystals will be used for this work.

The behavior of chromium in caustic waste leaching is also important to consider. The insoluble chromium content of the waste left after caustic leaching must be evaluated to determine if oxidative leaching is necessary. The removal of chromium from the waste forms is imperative because in vitrified wastes chromium forms crystalline compounds that limit the loading of the glass. Furthermore, by reducing chromium, it will reduce the operating life cycle of the WTP and decrease the number of canisters generated.

TESTING METHODS

Bench-scale testing involved small-scale parametric simulant studies using varying quantities of caustic to identify optimal operating conditions by trading off reactor size and caustic requirements. Battelle—Pacific Northwest Division (PNWD) performed bench-scale simulant tests to evaluate varying caustic and boehmite (AlOOH) concentrations and residence time to determine the extent of aluminum. Tests involved operating with batch feed and product removal, which simulated continuous flows, and examining the impact of changing reactor conditions on conversion (dissolution) of the boehmite. A statistically designed test matrix was used.

These continuous leaching tests, which are a finite-element version of this continuous process, were set up as shown in Fig. 4 using NaOH/boehmite/CrOOH slurry.

The slurry was added in increments that were comparatively small to the reactor residence time (once per hour) and heated to temperature (100°C) while stirring at 120 RPM in a 1-liter reaction vessel. The reaction vessel had a mechanical stirrer, a thermocouple, and a heating strap to keep the vessel at a constant temperature throughout the test. Two boehmite simulants were chosen: APYRAL AOH20 and AYPRAL AOH180E (14). APYRAL AOH20 was chosen based on the large particle size of this material which results in similar dissolution kinetics as those seen for the actual waste samples (12). An SEM micrograph of these crystals is shown in Fig. 5 and indicates that the crystals present in this boehmite are approximately 0.83 μm. Because the actual waste appears to have agglomerated (Figs. 2 and 3), an additional source

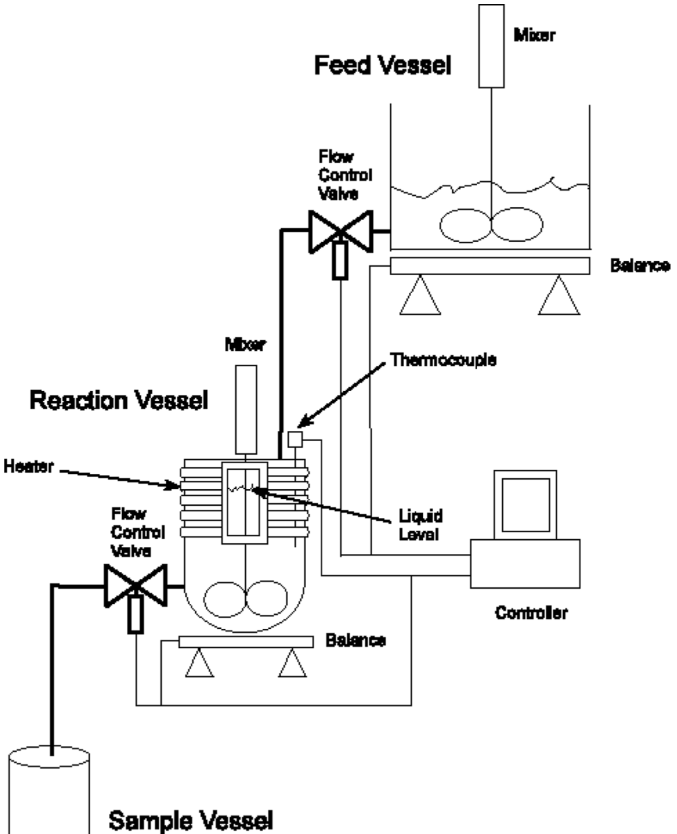
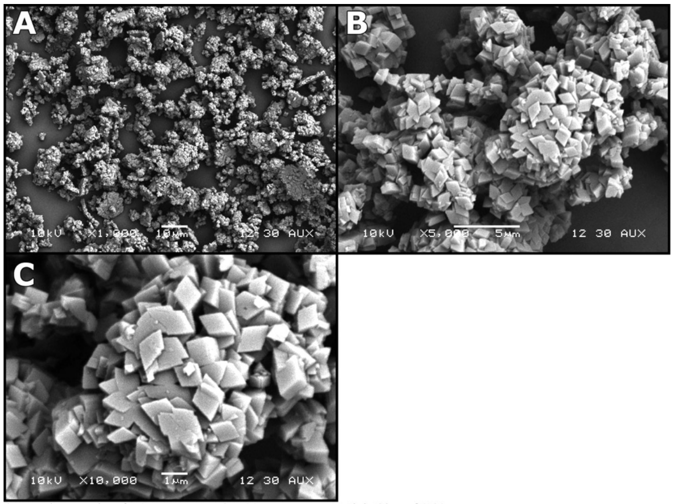


FIG. 4. Schematic drawing of the continuous sludge leaching (CSL) test setup.



SEM micrographs of B3 APYRAL AOH 20 . Average Particle Size of 0.83 µm.

FIG. 5. SEM micrograph of APYRAL AOH20 boehmite at 1,000×, 5,000×, and 10,000×.

of boehmite with a smaller crystal and larger surface area was chosen for testing as well (APYRAL AOH180E). Boehmite and CrOOH were added in the NaOH solution as slurry to the reaction vessel in 10-mL increments for the APYRAL AOH 20 boehmite and 100-mL, 50-mL, and 33-mL increments for the APYRAL AOH180E boehmite to meet residence time targets. The test solution was sampled at 0, 8, 24, 48, 72, and 100 hours and then every 24 hours after that for the APYRAL AOH20 boehmite tests. The test solution was sampled at 0, 2, 4, 6, 8, and 10 hours and then every 4 to 6 hours after that for the APYRAL AOH180E boehmite. Each sample taken consisted of 10 mL supernatant, which was filtered after being drawn from the reaction vessel and then analyzed for aluminum, chromium, and sodium content of the supernatant. Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was used to determine how much boehmite and CrOOH had dissolved.

The final three APYRAL AOH20 tests were performed by leaching a liter of slurry at 100°C in the reaction vessel for 24 hours, sampling, and then proceeding with the test as described above for only one tank turnover volume.

TABLE 1
CSL testing matrix with APYRAL AOH20 at 100°C

Test ID	OH Conc. (M)	Wt% Boehmite	Wt% CrOOH	Residence time (hr)
KA-1	5	2.53	0.25	100
KA-2	3	1.50	0.15	300
KA-3	3	2.26	0.23	100
KA-4	5	3.79	0.38	300
KA-5	4	2.62	0.26	200
KA-6	4	2.62	0.26	200

TABLE 2
CSL testing matrix with APYRAL AOH180E boehmite at 100°C

Test ID	OH Conc. (M)	Wt% Boehmite	Wt% CrOOH	Residence time (hr)
KB-1	5	2.53	0.25	10
KB-2	3	1.50	0.15	30
KB-3	3	2.26	0.23	10
KB-4	5	3.79	0.38	30
KB-5	4	2.62	0.26	20
KB-6	4	2.62	0.26	20

These test matrices were based on a statistical design with the residence time, leach solution concentration, and percent solubility (Tables 1 and 2). The time to achieve a specific dissolution percentage was the dependent variable, and the residence time and hydroxide concentration were the independent variables in this experimental design. For the purpose of this work, the leach solution hydroxide concentration was defined as the concentration before the start of testing.

To accelerate the approach to equilibrium, Tests KA-2 and KA-4 were batch leached for 24 hours before the continuous leaching began, and one reaction vessel turnover was performed for 300 hours to reach equilibrium. Test KA-6 was batch leached for 24 hours before continuous leaching began for one reaction vessel turnover in 200 hours. All other tests were leached continuously for three reaction vessel turnovers.

RESULTS

As can be seen in Table 3, the target dissolution of 90+% was achieved in test KA-2. The primary difference between KA-2 and KA-4 was the fraction of boehmite solubility. Prior tests have shown that the increasing fraction of boehmite solubility can result in slower reaction kinetics. Thus, to achieve the 90+% target dissolution with a 300-hour residence time, it is recommended that the fraction of boehmite solubility be limited to less than 0.5.

Figure 6 shows the impact of residence time on the leaching performance for the tests using the larger crystalline boehmite. As expected, extended residence times (up to 300 hours) are required to achieve the desired boehmite conversion. Note that the results have a significant scatter because of flow instabilities associated with the small scale of the tests. The analytical uncertainties associated with these tests are relatively small. Typical results obtained from this type of dissolution test result in less than 10% effort due to analytical error or temperature variability.

TABLE 3
Results from the KA series tests at 100°C

	Measured sodium molarity (M)	Fraction boehmite solubility	Residence time (hr)	Fraction boehmite dissolved	Fraction Cr dissolution
KA-1	7.11	0.16	100	0.53	0.209
KA-2	4.41	0.44	300	0.97	0.118
KA-3	5.22	0.24	100	0.60	0.107
KA-4	6.48	0.55	300	0.81	0.076
KA-5	4.71	0.19	200	0.61	0.267
KA-6	4.78	0.25	200	0.44	0.153

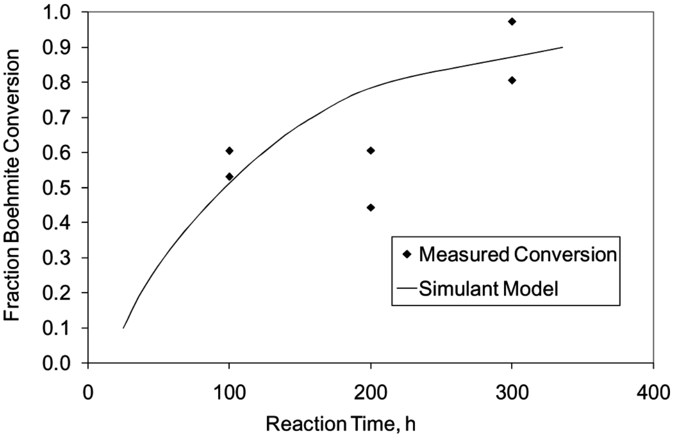


FIG. 6. APYRAL AOH20 Boehmite dissolution at 100°C.

However, due to the low flow rates, there was significant uncertainty associated with the measured flow rates. At this time, it is not possible to assess the impact of this flow rate uncertainty on the experimental results. However, the results are consistent with model Eqs. (4) and (5) developed from previous batch testing. These results indicate that the experimental results are consistent with the results expected based on the model developed for this system.

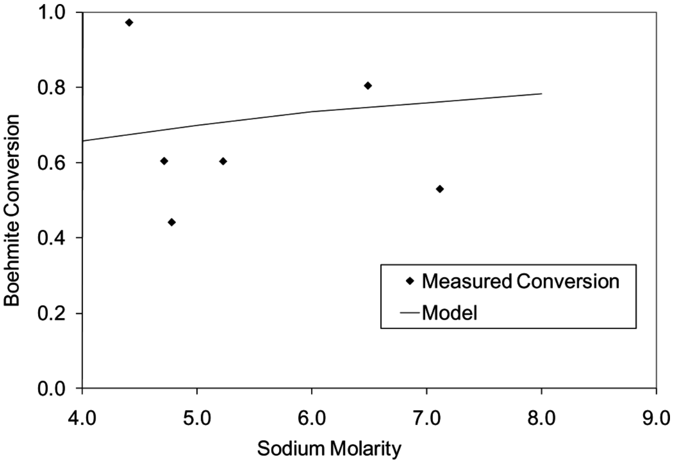


FIG. 7. Boehmite dissolution vs sodium molarity at 100°C.

TABLE 4
Results from the KB series tests at 100°C

	Hydroxide (M)	Residence time (hr)	Fraction boehmite dissolved	Fraction CrOOH dissolved
KB-1	5	10	0.65	0.004
KB-2	3	30	0.57	0.024
KB-3	3	10	0.67	0.005
KB-4	5	30	0.44	0.010
KB-5	4	20	0.37	0.012
KB-6	4	20	0.37	0.011

Figure 7 shows boehmite dissolution against measured sodium molarity. This plot indicates that data are consistent with the expectation that there would be a limited impact of sodium molarity on reaction kinetics. Also shown in Fig. 7 is the model behavior based on prior batch testing (Russell et al.). Note that this set of tests was performed with a very simple reaction matrix. Other species that may be present in actual waste were omitted in this initial phase of testing.

The results of the APYRAL AOH180E boehmite are shown in Table 4. As expected, the small particle size boehmite material reacts much faster, reaching equivalent conversions in an order of magnitude less time.

CONCLUSIONS

The target dissolution (90+%) was achieved in Test KA-2, and ~81% dissolution was obtained in KA-4. The primary difference between Tests KA-2 and KA-4 was the fraction of boehmite solubility (i.e., dissolved boehmite concentration divided by its solubility limits (Panias et al. (15)). Prior tests have shown that increasing the fraction of boehmite solubility can result in slower reaction kinetics.

Thus, to achieve the target dissolution of 90+% with a 300-hour residence time, it is recommended that the fraction of boehmite solubility be limited to less than 0.5. Testing also indicated that using boehmite crystals with significant smaller crystal sizes can result in up to an order of magnitude increase in the reaction rate.

The results from the model used indicate that there is a significant increase in the performance in boehmite dissolution from 0 to 100 hours and then incremental increases from 100 to 300 hours in reaction vessel residence time.

While there is little impact of sodium molarity on reaction kinetics, the Na:Al ratio is a key component. These results are consistent with the prior observed 1/2 order kinetics observed by Packter and provide the necessary basis for proceeding with pilot plant testing. The conditions required to achieve 90% dissolution of boehmite have been identified and are within the expected operating conditions of the CSL process. Initial pilot plan operations should employ a 300-hour residence time with a target boehmite solubility of 0.5. It should be noted that the simulant chosen (APYRAL AOH20) is expected to provide an upper bound on the anticipated performance of the CSL process. While this simulant provides the same reaction rate in batch testing at 100°C, the much larger crystal sizes suggest that the actual waste may experience faster reaction rates (Fig. 8, Shimskey et al. (16)).

The results, which were scattered because of experimental issues associated with the feed flowrates, are consistent with a previously developed model of boehmite dissolution kinetics. Based on Equation (2), the dissolution rate for boehmite is a function of residence time and hydroxide molarity. This dependence is shown in Fig. 9. The higher the ratio of Na:Al in the leachate, the lower the required residence time to achieve the given 90% dissolution. Note that the solubility limit for gibbsite at 25°C is shown on this graph. To maintain the aluminate ion in solution after leaching and cooling to 25°C, it is necessary to stay to the right of this solubility curve. Thus, for a 5 M NaOH leachate, the minimum Na:Al ratio to achieve 90% dissolution is approximately 8. However, if the sodium molarity of the leachate is increased to 8 M NaOH, then the minimum ratio can be reduced to 6.

However, there is a trade off to decreasing the Na:Al ratio. Equation (2) can also be used to assess the optimal target boehmite dissolution. Figure 10 shows the rate of aluminum dissolution per liter of reactor volume for various Na:Al ratios. The maximum quantity of Al dissolution is achieved at approximately 90% boehmite conversion for all Na:Al ratios. However, the rate of aluminum dissolution can be significantly improved by increasing the Na:Al ratio above 6. The rate of Al dissolution can be increased

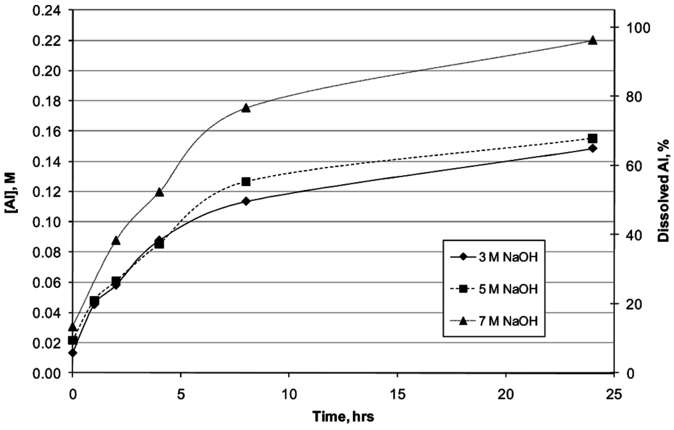


FIG. 8. Actual wastes solid aluminum dissolution at 100°C.

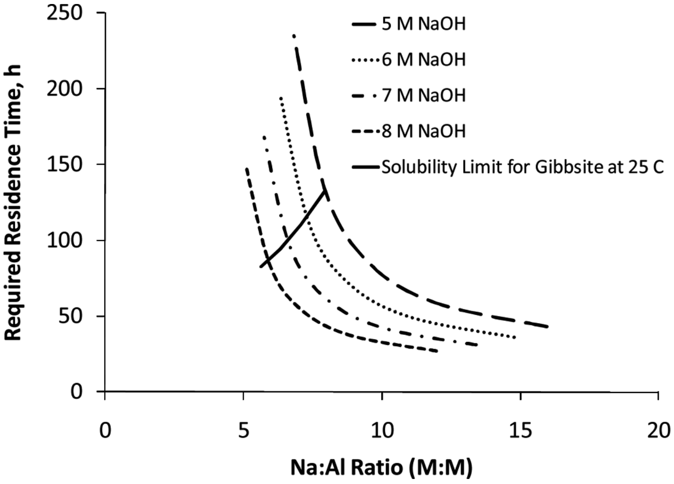


FIG. 9. Sodium/aluminum ratio vs. residence time.

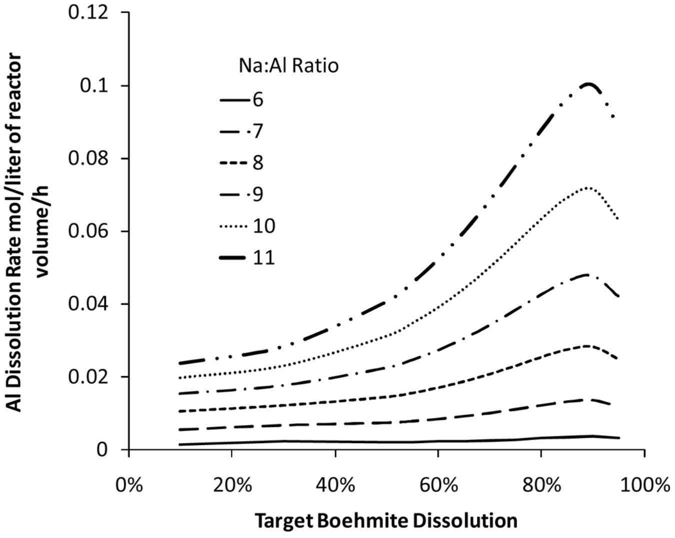


FIG. 10. Aluminum dissolution per liter of reactor volume.

by a factor of 20 by increasing the Na:Al ratio from 6 to 10. This is the result of a three-fold impact of increasing the Na:Al ratio: first, the approach to supersaturation is decreased; second, the hydroxide molarity is increased (increasing the reaction rate); and third, the hydroxide molarity increase also increases the Al solubility in a non-linear fashion.

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