EFFECT OF PHOSPHATE, FLUORIDE, AND NITRATE ON GIBBSITE DISSOLUTION RATE AND SOLUBILITY

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Acronyms and Abbreviations

AS	Analyzer Studio
ESP	Environmental Simulation Program
ICP-AES	inductively coupled plasma-atomic emission spectroscopy

Units

°C	degrees Celsius
g	gram
Kg	kilogram
µg	microgram
L	liter
m	molal
M	molar (moles per liter)
mL	milliliter
mol	mole

1 EXECUTIVE SUMMARY

Laboratory tests have been completed with simulated tank waste samples to investigate the effects of phosphate, fluoride, and nitrate on the dissolution rate and equilibrium solubility of gibbsite in sodium hydroxide solution at 22 and 40 ^{o}C. Results are compared to relevant literature data and to computer model predictions.

The presence of sodium nitrate (3 M) caused a reduction in the rate of gibbsite dissolution in NaOH, but a modest increase in the equilibrium solubility of aluminum. The increase in solubility was not as large, though, as the increase predicted by the computer model.

The presence of phosphate, either as sodium phosphate or sodium fluoride phosphate, had a negligible effect on the rate of gibbsite dissolution, but caused a slight increase in aluminum solubility. The magnitude of the increased solubility, relative to the increase caused by sodium nitrate, suggests that the increase is due to ionic strength (or water activity) effects, rather than being associated with the specific ion involved. The computer model predicted that phosphate would cause a slight decrease in aluminum solubility, suggesting some Al-PO_4 interaction. No evidence was found of such an interaction.

2 EXPERIMENTAL

Gibbsite dissolution tests were performed at ambient temperature (22 ±1 ^{o}C) and at 40 ±1 ^{o}C. Variables were OH^- (1.0, 2.0, and 3.0 M), PO_4^{3-} (absent or saturated as sodium phosphate or fluoride phosphate), F^- (absent or saturated as sodium fluoride phosphate), and NO_3^- (absent or 3.0 M). The chemicals used were:

- Gibbsite, $Al(OH)_3$, Almatis hydrated alumina C33
- Sodium hydroxide, NaOH, EMD, ACS grade
- Sodium phosphate, $Na_3PO_4 \bullet 12H_2O \bullet ¼NaOH$, J. T. Baker, ACS reagent grade
- Sodium fluoride, NaF, Sigma-Aldrich, ACS reagent grade
- Sodium nitrate, $NaNO_3$, Sigma-Aldrich, ACS reagent grade.

Samples were taken periodically, filtered, and analyzed for density, selected elements (Na, Al, P) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and free hydroxide by titration.

Initially, twelve samples were prepared at each temperature, labeled ALP2-1 – ALP2-12 for the ambient-temperature samples and ALP2-21 – ALP2-32 for the 40 ^{o}C samples. After preliminary analytical results showed that the samples were not coming to equilibrium within the original timeframe of the test, additional samples (ALP2-55 – APL-62 at ambient temperature,

ALP2-41 – ALP2-47 at 40 °C) were prepared to equilibrate over longer test periods. The final parametric matrix is shown in Table 1.

Consistency of data trends was used in place of sample duplicates to assess data quality. In addition, several samples contained zero phosphate, fluoride, and nitrate, so results could be compared to literature data for the pure-component phase diagram.

Table 1. Sample Matrix for Gibbsite Dissolution Tests.

Sample Number		Concentration, Molarity			
22 °C	**40 °C**	**OH^-**	**PO_4^{3-}**	**F^-**	**NO_3^-**
ALP2-1	ALP2-21/41	1.0	Saturated	Saturated	Absent
ALP2-2	ALP2-22/42	1.0	Saturated	Absent	Absent
ALP2-3	ALP2-23/43	1.0	Absent	Absent	Absent
ALP2-4	ALP2-24/44	1.0	Absent	Absent	3.0
ALP2-5/55	ALP2-25/45	2.0	Saturated	Saturated	Absent
ALP2-6/56	ALP2-26/46	2.0	Saturated	Absent	Absent
ALP2-7/57	ALP2-27/47	2.0	Absent	Absent	Absent
ALP2-8/58	ALP2-28	2.0	Absent	Absent	3.0
ALP2-9/59	ALP2-29	3.0	Saturated	Saturated	Absent
ALP2-10/60	ALP2-30	3.0	Saturated	Absent	Absent
ALP2-11/61	ALP2-31	3.0	Absent	Absent	Absent
ALP2-12/62	ALP2-32	3.0	Absent	Absent	3.0

Ambient-temperature samples, which were approximately 80 – 100 mL in volume, were kept in 125-mL polyethylene bottles on a rotator which tumbled the bottles continually. Slurries were sampled periodically by (a) recording the temperature of the slurry with a standardized thermometer, (b) allowing the slurry to settle briefly, (c) filtering a portion of the slurry through a syringe filter, (d) filling a 10-mL volumetric flask to determine the density of the filtrate, and (e) transferring the liquid from the volumetric flask to a sample vial for submission to the analytical laboratory for ICP-AES and free OH^- analyses.

Elevated temperature samples were kept in polyethylene bottles in a 40 °C shaker bath. Slurries were sampled periodically by the same method as the ambient-temperature slurries except that the liquid in the 10-mL volumetric flask was transferred quantitatively with water to a 25-mL flask to prevent precipitation of the sample when it cooled to ambient temperature. Densities of the diluted and undiluted liquids were recorded.

For the initial set of samples, the ambient temperature slurries (1 – 12) were sampled weekly for 5 weeks, and the 40 °C samples (21 – 27) were sampled at 1, 2, 3, 4, and 7 days. For the follow-up set, the ambient temperature slurries (55 – 62) were sampled once every two weeks for 10 weeks, and the 40 °C samples (28 – 32 and 41 - 47) were sampled at 1, 4 or 5, 7, 9 or 10, and 14 days.

3 DISSOLUTION TEST ANALYTICAL RESULTS

Periodic samples were analyzed for density (g/mL) and concentrations (µg/mL) of Al, Na, P, and free OH^-. Results are shown in Appendix A. Conversion of µg/mL concentrations to molar (M) concentrations (Appendix A) is a simple matter of converting units and dividing by the formula weight, as shown by the example in Equation 3-1:

$$1270\ \mu g/mL\ Al * (1\ g / 1E6\ \mu g) * (1000\ mL / 1\ L) * (1\ mol / 27.0\ g) = 0.047\ M\ Al \quad (3\text{-}1)$$

Conversion of molar concentrations to molal (m) concentrations requires information about the water content of the samples, which was determined by calculation (which is probably at least as accurate, for these samples, as percent water analytical results would be).

Step 1 of the molality conversion is to calculate the total mass of the liquid phase in each bottle, which is the sum of the water added plus the water-soluble portions of the chemicals that were added. For all of these samples, the NaOH and $NaNO_3$ are assumed to be completely soluble. For the ambient-temperature samples, the $Al(OH)_3$, $Na_3PO_4•12H_2O•¼NaOH$, and NaF are assumed to be 25% soluble. For the 40 °C samples, the $Al(OH)_3$, $Na_3PO_4•12H_2O•¼NaOH$, and NaF are assumed to be 50% soluble. (Comparison of observed liquid phase molalities with the corresponding theoretical molalities based on 100% dissolution of all salts shows that these 25% and 50% dissolution estimates are reasonable.)

Step 2 of the molality conversion is to calculate the total liquid phase volume, which is equal to the total liquid phase mass from Step 1 divided by the density measured for the individual samples. Step 3 is to calculate the total mass of H_2O in each bottle, which is set equal to the mass of H_2O added as H_2O plus the mass of H_2O derived from dissolution of 25% (or 50%) of the added $Na_3PO_4•12H_2O•¼NaOH$. Step 4 is to divide the mass of H_2O from Step 3 by the volume of the liquid phase from Step 2 to give kg H_2O per liter. Step 5, the final step, is to divide the molarity (mol/L) by the factor from Step 4 (kg H_2O/L) to give molality (mol/kg H_2O).

Tables in Appendix A show concentrations in all 3 units (µg/mL, molarity, molality) for all sub-samples as a function of time.

3.1 AMBIENT TEMPERATURE RESULTS

Slurry temperatures recorded during the ambient-temperature equilibration period averaged 22 °C. The highest temperature recorded for any individual sample was 22.9 °C and the lowest was 20.8 °C.

Runs 1 – 12 were conducted at ambient temperature with samples taken at 1-week intervals for a total of 5 weeks. Analytical results are shown in Tables A-1 through A-3 in Appendix A. Results show that none of the samples reached equilibrium (i.e., constant Al concentration).

Runs 5 – 12 were repeated as Runs 55 – 62 with sampling every 2 weeks for a total of 10 weeks. Analytical results are shown in Table A-4 through A-6 in Appendix A. Several of these re-run samples still had not reached equilibrium after 10 weeks.

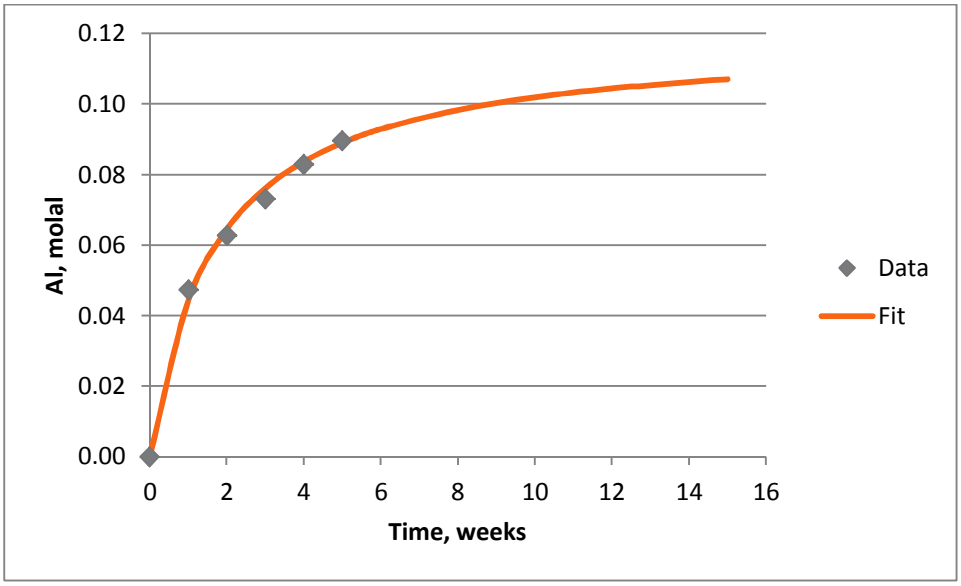
Figure 1 shows a plot of Al molality as a function of time for Run 1 (1.3 m hydroxide, saturated in fluoride and phosphate). Corresponding plots for other runs are shown in Appendix B. None of the plots fit a "standard" kinetic pattern (i.e., none of the plots fit zero-order, first-order, or second-order kinetics). However, because the Al concentration begins at zero molal at zero time, and reaches some constant value at equilibrium (at infinite time), the data can be fit using an asymptotic function like Equation 3-2

$$y = ax / (b+x) \tag{3-2}$$

where y = Al molality, x = time (weeks for ambient temperature runs, days for 40 °C runs), and a and b are parameters that are adjusted to optimize the fit to the data points. Parameter a is also equal to the value of y at infinite time, and therefore represents the equilibrium concentration of Al predicted by the equation. The resulting equation for Run 1 is shown as the solid line labeled "Fit" in Figure 1.

Figure 1. Rate of Gibbsite Dissolution in Run 1.

(22 °C, 1.3 m NaOH, saturated in fluoride and phosphate, no nitrate)



The "Solver" function in Microsoft Excel was used to optimize the values of the parameters in Equation 3-2. The process is shown in Table 2, which represents an Excel spreadsheet. Column A contains the sample time in weeks (x). Column B contains the measured Al molality (y). Column C contains, initially, a reasonable-guess value for parameter a, the equilibrium concentration of Al. Column D contains, initially, a reasonable-guess value for parameter b, which determines the shape of the curve. Column E contains the y result of Equation 3-2, the

predicted Al concentration at time *x*. Column F contains the square of the difference between the measured and predicted Al concentrations (Columns B and E). Cell F8 contains the sum of the squared differences in Column F, with added weight placed on the final data point (cell F7). The Solver is then used to minimize the value of cell F8 using cells C2 and D2 as input variables. The resulting values are entered into cells F8, C2, and D2. This process was repeated for all of the runs in this study.

Table 2. Spreadsheet Used to Calculate Parameters for Equation 3-2, Run 1.

	A	B	C	D	E	F
1	x = time	$y = Al_{measured}$	'a'	'b'	y=ax/(b+x)	$(B - E)^2$
2	0	0	0.119	1.695	0	0
3	1	0.047	--	--	0.044	9.99E-6
4	2	0.063	--	--	0.065	3.36E-6
5	3	0.073	--	--	0.076	9.20E-6
6	4	0.083	--	--	0.084	7.86E-7
7	5	0.090	--	--	0.089	2.82E-7
8					SUM(F3..F6)+5*F7 =	2.50E-5

It is clear from the plots in Appendix B that the gibbsite dissolution rate is not a perfect fit to the asymptotic function of Equation 3-2. In nearly all cases, there appear to be two distinct regions – a brief initial period of very rapid dissolution, followed by an extended period of much slower dissolution at a nearly linear rate. Nevertheless, the asymptotic function does appear to provide a reasonable estimate of the equilibrium Al concentration in most runs. These predicted values are collected in Table 3 along with the measured (or calculated) concentrations of the other solution components at the final sampling point (t = 5 weeks or t = 10 weeks) for all of the ambient-temperature runs.

Table 3. Concentrations (in molality) at Final Sampling Point for 22 °C Samples.

Run	Time, weeks	Na^+	PO_4^{3-} [a]	F^- [b]	NO_3^- [c]	OH^-	$Al_{measured}$	Al_{equil} [d]
1	5	1.87	0.107	0.054	0.00	1.30	0.090	0.119
2	5	1.89	0.145	0.000	0.00	1.24	0.090	0.133
3	5	1.47	0.000	0.000	0.00	1.30	0.075	0.100
4	5	5.39	0.000	0.000	3.76	1.30	0.072	0.106
5	5	3.15	0.058	0.029	0.00	2.53	0.201	0.249
55	10	3.04	0.050	0.025	0.00	2.50	0.205	0.225
6	5	3.06	0.060	0.000	0.00	2.48	0.200	0.255
56	10	2.94	0.052	0.000	0.00	2.45	0.201	0.220
7	5	2.94	0.000	0.000	0.00	2.54	0.178	0.213
57	10	2.84	0.000	0.000	0.00	2.51	0.188	0.215
8	5	6.97	0.000	0.000	3.75	2.53	0.186	0.237
58	10	6.75	0.000	0.000	3.75	2.52	0.204	0.259
9	5	4.45	0.034	0.017	0.00	3.76	0.321	0.376
59	10	4.33	0.030	0.015	0.00	3.67	0.339	0.357
10	5	4.33	0.033	0.000	0.00	3.75	0.311	0.376
60	10	4.28	0.030	0.000	0.00	3.73	0.338	0.356
11	5	4.26	0.000	0.000	0.00	3.76	0.319	0.330
61	10	4.20	0.000	0.000	0.00	3.71	0.323	0.334
12	5	8.11	0.000	0.000	3.76	3.75	0.328	0.386
62	10	8.05	0.000	0.000	3.75	3.67	0.365	0.418

[a]Phosphate concentration based on P analysis result from inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.
[b2]Fluoride not measured; assumed equal to one-half of phosphate concentration if NaF added to sample.
[c]Nitrate concentration not measured; calculated from input weights of $NaNO_3$ and H_2O.
[d]Aluminum concentration at equilibrium, as predicted from Equation 3-2.

Equation 3-2 is similar to, but more empirical than, a model used in a 2009 study ("The kinetics of gibbsite dissolution in NaOH" [Pereira et al 2009]) of gibbsite dissolution rates at 60 to 100 °C. Equation 3-3 is the model that those researchers found provided the best fit to their data. Their lower-case *k* is described as a kinetic rate constant and is equivalent to parameter *b* in Equation 3-2. Their upper-case *K* is described as an equilibrium constant ($K=C_{Al}/C_{OH}$), and is equivalent to parameter *a* in Equation 3-2.

$$dC_{Al}/dt = k(1-C_{Al}/C^{o}_{gibb})^{2/3}C_{OH}(1-C_{Al}/KC_{OH}) \qquad (3\text{-}3)$$

3.1.1 Evaluation of Experimental Error for 22 °C Samples

Experimental error derived from analytical uncertainty (ICP-AES and free hydroxide analyses) is expected to be small. Of the 100 ambient-temperature samples submitted for analysis, 8 ICP-AES samples and 7 OH samples were run in duplicate (one sample per batch). The average relative percent difference for these duplicate samples was 1.3% for Al, 1.4% for Na, 1.2% for P, and 0.9% for OH.

Errors derived from the weights of reagents added to the sample bottles are expected to be very small. Reagents were weighed on a balance accurate to ±0.01 g, and weights ranged from 0.42 g

(NaF) to 80.0 g (H_2O). The gross and tare weights of the sample bottles were used to calculate the total mass added to each bottle, which was compared to the sum of the reagents added to the bottle. The difference between the computed sum and measured sum was never greater than 0.05 g and was generally less than 0.03 g.

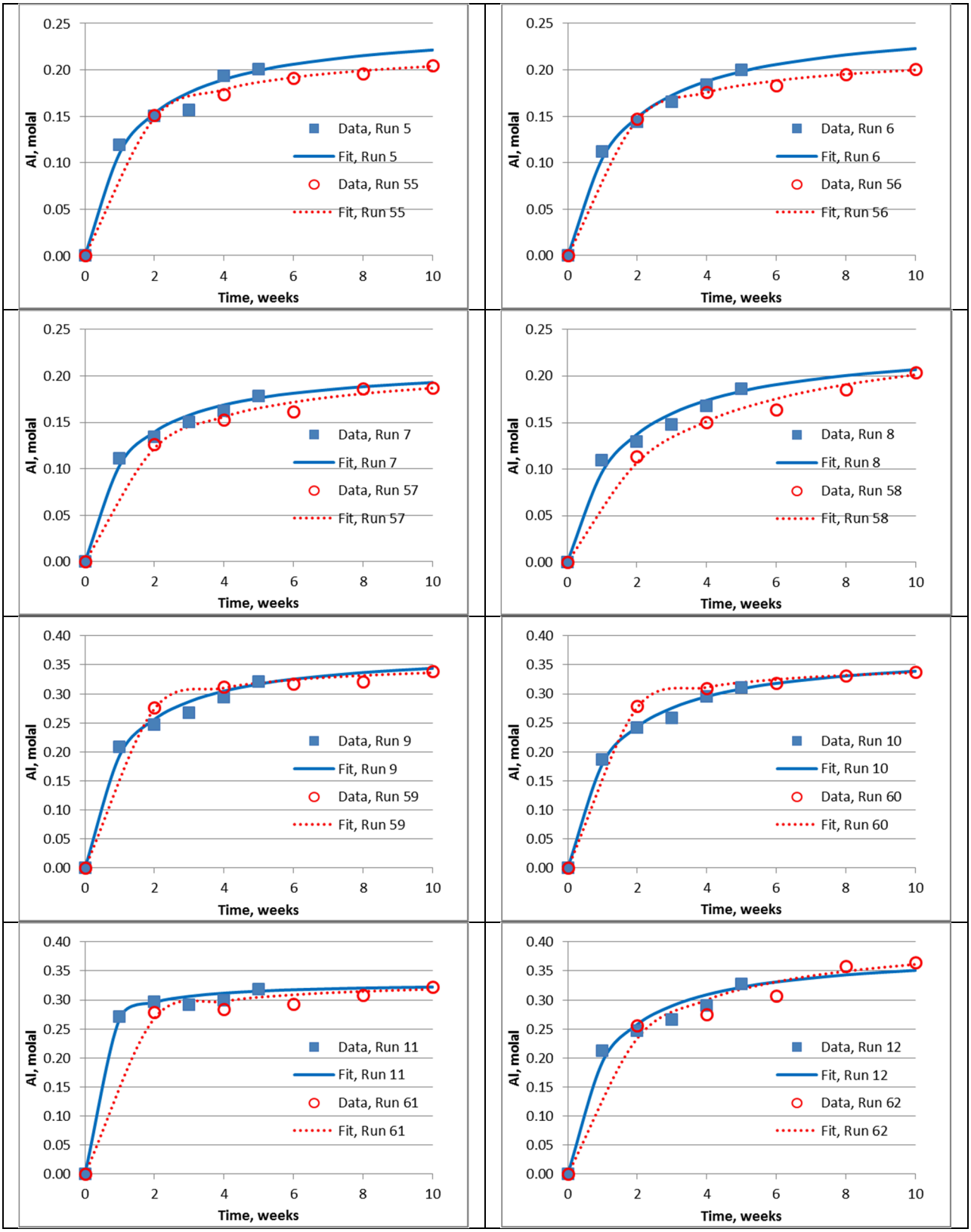
Errors derived from temperature excursions are expected to be small. The temperature of the solution in the sample bottle was recorded each time a sample was taken. These temperatures ranged from 20.8 to 22.9 ^oC and were typically at 22.0 ±0.5 ^oC.

Errors derived from sample preparation are likely to be more significant than the errors described above. Some evaporation of water is inevitable when sample bottles are opened and during the filtration process.

Errors derived from conversion of molarity (or μg/mL) to molality are also expected to be significant. This conversion depends on the calculated mass of H_2O in each sample bottle, which depends, in turn, on the measured density (small error) and an estimate of the amount of H_2O in the solid phase in each bottle as $Na_3PO_4•12H_2O$ or $Na_7F(PO_4)_2•19H_2O$ (larger error).

The overall impact of the combined effects of these errors can be evaluated by comparing the results for duplicate test runs. Figure 2 shows the Al molality vs. time plots (data points and curve fits) for the 8 sets of duplicate runs. In all 8 sets of duplicate runs, the individual data points at 2 weeks and 4 weeks and the projected data at 10 weeks (blue solid line vs. red dotted line), are approximately within ±10% of each other and in most cases are much better than that. Note that the same can be said about the agreement between the duplicate values in Table 10 for the equilibrium concentration of Al in runs 5/55 through 12/62.

Figure 2. Reproducibility of Ambient Temperature Runs.

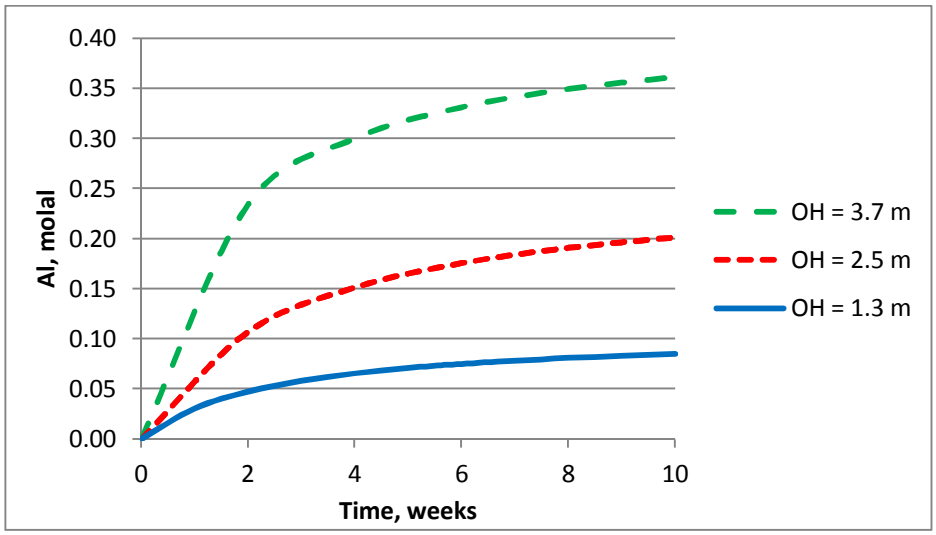


3.1.2 Effect of Hydroxide Concentration

Clearly, and as expected, hydroxide concentration had the largest impact of all the parameters (at constant temperature) on the equilibrium Al concentration. In terms of rate of approach to equilibrium, however, there is little indication that hydroxide concentration had much impact. All of the samples at ambient temperature took more-or-less the same amount of time to reach equilibrium, regardless of the hydroxide concentration. This matches the finding of a 2009 study (Pereira et al 2009), which found that hydroxide concentration over the range of 5 to 9 wt% NaOH had no significant effect on the rate of gibbsite dissolution over the temperature range of 60 to 100 ^{o}C. It also matches the finding of a 2000 study ("The Dissolution and Interactions of Gibbsite Particles in Alkaline Media" [Addai-Mensah et al 2000]), which found that hydroxide concentration over the range of 1 to 8 M NaOH had no significant effect on the rate of gibbsite dissolution over the temperature range of 25 to 65 ^{o}C. See Figure 3 for the dissolution rate data for the current runs 4, 58, and 62, all of which were at 3.75 m nitrate and no fluoride or phosphate.

Figure 3. Effect of Hydroxide on Gibbsite Dissolution at Ambient Temperature.

(Asymptotic Fit Data, Runs at 3.75 m nitrate, no fluoride or phosphate.)



Run 4 at 1.3 m OH; Run 58 at 2.5 m OH; Run 62 at 3.7 m OH

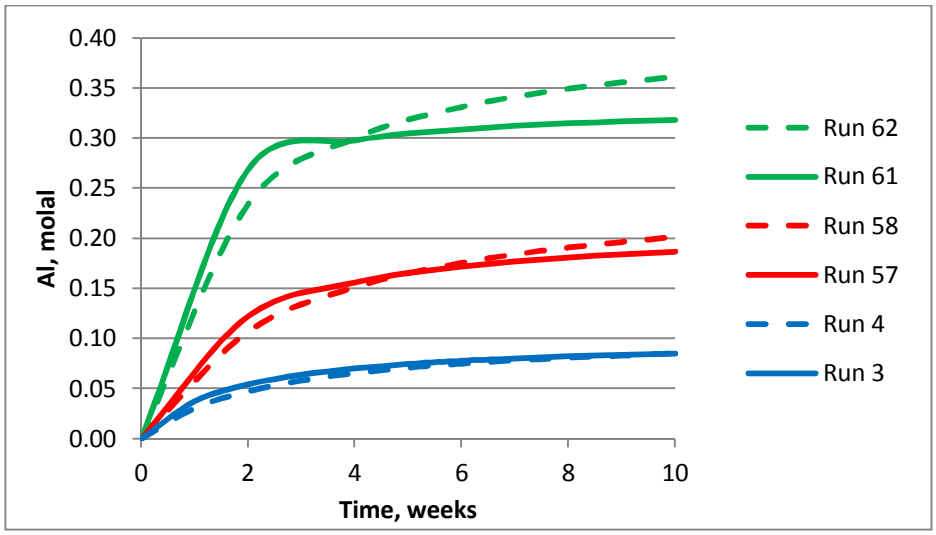
3.1.3 Effect of Nitrate Concentration

The presence of 3.75 m sodium nitrate had a subtle but consistent effect on the gibbsite dissolution rate and on the equilibrium Al concentration in solution, as shown in Figure 4. The dashed lines in this figure represent the asymptotic fits for runs 4, 58, and 62, at 1.3 m, 2.5 m, and 3.7 m OH, all of which contained 3.75 m nitrate and no fluoride or phosphate. The corresponding solids lines show runs 3, 57, and 61 at the same OH concentrations but without any nitrate, phosphate, or fluoride. In all 3 sets of lines, the nitrate had the effect of slowing the approach to equilibrium (i.e., the dashed lines are below the solid lines for the first 2-4 weeks), but increasing the final equilibrium Al concentration. The magnitude of the effect increases with increasing OH (and increasing Al). Based on the values in Table 3, the presence of 3.75 m nitrate results in a 7% increase in Al_{equil} at 1.3 m OH, a 16% increase at 2.5 m OH, and a 21% increase at 3.7 m OH.

The effect of nitrate on the dissolution rate is in agreement with an Oak Ridge National Laboratory study ("Experimental Studies of the Solubilities of Aluminum Oxy-Hydroxy Phases to 300 oC" [Palmer et al 2001]), which found that increasing nitrate concentration from 1 to 5 m caused a reduction in the rate of boehmite dissolution in 1 m NaOH at 30 ^{o}C. The authors also said that though "the relative rates could not be quantified," increasing ionic strength caused a "marked reduction" in the rate of gibbsite dissolution.

Figure 4. Effect of Nitrate on Gibbsite Dissolution at Ambient Temperature.

(Asymptotic Fit Data, no F or PO_4; solid lines – NO_3 absent; dashed lines – 3.75 m NO_3.)
(Same OH levels as Figure 3.)



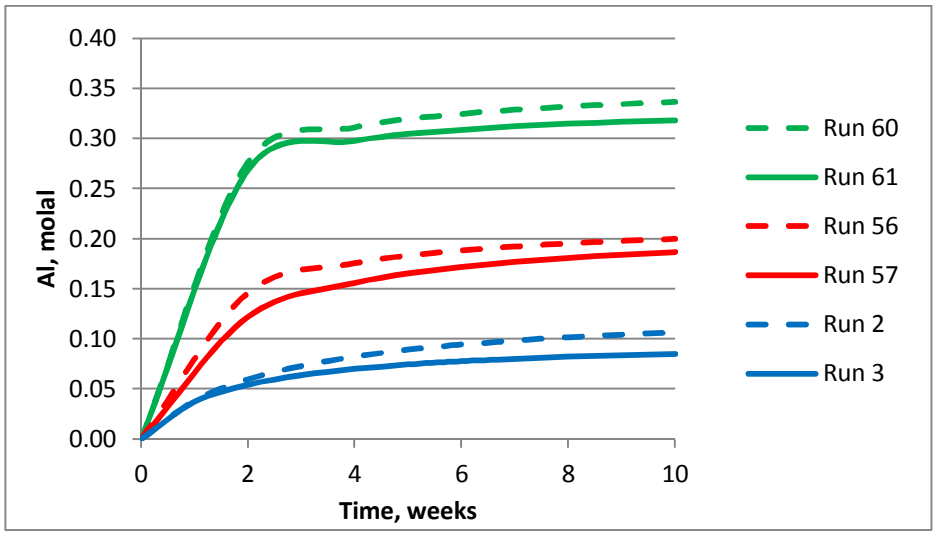
3.1.4 Effect of Phosphate

The presence of sodium phosphate had almost no effect on gibbsite dissolution rate, but it did have a subtle but consistent effect on the equilibrium Al concentration in solution, as shown in Figure 5. The dashed lines in this figure represent the asymptotic fits for runs 2, 56, and 60 at saturated sodium phosphate conditions (0.14 m, 0.05 m, and 0.03 m PO_4, respectively). The corresponding solids lines show runs 3, 57, and 61, all of which contained no phosphate, nitrate, or fluoride. In all 3 sets of lines, the phosphate had the effect of increasing the final equilibrium Al concentration by a small amount. The effect appears to be independent of hydroxide concentration (i.e., the magnitude of the change is roughly the same in all 3 sets of curves). However, considering the change in phosphate solubility with increasing hydroxide (i.e., the change from 0.10 m PO_4 at the lowest OH level to 0.03 m PO_4 at the highest OH level), the effect does increase with increasing OH, as did the nitrate effect. In other words, the effect of enhancing the Al solubility is more likely due to an ionic strength (or water activity) effect than it is to the anions themselves.

There was never any indication from microscopic observation of the solids that there was any incorporation of phosphate into any Al-containing solid phase. The only solid phases observed were gibbsite and $Na_3PO_4 \cdot 12H_2O$.

Figure 5. Effect of Phosphate on Gibbsite Dissolution at Ambient Temperature.

(Asymptotic Fit Data, no F or NO_3; solid lines – PO_4 absent; dashed lines – saturated in PO_4.)
(Same OH levels as Figure 3.)



3.1.5 Fluoride Effect

Samples that contained fluoride (Runs 1, 5/55, 9/59) were saturated in the sodium fluoride phosphate double salt, $Na_7F(PO_4)_2 \cdot 19H_2O$. The effect of the fluoride phosphate on gibbsite dissolution rate (none) and gibbsite solubility (slight enhancement) were the same as for phosphate alone, as shown in Figure 6. Figures 5 and 6 appear to be near duplicates of one another. Phosphate concentrations were nearly the same in samples with and without fluoride, as shown in Table 4.

Figure 6. Effect of Fluoride/Phosphate on Gibbsite Dissolution at Ambient Temperature.

(Asymptotic Fit Data; solid lines – F and PO_4 absent; dashed lines – saturated in $Na_7F(PO_4)_2 \cdot 19H_2O$.)
(Same OH levels as Figure 9; nitrate absent.)

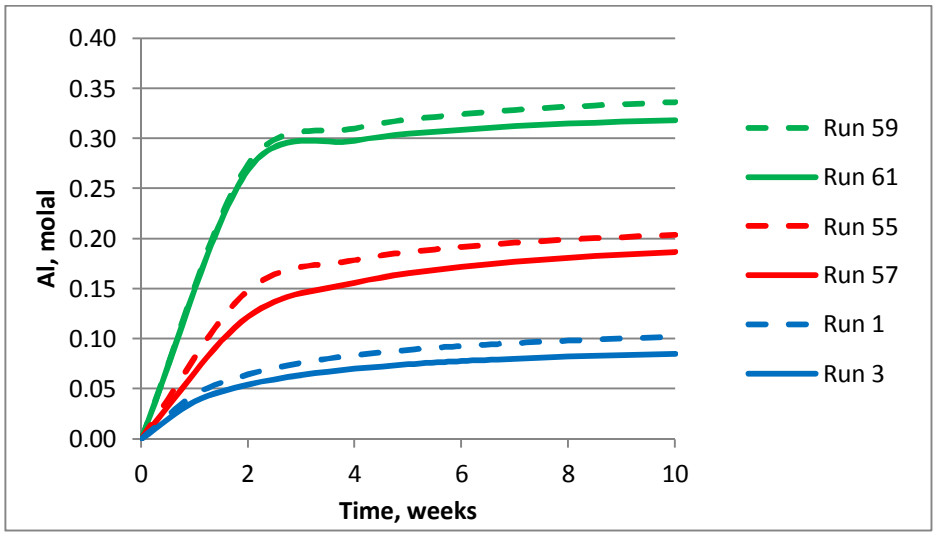


Table 4. Concentration (in molality) of Phosphate in Ambient Temperature Samples.

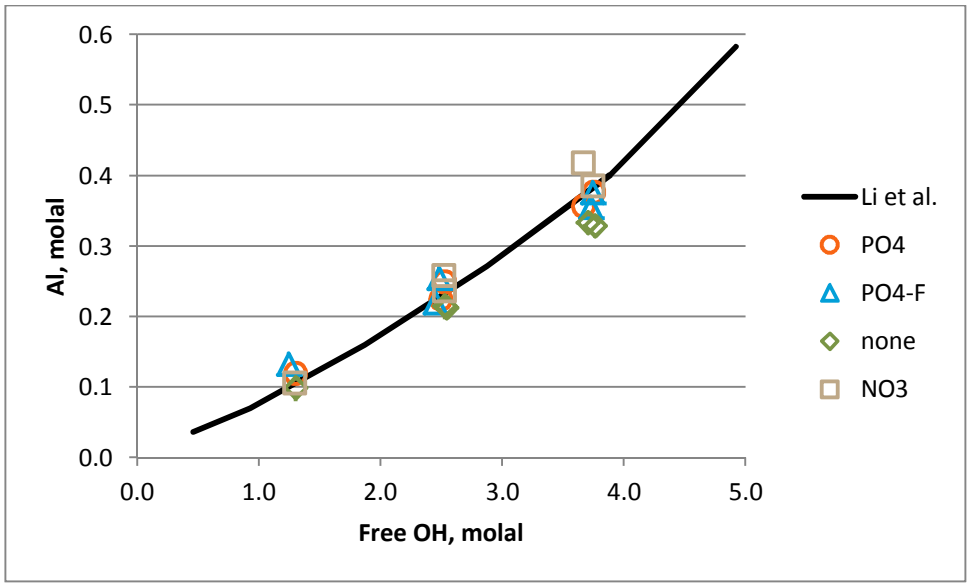
OH, molal	F Present (Runs 1, 5/55, 9/59)	F Absent (Runs 2, 6/56, 10/60)
1.3	0.10	0.14
2.5	0.05	0.05
3.7	0.03	0.03

3.1.6 Comparison to Literature Data

Equilibrium aluminum concentrations (in molality) from Table 3 are compared to literature data for gibbsite solubility at 25 °C ("The influence of Al(III) supersaturation and NaOH concentration on the rate of crystallization of Al(OH)3 precursor particles from sodium aluminate solutions" [Li et al 2005]) in Figure 7. The solid line represents the literature data. The diamond-shaped points represent samples with no phosphate, fluoride, or nitrate added (samples ALP2-3, -7, -11, -57, -61). These points generally fall slightly below the literature

curve, possibly due to the 3 °C temperature difference (25 °C for the literature data, 22 °C for the current samples). The square data points represent samples containing 3.75 m sodium nitrate (samples ALP2-4, -8, -12, -58, -62). These points generally fall above the literature line, representing the influence of nitrate (or ionic strength or water activity) on the gibbsite solubility. Points representing samples saturated in $Na_3PO_4 \cdot 12H_2O$ (circles) or $Na_7F(PO_4)_2 \cdot 19H_2O$ (triangles) fall virtually on the literature curve, intermediate between the diamonds and squares.

Figure 7. Comparison of Sample Data (22 °C) to Literature Data (25 °C) for Gibbsite Solubility.



(Li et al. 2005 data as amended by personal communication from Jacob Reynolds)

3.2 ELEVATED TEMPERATURE RESULTS

Runs 21 – 27 were conducted at 40 ^{o}C with samples taken at 1-day intervals for 4 days plus a final sample at 7 days. Analytical results are shown in Tables A-7 through A-9 in Appendix A. Results show that none of the samples reached equilibrium (i.e., constant Al concentration).

Runs 28 – 32 were done with sampling at intervals of 1, 4, 7, 10, and 14 days. Runs 41 – 47 (repeat of Runs 21 – 27) were done with sampling at intervals of 1, 5, 7, 9, and 14 days. Analytical results are shown in Tables A-10 through A-12 in Appendix A.

Several of the samples still had not reached equilibrium after 14 days. Plots of Al molality as a function of time are shown in Appendix B. As with the ambient-temperature runs, the 40 ^{o}C plots were fitted with the asymptotic function in Equation 3-2, and the "Solver" function in Microsoft Excel was used to optimize the values of the parameters. (For Run 47, the Solver returned a "division by zero" error, so the fit was made manually in that case.) The predicted values for Al_{equil} are collected in Table 5 along with the measured (or calculated) concentrations of the other solution components at the final sampling point (t = 7 days or t = 14 days) for all of the 40 ^{o}C runs.

Table 5. Concentrations (in molality) at Final Sampling Point for 40 °C Samples.

Run	Time, Days	Na^+ molal	PO_4^{3-} molal[a]	F^- molal[b]	NO_3^- molal[c]	OH^- molal	$Al_{measured}$ molal	Al_{equil} molal[d]
21	7	2.23	0.19	0.09	0.00	1.34	0.21	0.23
41	14	2.23	0.20	0.10	0.00	1.33	0.18	0.21
22	7	2.79	0.40	0.00	0.00	1.28	0.20	0.21
42	14	2.72	0.44	0.00	0.00	1.20	0.16	0.18
23	7	1.69	0.00	0.00	0.00	1.40	0.19	0.21
43	14	1.53	0.00	0.00	0.00	1.34	0.16	0.16
24	7	5.98	0.00	0.00	3.75	1.34	0.17	0.20
44	14	5.33	0.00	0.00	3.75	1.33	0.18	0.20
25	7	3.72	0.10	0.05	0.00	2.62	0.38	0.45
45	14	3.44	0.11	0.05	0.00	2.65	0.37	0.42
26	7	3.86	0.20	0.00	0.00	2.53	0.37	0.43
46	14	3.46	0.21	0.00	0.00	2.49	0.36	0.38
27	7	3.45	0.00	0.00	0.00	2.63	0.38	0.40
47	14	3.09	0.00	0.00	0.00	2.52	0.45	0.46
28	14	6.52	0.00	0.00	3.75	2.41	0.41	0.44
29	14	4.78	0.08	0.04	0.00	3.77	0.65	0.66
30	14	4.81	0.14	0.00	0.00	3.66	0.65	0.65
31	14	4.52	0.00	0.00	0.00	3.81	0.64	0.66
32	14	8.16	0.00	0.00	3.75	3.60	0.76	0.79

[a]Phosphate concentration based on P analysis result from inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.
[b]Fluoride not measured; assumed equal to one-half of phosphate concentration if NaF added to sample.
[c]Nitrate concentration not measured; calculated from input weights of $NaNO_3$ and H_2O.
[d]Aluminum concentration at equilibrium, as predicted from Equation 3-2.

3.2.1 Evaluation of Experimental Error

Experimental error derived from analytical uncertainty (ICP-AES and free hydroxide analyses) for the 40 ^{o}C samples, like the ambient-temperature samples, is expected to be small. Of the 95 samples submitted for analysis, 6 ICP-AES samples and 11 OH samples were run in duplicate (one sample per batch). The average relative percent difference for these duplicate samples was 2.8% for Al, 2.2% for Na, 3.7% for P, and 1.3% for OH.

Errors derived from the weights of reagents added to the sample bottles are expected to be very small. The reagents were weighed on a balance accurate to ±0.01 g, and weights ranged from 0.84 g (NaF) to 80.0 g (H_2O). The gross and tare weights of the sample bottles were used to calculate the total mass added to each bottle, which was compared to the sum of the reagents added to the bottle. The difference between the computed sum and measured sum was never greater than 0.11 g and was generally less than 0.06 g.

Errors derived from temperature excursions are expected to be small. The temperature of the solution in the sample bottle was recorded each time a sample was taken. These temperatures ranged from 38.4 to 41.2 ^{o}C, and were typically at 40.0 ±1.0 ^{o}C.

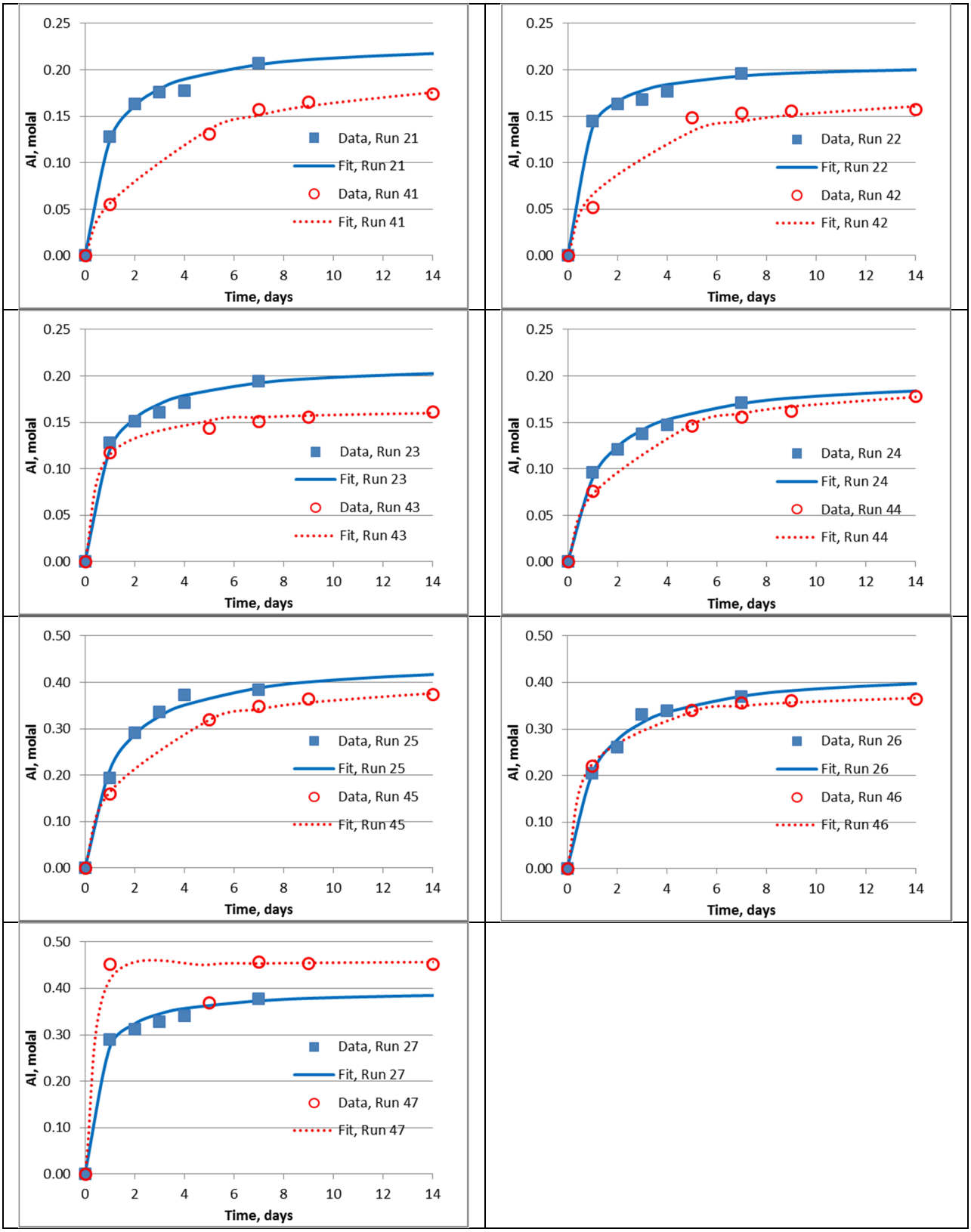
Errors derived from sample preparation are likely to be more significant than the errors described above. Some evaporation of water is inevitable when sample bottles are opened and during the filtration process, and sample dilutions were necessary to prevent precipitation of salts before the samples were analyzed.

Errors derived from conversion of molarity (or μg/mL) to molality are also expected to be significant. This conversion depends on the calculated mass of H_2O in each sample bottle, which depends, in turn, on the measured density (small error) and an estimate of the amount of H_2O in the solid phase in each bottle as $Na_3PO_4 \cdot 12H_2O$ or $Na_7F(PO_4)_2 \cdot 19H_2O$ (larger error).

One potential source of error for the 40 ^{o}C samples that was not present for the ambient-temperature samples was the degree of mixing. Ambient-temperature samples were continually rotated using a Labquake mixer, which provided nearly perfect mixing of solid and liquid phases during the test. The 40 ^{o}C samples were kept in a shaking water bath which provided generally poorer contact of the settled solids with the liquid phase. This is likely the dominant source or discrepancy between duplicate sample runs for the 40 ^{o}C samples.

The overall impact of the combined effects of these errors can be evaluated by comparing the results for duplicate test runs. Figure 8 shows the Al molality vs. time plots (data points and curve fits) for the 7 sets of duplicate runs. (Note that, based on the Day 5 sample and the Day 1 results for similar samples, the reported Al concentration for Run 47 Day 1 appears to be too high by a factor of two. Re-examination of the analytical data failed to uncover any inconsistencies.)

Figure 8. Reproducibility of 40 °C Runs.

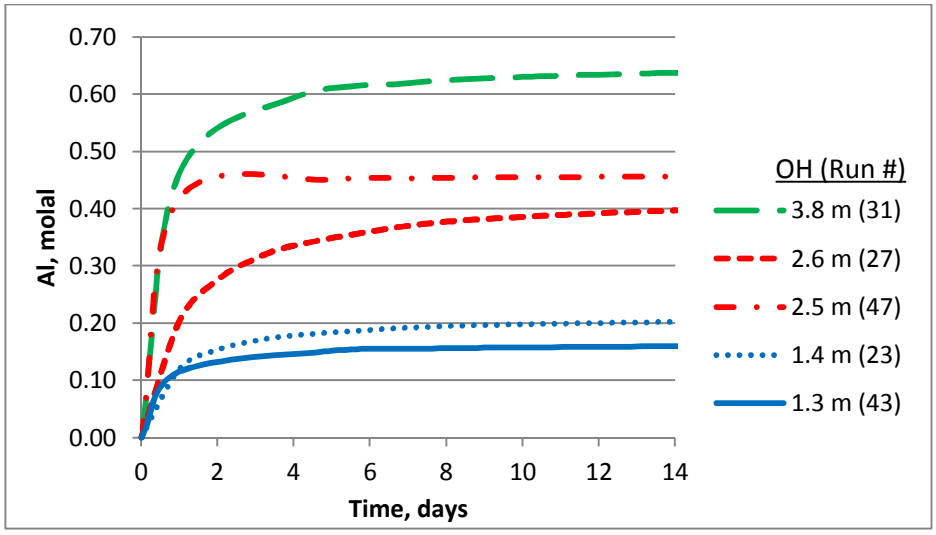


3.2.2 Effect of Hydroxide Concentration

Clearly, as with the ambient-temperature runs, hydroxide concentration had the largest impact of all the parameters on the equilibrium Al concentration. In terms of rate of approach to equilibrium, however, there is little indication that hydroxide concentration had much impact. All of the samples at 40 °C took more-or-less the same amount of time to reach equilibrium, regardless of the hydroxide concentration. See Figure 9 for the dissolution rate data for runs 23/43, 27/47, and 31, all of which were at zero fluoride, phosphate, and nitrate.

Figure 9. Effect of Hydroxide on Gibbsite Dissolution at 40 °C.

(Asymptotic Fit Data, Runs at zero fluoride, phosphate, and nitrate.)

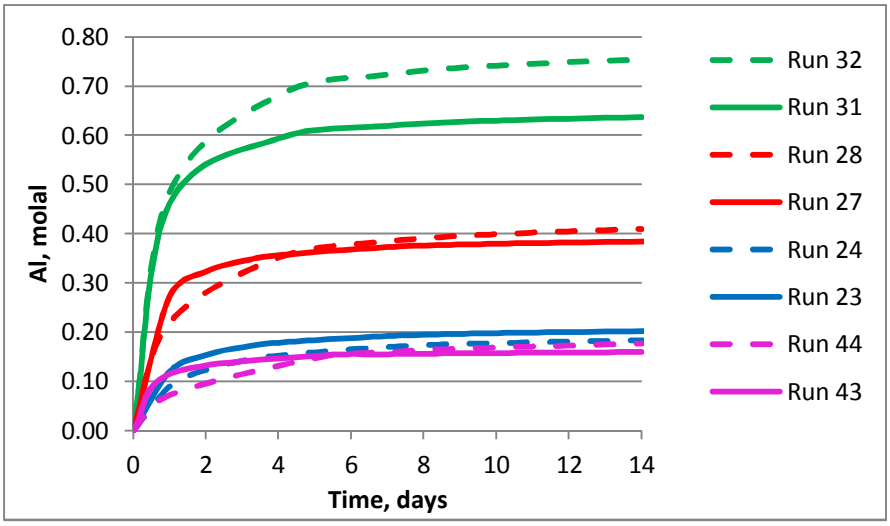


3.2.3 Effect of Nitrate Concentration

The presence of 3.75 m sodium nitrate had a subtle effect on gibbsite dissolution rate at 40 °C and on the equilibrium Al concentration in solution, as shown in Figure 10. The dashed lines in this figure represent the asymptotic fits for runs 24/44, 28, and 32, at 1.3 m, 2.5 m, and 3.7 m OH, all of which contained 3.75 m nitrate. The corresponding solid lines show runs 23/43, 27, and 31 at the same OH concentrations but without any nitrate, phosphate, or fluoride. At 1.3 m and 2.5 m OH, the nitrate had the effect of slowing the approach to equilibrium (i.e., the dashed lines are below the solid lines for the first 1-5 days), but the final equilibrium Al concentration was the same, within the analytical uncertainty in these runs. At 3.7 m OH, the nitrate appeared to have no effect on the rate of dissolution, but like the ambient-temperature samples, it did increase the gibbsite solubility by about 20%.

Figure 10. Effect of Nitrate on Gibbsite Dissolution at 40 °C.

(Asymptotic Fit Data, no F or PO_4; solid lines – NO_3 absent; dashed lines – 3.75 m NO_3.)
(Same OH levels as Figure 9.)



3.2.4 Effect of Phosphate and Fluoride

The presence of sodium phosphate (or the sodium fluoride phosphate double salt) had no discernable effect on gibbsite dissolution rate or equilibrium Al concentration at 40 °C, as shown in Figures 11 and 12. The dashed lines in Figure 11 represent the asymptotic fits for runs 22, 26, and 30 at saturated sodium phosphate conditions (0.42 m, 0.20 m, and 0.14 m PO_4, respectively). The corresponding solid lines show runs 23, 27, and 31, all of which contained no phosphate, nitrate, or fluoride. In all 3 sets of lines, the difference between the dashed lines and solid lines is either inconsistent or within experimental error.

The dashed lines in Figure 12 represent the asymptotic fits for runs 21, 25, and 29 at saturated sodium fluoride phosphate conditions (0.19 m, 0.10 m, and 0.08 m PO_4, respectively). The corresponding solid lines are the same as they were in Figure 9 (no nitrate, fluoride, or phosphate). Although the equilibrium Al concentration is higher for the dashed line in all 3 cases (i.e., at all 3 OH levels), the difference does not exceed experimental error.

Figure 11. Effect of Phosphate on Gibbsite Dissolution at 40 °C.

(Asymptotic Fit Data, no F or NO_3; solid lines – PO_4 absent; dashed lines – saturated in PO_4.)
(Same OH levels as Figure 9.)

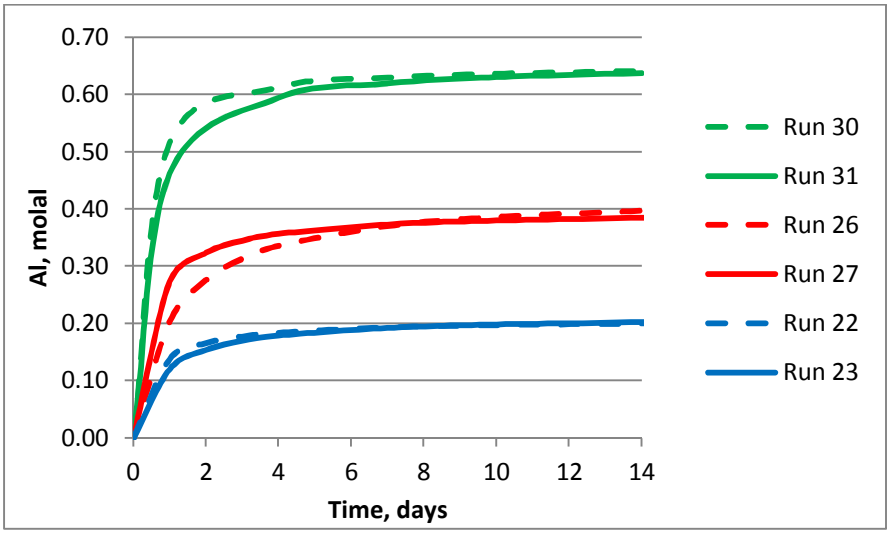
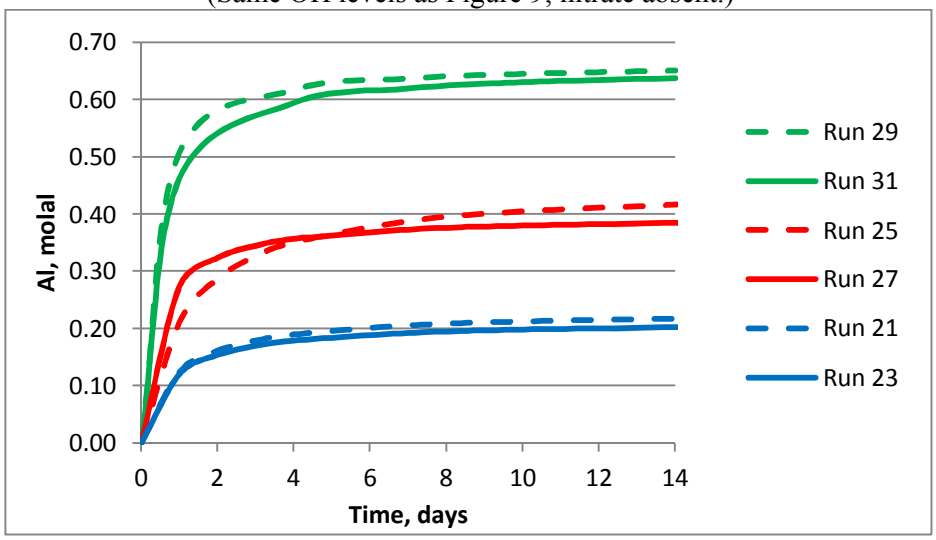


Figure 12. Effect of Fluoride/Phosphate on Gibbsite Dissolution at 40 °C.

(Asymptotic Fit Data; solid lines – F and PO_4 absent; dashed lines – saturated in $Na_7F(PO_4)_2 \cdot 19H_2O$.)
(Same OH levels as Figure 9; nitrate absent.)



At ambient temperature, the presence of fluoride had little effect on the overall solubility of phosphate (see Table 4). At 40 °C, however, the fluoride had a strongly inhibiting effect on phosphate solubility, as shown in Table 6.

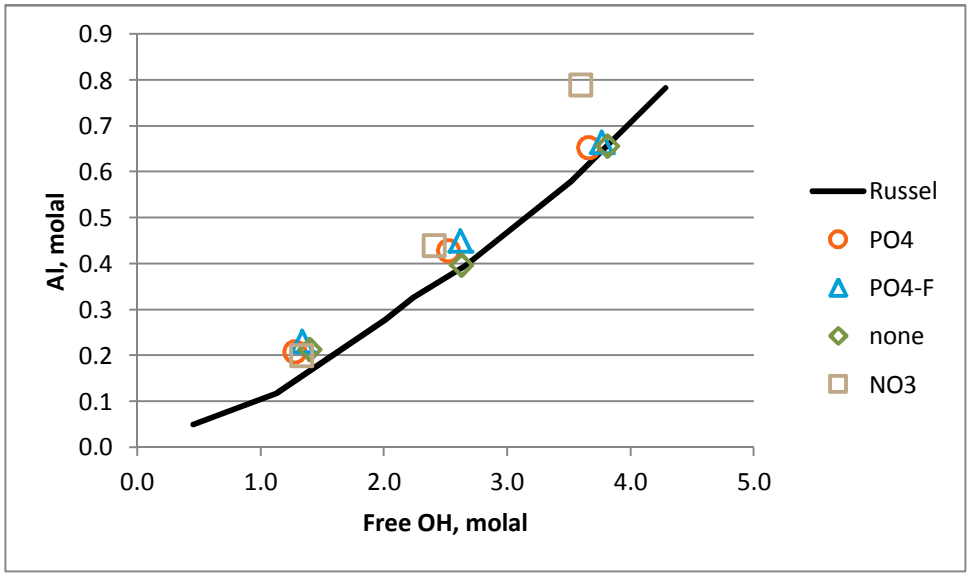
Table 6. Concentrations (in molality) of Phosphate in 40 °C Samples.

OH, molal	F Present (Runs 21/41, 25/45, 29)	F Absent (Runs 22/42, 26/46, 30)
1.3	0.19	0.42
2.5	0.10	0.20
3.7	0.08	0.14

3.2.5 Comparison to 40 °C Literature Data

Equilibrium aluminum concentrations (in molality) from Table 5 are compared to literature data for gibbsite solubility at 40 °C ("Solubility and Density of Hydrated Aluminas in NaOH Solutions" [Russell et al. 1955]) in Figure 13. The solid line represents the literature data. The diamond-shaped points represent samples with no phosphate, fluoride, or nitrate added (samples ALP2-23, -27, -31). These points generally fall very close to the literature curve. The square data points represent samples containing 3.75 m sodium nitrate (samples ALP2-24, -28, -32). These points generally fall above the literature line, representing the influence of nitrate (or ionic strength or water activity) on the gibbsite solubility. Points representing samples saturated in $Na_3PO_4 \cdot 12H_2O$ (circles) or $Na_7F(PO_4)_2 \cdot 19H_2O$ (triangles) are generally intermediate between the diamonds and squares.

Figure 13. Comparison of Sample Data (40 °C) to Literature Data (40 °C) for Gibbsite Solubility.



(Russell et al. 1955 data as amended by personal communication from Jacob Reynolds)

4 COMPARISON TO COMPUTER MODEL PREDICTIONS

Experimental results for Runs 1 – 12 (ambient temperature) and 21 – 32 (40 ^{o}C) were provided to System Planning and Modeling for the purpose of comparing experimental aluminum solubility data with numbers predicted by the Environmental Simulation Program (ESP) computer model. The data provided included the measured concentrations (in molarity) of hydroxide and phosphate, and the solution density in g/mL. Fluoride concentration was assumed to be exactly half of the measured phosphate concentration (for samples that included fluoride). Nitrate concentration was assumed to be the calculated value based on the mass of $NaNO_3$ added to the samples.

The experimental data were used as input to the Analyzer Studio (AS) function of the ESP software. The steps involved in calculating the aluminum solubility were:

1. Enter the sample compositions (in molarity) into AS 9.0.
2. Perform an equilibrium calculation.
3. Create an output stream composition.
4. Let AS calculate the Al precipitation point for this new stream.
5. Compare the resulting free OH concentration of the new stream with the input stream; increase the free OH in the new stream to match (or exceed) the input stream.
6. Iterate the Al precipitation point calculation until the resulting free OH concentration matches the original input stream.
7. Record the final output stream composition.

The AS software provided equilibrium concentrations (in molarity) of hydroxide, phosphate, fluoride, nitrate, and aluminate, plus solution density in g/mL and weight percent water. The density and $\%H_2O$ values were used to convert the molarity data to molality units. Results are shown in Table 7 beside the experimental Al_{equil} values from Table 3 and Table 5.

The agreement between the ESP-predicted results and the experimental results is generally good, but there are some consistent discrepancies.

ESP tended to predict that phosphate and/or phosphate/fluoride would lower the Al solubility by a very small amount. Experimentally, the opposite is true. The ESP results imply that there is some Al-PO4 interaction, which would cause the Al solubility to decrease, rather than increase due to the ionic strength effect. However, such an interaction does not appear to be present.

ESP correctly predicts that adding $NaNO_3$ would increase the Al solubility. Experimentally, however, the magnitude of the increase is not as great as ESP predicts, especially at 40 ^{o}C.

Finally, the effect of hydroxide concentration is not as great experimentally as the ESP results would predict. Thus, the Al/OH curve is “flatter” for the experimental data than it is for the ESP results, as shown in Figure 14, for both the 22 ^{o}C and 40 ^{o}C data.

Table 7. Comparison of Experimental Data[1] (Al_{equil}) with Environmental Simulation Program-Predicted Data (Al_{ESP}).

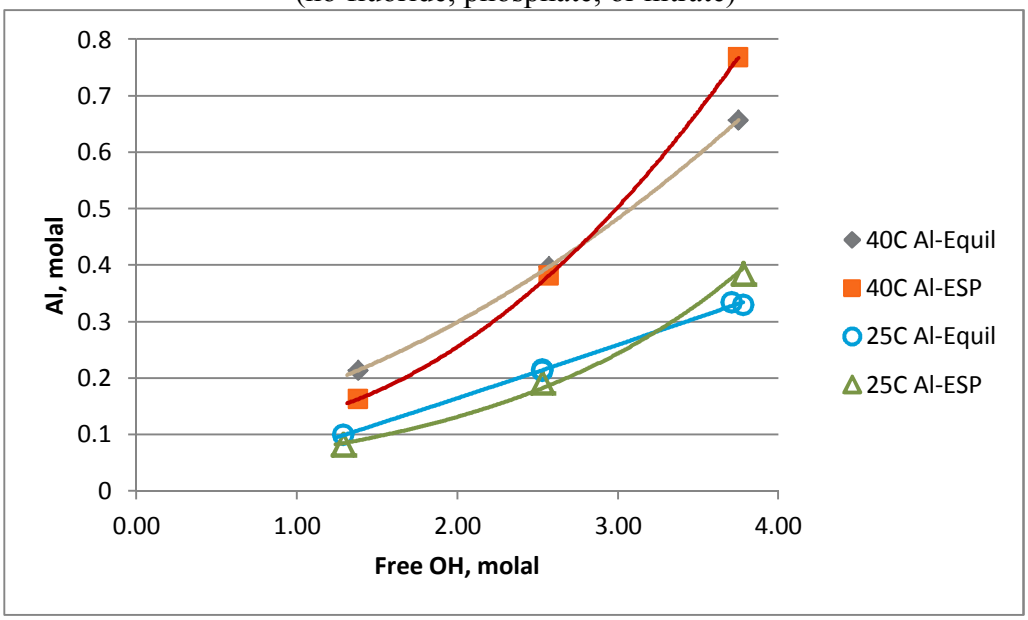
(Concentrations in Molality)

Run	T (^oC)	OH	Added Salt	Al_{equil}	Al_{ESP}
1	22	1.30	PO_4 - F	0.119	0.079
2	22	1.24	PO_4	0.133	0.074
3	22	1.30	None	0.100	0.083
4	22	1.30	NO_3	0.106	0.100
5	22	2.53	PO_4 – F	0.249	0.190
6	22	2.48	PO_4	0.255	0.184
7	22	2.54	None	0.213	0.192
8	22	2.53	NO_3	0.237	0.224
9	22	3.76	PO_4 – F	0.376	0.383
10	22	3.75	PO_4	0.376	0.383
11	22	3.76	None	0.330	0.385
12	22	3.75	NO_3	0.386	0.421
21	40	1.34	PO_4 – F	0.231	0.146
22	40	1.28	PO_4	0.207	0.142
23	40	1.40	None	0.214	0.163
24	40	1.34	NO_3	0.200	0.243
25	40	2.62	PO_4 – F	0.451	0.372
26	40	2.53	PO_4	0.429	0.359
27	40	2.63	None	0.397	0.382
28	40	2.41	NO_3	0.440	0.549
29	40	3.77	PO_4 - F	0.665	0.746
30	40	3.66	PO_4	0.653	0.723
31	40	3.81	None	0.657	0.768
32	40	3.60	NO_3	0.789	1.180

[1]OH molality is taken from the last-measured data point for each run. Al_{equil} molality is taken from a fit to the experimental data using Equation 4-2, as described earlier.

Figure 14. Comparison of Experimental Data with Environmental Simulation Program Predictions.

(no fluoride, phosphate, or nitrate)



5 ACKNOWLEDGEMENTS

Nearly all of the laboratory work for this study (sample preparation, mixing, filtration, density measurement, etc.) was skillfully performed by Margaret LaMothe. Sample analyses (ICP-AES, OH titrations) were performed by Advanced Technologies and Laboratories International, Inc., personnel. Computer modeling work (ESP) was performed by Kayla Pierson and Q. D. Ho of WRPS System Planning and Modeling.

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Appendix A

Analytical Results for Gibbsite Dissolution Samples.

Table A-1. Analytical Results for Ambient-Temperature Samples ALP2-1 through ALP2-12.

Week	1	2	3	4	5	6	7	8	9	10	11	12
	Density, g/mL											
1	1.076	1.072	(1.255)	1.216	1.118	1.114	1.102	1.251	1.155	1.158	1.154	1.287
2	1.075	1.078	1.055	1.214	1.117	1.115	1.111	1.251	1.160	1.162	1.159	1.294
3	1.076	1.077	1.056	1.219	1.116	1.114	1.105	1.250	1.160	1.160	1.158	1.295
4	1.078	1.076	1.055	1.213	1.115	1.116	1.105	1.251	1.162	1.160	1.158	1.294
5	1.077	1.078	1.057	1.218	1.117	1.115	1.107	1.254	1.165	1.161	1.158	1.295
	Al, µg/mL											
1	1270	1120	1080	801	3160	2970	2950	2560	5460	4900	7160	4920
2	1680	1580	1450	1110	3980	3810	3570	3030	6470	6350	7820	5730
3	1960	1870	1580	1300	4150	4380	4000	3460	7020	6780	7670	6180
4	2220	2200	1860	1530	5120	4870	4310	3930	7700	7750	7870	6730
5	2400	2410	2020	1700	5310	5280	4730	4360	8410	8140	8400	7600
	Na, µg/mL											
1	42100	41400	32900	111000	68400	68200	64400	138000	96900	94200	94100	161000
2	41500	41400	33100	108000	70400	67500	64700	134000	97500	98100	97700	158000
3	42100	40600	31800	104000	65500	66900	64900	133000	95900	94100	93400	155000
4	41900	41500	33100	107000	72100	66600	64000	135000	95900	97700	91600	151000
5	42700	43300	33500	109000	71000	69000	66500	139000	99300	96600	95500	160000
	P, µg/mL											
1	3180	4170	0	0	1610	1660	0	0	925	947	0	0
2	3270	4200	0	0	1730	1800	0	0	1010	1010	0	0
3	3120	4180	0	0	1620	1670	0	0	918	926	0	0
4	3140	4120	0	0	1660	1620	0	0	939	976	0	0
5	3300	4460	0	0	1760	1810	0	0	1010	1000	0	0
	OH, µg/mL											
1	22900	21900	22700	19900	43700	43300	43200	38300	63300	63700	62600	56300
2	22700	21600	22400	19900	43000	42400	43200	37900	63300	63200	63100	56000
3	22300	21300	22400	19700	43000	42300	43200	37900	62800	62800	62600	55600
4	22200	21000	22000	19600	42200	41600	42500	37600	62300	59000	60700	55100
5	22000	21000	22000	19400	42100	41300	42500	37300	61900	61800	62400	54700

Table A-2. Samples ALP2-1 through ALP2-12, Concentrations in Molarity.

Week	1	2	3	4	5	6	7	8	9	10	11	12
	Al, M											
1	0.047	0.041	0.040	0.030	0.117	0.110	0.109	0.095	0.202	0.181	0.265	0.182
2	0.062	0.059	0.054	0.041	0.147	0.141	0.132	0.112	0.240	0.235	0.290	0.212
3	0.073	0.069	0.059	0.048	0.154	0.162	0.148	0.128	0.260	0.251	0.284	0.229
4	0.082	0.081	0.069	0.057	0.190	0.180	0.160	0.146	0.285	0.287	0.291	0.249
5	0.089	0.089	0.075	0.063	0.197	0.196	0.175	0.161	0.311	0.301	0.311	0.281
	Na, M											
1	1.830	1.800	1.430	4.826	2.974	2.965	2.800	6.000	4.213	4.096	4.091	7.000
2	1.804	1.800	1.439	4.696	3.061	2.935	2.813	5.826	4.239	4.265	4.248	6.870
3	1.830	1.765	1.383	4.522	2.848	2.909	2.822	5.783	4.170	4.091	4.061	6.739
4	1.822	1.804	1.439	4.652	3.135	2.896	2.783	5.870	4.170	4.248	3.983	6.565
5	1.857	1.883	1.457	4.739	3.087	3.000	2.891	6.043	4.317	4.200	4.152	6.957
	P, M											
1	0.103	0.135	0.000	0.000	0.052	0.054	0.000	0.000	0.030	0.031	0.000	0.000
2	0.105	0.135	0.000	0.000	0.056	0.058	0.000	0.000	0.033	0.033	0.000	0.000
3	0.101	0.135	0.000	0.000	0.052	0.054	0.000	0.000	0.030	0.030	0.000	0.000
4	0.101	0.133	0.000	0.000	0.054	0.052	0.000	0.000	0.030	0.031	0.000	0.000
5	0.106	0.144	0.000	0.000	0.057	0.058	0.000	0.000	0.033	0.032	0.000	0.000
	OH, M											
1	1.347	1.288	1.335	1.171	2.571	2.547	2.541	2.253	3.724	3.747	3.682	3.312
2	1.335	1.271	1.318	1.171	2.529	2.494	2.541	2.229	3.724	3.718	3.712	3.294
3	1.312	1.253	1.318	1.159	2.529	2.488	2.541	2.229	3.694	3.694	3.682	3.271
4	1.306	1.235	1.294	1.153	2.482	2.447	2.500	2.212	3.665	3.471	3.571	3.241
5	1.294	1.235	1.294	1.141	2.476	2.429	2.500	2.194	3.641	3.635	3.671	3.218

Table A-3. Samples ALP2-1 through ALP2-12, Concentrations in Molality.

	1	2	3	4	5	6	7	8	9	10	11	12
	Conversion Factors											
g[1]	89.15	88.97	85.08	110.59	93.07	92.92	90.00	115.54	97.02	96.93	94.98	120.54
mL[2]	82.82	82.68	80.58	90.93	83.34	83.36	81.39	92.33	83.61	83.55	82.06	93.22
g[3]	82.17	82.19	80.02	80.01	81.63	81.63	80.01	80.03	81.08	81.08	80.01	80.00
kg/L[4]	0.992	0.994	0.993	0.880	0.979	0.979	0.983	0.867	0.970	0.971	0.975	0.858
Week	**Al, m**											
1	0.047	0.042	0.040	0.034	0.119	0.112	0.111	0.109	0.209	0.187	0.272	0.212
2	0.063	0.059	0.054	0.047	0.150	0.144	0.134	0.129	0.247	0.242	0.297	0.247
3	0.073	0.070	0.059	0.055	0.157	0.166	0.151	0.148	0.268	0.259	0.291	0.267
4	0.083	0.082	0.069	0.064	0.194	0.184	0.162	0.168	0.294	0.296	0.299	0.290
5	0.090	0.090	0.075	0.072	0.201	0.200	0.178	0.186	0.321	0.311	0.319	0.328
	Na, m											
1	1.845	1.811	1.440	5.485	3.036	3.028	2.848	6.922	4.344	4.220	4.196	8.157
2	1.819	1.811	1.449	5.337	3.125	2.997	2.861	6.721	4.371	4.395	4.357	8.005
3	1.845	1.776	1.392	5.139	2.908	2.971	2.870	6.671	4.299	4.216	4.165	7.853
4	1.836	1.815	1.449	5.287	3.201	2.957	2.830	6.772	4.299	4.377	4.085	7.650
5	1.871	1.894	1.467	5.386	3.152	3.064	2.941	6.972	4.452	4.328	4.259	8.106
	P, m											
1	0.103	0.135	0.000	0.000	0.053	0.055	0.000	0.000	0.031	0.031	0.000	0.000
2	0.106	0.136	0.000	0.000	0.057	0.059	0.000	0.000	0.034	0.034	0.000	0.000
3	0.101	0.136	0.000	0.000	0.053	0.055	0.000	0.000	0.031	0.031	0.000	0.000
4	0.102	0.134	0.000	0.000	0.055	0.053	0.000	0.000	0.031	0.032	0.000	0.000
5	0.107	0.145	0.000	0.000	0.058	0.060	0.000	0.000	0.034	0.033	0.000	0.000
	OH, m											
1	1.358	1.296	1.345	1.330	2.624	2.601	2.585	2.599	3.839	3.861	3.777	3.859
2	1.346	1.278	1.327	1.330	2.582	2.547	2.585	2.572	3.839	3.831	3.807	3.838
3	1.322	1.260	1.327	1.317	2.582	2.541	2.585	2.572	3.809	3.806	3.777	3.811
4	1.316	1.243	1.303	1.310	2.534	2.499	2.543	2.552	3.779	3.576	3.662	3.777
5	1.304	1.243	1.303	1.297	2.528	2.481	2.543	2.531	3.755	3.746	3.765	3.749

[1]Mass (g) of liquid phase based on mass of reagents added, assuming 25% dissolution of gibbsite, sodium phosphate, and sodium fluoride.
[2]Volume (mL) of liquid phase, based on calculated total mass and measured density.
[3]Mass (g) of H_2O, assuming 25% dissolution of sodium phosphate reagent.
[4]Mass (kg) of H_2O per L of liquid phase.

Table A-4. Analytical Results for Ambient-Temperature Samples ALP2-55 through ALP2-62.

Week	55	56	57	58	59	60	61	62
	Density, g/mL							
2	1.117	1.112	1.110	1.255	1.158	1.160	1.159	1.292
4	1.117	1.112	1.110	1.255	1.158	1.160	1.159	1.292
6	1.119	1.116	1.108	1.256	1.162	1.162	1.162	1.293
8	1.117	1.115	1.113	1.255	1.163	1.163	1.160	1.294
10	1.119	1.115	1.113	1.256	1.162	1.163	1.158	1.296
	Al, µg/mL							
2	4010	3890	3380	2670	7240	7320	7370	5940
4	4600	4660	4070	3540	8170	8130	7480	6390
6	5060	4850	4320	3850	8300	8350	7720	7110
8	5190	5150	4980	4360	8400	8690	8130	8310
10	5420	5300	5000	4780	8880	8860	8520	8460
	Na, µg/mL							
2	65500	64400	59400	124000	91600	92800	93400	151000
4	65100	63900	60900	128000	95500	93600	91400	141000
6	67400	62700	60700	123000	93200	93000	90300	146000
8	66600	64800	65500	128000	90800	92500	89800	157000
10	68600	66300	64400	135000	96600	95600	94400	159000
	P, µg/mL							
2	1620	1690	0	0	927	961	966	0
4	1660	1600	0	0	969	922	0	0
6	1500	1440	0	0	868	837	0	0
8	1470	1520	0	0	878	868	0	0
10	1520	1590	0	0	895	900	0	0
	OH, µg/mL							
2	42500	42100	43600	38700	61700	61700	61700	55300
4	42200	41500	42900	37700	61400	61600	62500	54600
6	41400	40500	42800	37900	61500	75200	62600	52600
8	41800	41300	42400	37500	61000	60700	62100	53700
10	41600	40800	42500	37300	60500	61600	61600	53600

Table A-5. Samples ALP2-1 through ALP2-12, Concentrations in Molarity.

Week	55	56	57	58	59	60	61	62
	Al, M							
2	0.149	0.144	0.125	0.099	0.268	0.271	0.273	0.220
4	0.170	0.173	0.151	0.131	0.303	0.301	0.277	0.237
6	0.187	0.180	0.160	0.143	0.307	0.309	0.286	0.263
8	0.192	0.191	0.184	0.161	0.311	0.322	0.301	0.308
10	0.201	0.196	0.185	0.177	0.329	0.328	0.316	0.313
	Na, M							
2	2.848	2.800	2.583	5.391	3.983	4.035	4.061	6.565
4	2.830	2.778	2.648	5.565	4.152	4.070	3.974	6.130
6	2.930	2.726	2.639	5.348	4.052	4.043	3.926	6.348
8	2.896	2.817	2.848	5.565	3.948	4.022	3.904	6.826
10	2.983	2.883	2.800	5.870	4.200	4.157	4.104	6.913
	P, M							
2	0.052	0.055	0.000	0.000	0.030	0.031	0.031	0.000
4	0.054	0.052	0.000	0.000	0.031	0.030	0.000	0.000
6	0.048	0.046	0.000	0.000	0.028	0.027	0.000	0.000
8	0.047	0.049	0.000	0.000	0.028	0.028	0.000	0.000
10	0.049	0.051	0.000	0.000	0.029	0.029	0.000	0.000
	OH, M							
2	2.500	2.476	2.565	2.276	3.629	3.629	3.629	3.253
4	2.482	2.441	2.524	2.218	3.612	3.624	3.676	3.212
6	2.435	2.382	2.518	2.229	3.618	4.424	3.682	3.094
8	2.459	2.429	2.494	2.206	3.588	3.571	3.653	3.159
10	2.447	2.400	2.500	2.194	3.559	3.624	3.624	3.153

Table A-6. Samples ALP2-1 through ALP2-12, Concentrations in Molality.

	55	56	57	58	59	60	61	62
	Conversion Factors							
g[1]	93.07	92.92	90.01	115.51	97.03	96.96	94.97	120.49
mL[2]	83.28	83.41	81.02	92.01	83.60	83.48	81.89	93.16
g[3]	81.63	81.63	80.02	80.01	81.10	81.10	80.01	80.01
kg/L[4]	0.980	0.979	0.988	0.870	0.970	0.972	0.977	0.859
Week	**Al, m**							
2	0.152	0.147	0.127	0.114	0.276	0.279	0.279	0.256
4	0.174	0.176	0.153	0.151	0.312	0.310	0.284	0.276
6	0.191	0.184	0.162	0.164	0.317	0.318	0.293	0.307
8	0.196	0.195	0.187	0.186	0.321	0.331	0.308	0.358
10	0.205	0.201	0.188	0.204	0.339	0.338	0.323	0.365
	Na, m							
2	2.905	2.861	2.615	6.200	4.105	4.153	4.157	7.644
4	2.888	2.839	2.681	6.400	4.280	4.189	4.068	7.138
6	2.990	2.785	2.672	6.150	4.177	4.162	4.019	7.391
8	2.954	2.879	2.884	6.400	4.069	4.139	3.996	7.948
10	3.043	2.945	2.835	6.750	4.329	4.278	4.201	8.049
	P, m							
2	0.053	0.056	0.000	0.000	0.031	0.032	0.032	0.000
4	0.055	0.053	0.000	0.000	0.032	0.031	0.000	0.000
6	0.049	0.047	0.000	0.000	0.029	0.028	0.000	0.000
8	0.048	0.050	0.000	0.000	0.029	0.029	0.000	0.000
10	0.050	0.052	0.000	0.000	0.030	0.030	0.000	0.000
	OH, m							
2	2.551	2.530	2.597	2.618	3.741	3.736	3.715	3.787
4	2.533	2.494	2.555	2.550	3.723	3.730	3.763	3.739
6	2.485	2.434	2.549	2.564	3.729	4.553	3.769	3.603
8	2.509	2.482	2.525	2.537	3.699	3.675	3.739	3.678
10	2.497	2.452	2.531	2.523	3.668	3.730	3.709	3.671

[1]Mass (g) of liquid phase based on mass of reagents added, assuming 25% dissolution of gibbsite, sodium phosphate, and sodium fluoride.
[2]Volume (mL) of liquid phase, based on calculated total mass and measured density.
[3]Mass (g) of H_2O, assuming 25% dissolution of sodium phosphate reagent.
[4]Mass (kg) of H_2O per L of liquid phase.

Table A-7. Analytical Results for 40 °C Samples ALP2-21 through ALP2-27.

Day	21	22	23	24	25	26	27
	Density, g/mL (Undiluted Sample)						
1	1.091	1.125	1.059	1.211	1.126	1.133	1.111
2	1.093	1.125	1.058	1.210	1.127	1.137	1.114
3	1.095	1.125	1.058	1.213	1.128	1.137	1.115
4	1.092	1.112	1.064	1.211	1.128	1.141	1.116
7	1.092	1.126	1.066	1.212	1.129	1.139	1.115
	Al, µg/mL (Diluted Sample 10/25)						
1	1330	1560	1340	893	1960	2090	2970
2	1700	1760	1590	1120	2940	2650	3200
3	1830	1810	1690	1280	3380	3370	3360
4	1850	1910	1800	1370	3760	3450	3500
7	2160	2110	2040	1590	3870	3760	3880
	Na, µg/mL (Diluted Sample 10/25)						
1	18900	25600	13500	45600	31800	33200	28700
2	19800	24800	14300	47300	31900	33800	29100
3	20200	25400	14300	46900	30700	33400	28800
4	19500	22700	14500	46500	32900	33300	28900
7	19800	25600	15100	47300	31900	33500	30500
	P, µg/mL (Diluted Sample 10/25)						
1	2260	5760	0	0	1100	2140	0
2	2390	5200	0	0	1170	2230	0
3	2420	5390	0	0	1140	2300	0
4	2270	4050	0	0	1210	2350	0
7	2230	5000	0	0	1170	2290	0
	OH, µg/mL (Diluted Sample 10/25)						
1	9140	8670	9320	8280	18200	17400	17300
2	8990	8520	9170	8030	17700	17100	17400
3	8940	8560	9140	8080	16900	16600	17300
4	8930	8740	8790	8050	16800	16300	17200
7	8770	8700	9240	7820	16600	16200	17000

Table A-8. Samples ALP2-21 through ALP2-27, Concentrations in Molarity.

Day	21	22	23	24	25	26	27
	Al, M (Undiluted Sample)						
1	0.123	0.144	0.124	0.083	0.181	0.194	0.275
2	0.157	0.163	0.147	0.104	0.272	0.245	0.296
3	0.169	0.168	0.156	0.119	0.313	0.312	0.311
4	0.171	0.177	0.167	0.127	0.348	0.319	0.324
7	0.200	0.195	0.189	0.147	0.358	0.348	0.359
	Na, M (Undiluted Sample)						
1	2.054	2.783	1.467	4.957	3.457	3.609	3.120
2	2.152	2.696	1.554	5.141	3.467	3.674	3.163
3	2.196	2.761	1.554	5.098	3.337	3.630	3.130
4	2.120	2.467	1.576	5.054	3.576	3.620	3.141
7	2.152	2.783	1.641	5.141	3.467	3.641	3.315
	P, M (Undiluted Sample)						
1	0.182	0.465	0.000	0.000	0.089	0.173	0.000
2	0.193	0.419	0.000	0.000	0.094	0.180	0.000
3	0.195	0.435	0.000	0.000	0.092	0.185	0.000
4	0.183	0.327	0.000	0.000	0.098	0.190	0.000
7	0.180	0.403	0.000	0.000	0.094	0.185	0.000
	OH, M (Undiluted Sample)						
1	1.344	1.275	1.371	1.218	2.676	2.559	2.544
2	1.322	1.253	1.349	1.181	2.603	2.515	2.559
3	1.315	1.259	1.344	1.188	2.485	2.441	2.544
4	1.313	1.285	1.293	1.184	2.471	2.397	2.529
7	1.290	1.279	1.359	1.150	2.441	2.382	2.500

Table A-9. Samples ALP2-21 through ALP2-27, Concentrations in Molality.

	21	22	23	24	25	26	27
	Conversion Factors						
g[1]	95.37	95.02	87.23	112.73	101.76	101.34	93.53
mL[2]	87.44	84.42	82.34	93.10	90.39	89.42	84.20
g[3]	84.32	84.33	80.00	80.01	84.34	84.33	80.02
kg/L[4]	0.964	0.999	0.972	0.859	0.933	0.943	0.950
Day	**Al, m (Undiluted Sample)**						
1	0.128	0.145	0.128	0.096	0.194	0.205	0.289
2	0.163	0.163	0.152	0.121	0.292	0.260	0.312
3	0.176	0.168	0.161	0.138	0.335	0.331	0.327
4	0.178	0.177	0.172	0.148	0.373	0.339	0.341
7	0.207	0.196	0.194	0.171	0.384	0.369	0.378
	Na, m (Undiluted Sample)						
1	2.130	2.786	1.510	5.768	3.704	3.827	3.283
2	2.232	2.699	1.600	5.983	3.716	3.896	3.328
3	2.277	2.764	1.600	5.932	3.576	3.850	3.294
4	2.198	2.470	1.622	5.881	3.833	3.838	3.306
7	2.232	2.786	1.689	5.983	3.716	3.861	3.489
	P, m (Undiluted Sample)						
1	0.189	0.465	0.000	0.000	0.095	0.183	0.000
2	0.200	0.420	0.000	0.000	0.101	0.191	0.000
3	0.202	0.435	0.000	0.000	0.099	0.197	0.000
4	0.190	0.327	0.000	0.000	0.105	0.201	0.000
7	0.186	0.404	0.000	0.000	0.101	0.196	0.000
	OH, m (Undiluted Sample)						
1	1.394	1.276	1.411	1.417	2.868	2.713	2.677
2	1.371	1.254	1.388	1.374	2.790	2.667	2.693
3	1.363	1.260	1.383	1.383	2.664	2.589	2.677
4	1.362	1.287	1.330	1.378	2.648	2.542	2.662
7	1.337	1.281	1.398	1.338	2.616	2.526	2.631

[1]Mass (g) of liquid phase based on mass of reagents added, assuming 25% dissolution of gibbsite, sodium phosphate, and sodium fluoride.
[2]Volume (mL) of liquid phase, based on calculated total mass and measured density.
[3]Mass (g) of H_2O, assuming 25% dissolution of sodium phosphate reagent.
[4]Mass (kg) of H_2O per L of liquid phase.

Table A-10. Analytical Results for 40 °C Samples ALP2-28 through ALP2-47.

Day	28	29	30	31	32	Day	41	42	43	44	45	46	47
	Density, g/mL (Undiluted Sample)												
1	1.252	1.171	1.174	1.160	1.293	1	1.086	1.120	1.060	1.213	1.120	1.136	1.117
4	1.258	1.172	1.179	1.167	1.296	5	1.090	1.127	1.060	1.216	1.130	1.138	1.119
7	1.256	1.174	1.183	1.170	1.300	7	1.091	1.126	1.061	1.214	1.127	1.138	1.118
10	1.254	1.177	1.182	1.169	1.301	9	1.092	1.126	1.060	1.212	1.130	1.143	1.113
14	1.248	1.176	1.178	1.171	1.298	14	1.095	1.124	1.061	1.215	1.130	1.142	1.120
	Al, µg/mL (Diluted Sample 10/25)												
1	1990	5130	5210	4710	4460	1	571	565	1240	705	1600	2260	4670
4	3160	5600	5850	5790	5830	5	1360	1600	1510	1360	3200	3490	3820
7	3540	6310	6070	6090	6220	7	1630	1650	1590	1450	3490	3640	4720
10	3810	6530	6290	6330	6520	9	1720	1680	1640	1510	3660	3700	4680
14	3700	6450	6430	6440	6800	14	1810	1690	1700	1660	3750	3720	4670
	Na, µg/mL (Diluted Sample 10/25)												
1	56100	41800	41900	41200	67600	1	19100	25000	13300	45300	27900	31400	26900
4	56600	43200	43600	41300	66000	5	19400	24600	13500	44200	29700	31900	22100
7	55300	42300	43000	37100	63500	7	19700	25900	13800	43000	29700	31300	27300
10	52800	40200	39800	36900	60800	9	19600	25500	13700	42100	29800	30800	27100
14	50500	40200	40700	38600	61900	14	19700	24900	13700	42200	29400	30100	27200
	P, µg/mL (Diluted Sample 10/25)												
1	0	772	1290	0	0	1	1940	5400	0	0	989	2430	0
4	0	986	1660	0	0	5	2320	5350	0	0	1290	2440	0
7	0	957	1600	0	0	7	2390	5550	0	0	1310	2500	0
10	0	912	1510	0	0	9	2330	5430	0	0	1290	2460	0
14	0	918	1600	0	0	14	2340	5380	0	0	1280	2420	0
	OH, µg/mL (Diluted Sample 10/25)												
1	15600	24400	23800	25200	21800	1	9480	8960	9170	8550	17800	16900	16400
4	14900	23800	23400	24500	20000	5	9000	8300	9000	8350	17000	16300	16500
7	14700	23500	22900	23000	19700	7	8830	8260	8920	7930	16700	16000	16300
10	14300	23600	23300	24200	20500	9	8670	8530	8930	7950	17000	16000	16300
14	13800	23400	22900	24100	20200	14	8680	8100	8870	7810	16700	16000	16400

Table A-11. Samples ALP2-28 through ALP2-47, Concentrations in Molarity.

Day	28	29	30	31	32	Day	41	42	43	44	45	46	47
	Al, M (Undiluted Sample)												
1	0.184	0.475	0.482	0.436	0.413	1	0.053	0.052	0.115	0.065	0.148	0.209	0.432
4	0.293	0.519	0.542	0.536	0.540	5	0.126	0.148	0.140	0.126	0.296	0.323	0.354
7	0.328	0.584	0.562	0.564	0.576	7	0.151	0.153	0.147	0.134	0.323	0.337	0.437
10	0.353	0.605	0.582	0.586	0.604	9	0.159	0.156	0.152	0.140	0.339	0.343	0.433
14	0.343	0.597	0.595	0.596	0.630	14	0.168	0.156	0.157	0.154	0.347	0.344	0.432
	Na, M (Undiluted Sample)												
1	6.098	4.543	4.554	4.478	7.348	1	2.076	2.717	1.446	4.924	3.033	3.413	2.924
4	6.152	4.696	4.739	4.489	7.174	5	2.109	2.674	1.467	4.804	3.228	3.467	2.402
7	6.011	4.598	4.674	4.033	6.902	7	2.141	2.815	1.500	4.674	3.228	3.402	2.967
10	5.739	4.370	4.326	4.011	6.609	9	2.130	2.772	1.489	4.576	3.239	3.348	2.946
14	5.489	4.370	4.424	4.196	6.728	14	2.141	2.707	1.489	4.587	3.196	3.272	2.957
	P, M (Undiluted Sample)												
1	0.000	0.062	0.104	0.000	0.000	1	0.156	0.435	0.000	0.000	0.080	0.196	0.000
4	0.000	0.080	0.134	0.000	0.000	5	0.187	0.431	0.000	0.000	0.104	0.197	0.000
7	0.000	0.077	0.129	0.000	0.000	7	0.193	0.448	0.000	0.000	0.106	0.202	0.000
10	0.000	0.074	0.122	0.000	0.000	9	0.188	0.438	0.000	0.000	0.104	0.198	0.000
14	0.000	0.074	0.129	0.000	0.000	14	0.189	0.434	0.000	0.000	0.103	0.195	0.000
	OH, M (Undiluted Sample)												
1	2.294	3.588	3.500	3.706	3.206	1	1.394	1.318	1.349	1.257	2.618	2.485	2.412
4	2.191	3.500	3.441	3.603	2.941	5	1.324	1.221	1.324	1.228	2.500	2.397	2.426
7	2.162	3.456	3.368	3.382	2.897	7	1.299	1.215	1.312	1.166	2.456	2.353	2.397
10	2.103	3.471	3.426	3.559	3.015	9	1.275	1.254	1.313	1.169	2.500	2.353	2.397
14	2.029	3.441	3.368	3.544	2.971	14	1.276	1.191	1.304	1.149	2.456	2.353	2.412

Table A-12. Samples ALP2-28 through ALP2-47, Concentrations in Molality.

Day	28	29	30	31	32	Day	41	42	43	44	45	46	47
	Conversion Factors												
g[1]	119.0	108.1	107.7	99.9	125.4	--	95.4	95.0	87.2	112.7	101.8	101.3	93.5
mL[2]	95.1	92.3	91.7	86.1	97.0	--	87.9	84.8	82.3	92.9	90.9	89.1	83.7
g[3]	80.0	84.3	84.3	80.0	80.0	--	84.3	84.3	80.0	80.0	84.3	84.3	80.0
kg/L[4]	0.842	0.914	0.920	0.929	0.825	--	0.959	0.994	0.972	0.861	0.928	0.946	0.956
	Al, m (Undiluted Sample)												
1	0.219	0.520	0.524	0.469	0.501	1	0.055	0.053	0.118	0.076	0.160	0.221	0.453
4	0.348	0.568	0.589	0.577	0.655	5	0.131	0.149	0.144	0.146	0.319	0.342	0.370
7	0.389	0.640	0.611	0.607	0.698	7	0.157	0.154	0.151	0.156	0.348	0.356	0.457
10	0.419	0.662	0.633	0.631	0.732	9	0.166	0.156	0.156	0.162	0.365	0.362	0.453
14	0.407	0.654	0.647	0.642	0.763	14	0.175	0.157	0.162	0.179	0.374	0.364	0.453
	Na, m (Undiluted Sample)												
1	7.246	4.974	4.952	4.819	8.909	1	2.164	2.733	1.487	5.719	3.268	3.608	3.060
4	7.310	5.140	5.153	4.831	8.698	5	2.198	2.689	1.509	5.580	3.479	3.665	2.514
7	7.143	5.033	5.082	4.340	8.369	7	2.232	2.831	1.542	5.428	3.479	3.596	3.105
10	6.820	4.783	4.704	4.316	8.013	9	2.220	2.787	1.531	5.315	3.491	3.539	3.083
14	6.523	4.783	4.810	4.515	8.158	14	2.232	2.722	1.531	5.327	3.444	3.458	3.094
	P, m (Undiluted Sample)												
1	0.000	0.068	0.113	0.000	0.000	1	0.163	0.438	0.000	0.000	0.086	0.207	0.000
4	0.000	0.087	0.146	0.000	0.000	5	0.195	0.434	0.000	0.000	0.112	0.208	0.000
7	0.000	0.084	0.140	0.000	0.000	7	0.201	0.450	0.000	0.000	0.114	0.213	0.000
10	0.000	0.081	0.132	0.000	0.000	9	0.196	0.440	0.000	0.000	0.112	0.210	0.000
14	0.000	0.081	0.140	0.000	0.000	14	0.197	0.436	0.000	0.000	0.111	0.206	0.000
	OH, m (Undiluted Sample)												
1	2.726	3.928	3.805	3.988	3.887	1	1.453	1.325	1.387	1.460	2.821	2.627	2.524
4	2.604	3.831	3.741	3.877	3.566	5	1.379	1.227	1.361	1.426	2.694	2.534	2.539
7	2.569	3.783	3.661	3.640	3.513	7	1.353	1.222	1.349	1.354	2.647	2.487	2.509
10	2.499	3.799	3.725	3.830	3.655	9	1.329	1.262	1.350	1.358	2.694	2.487	2.509
14	2.411	3.767	3.661	3.814	3.602	14	1.330	1.198	1.341	1.334	2.647	2.487	2.524

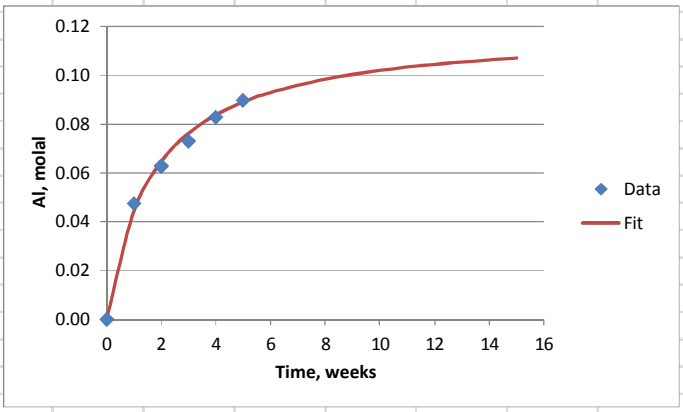
[1]Mass (g) of liquid phase based on mass of reagents added, assuming 25% dissolution of gibbsite, sodium phosphate, and sodium fluoride.
[2]Volume (mL) of liquid phase, based on calculated total mass and measured density.
[3]Mass (g) of H_2O, assuming 25% dissolution of sodium phosphate reagent.
[4]Mass (kg) of H_2O per L of liquid phase.

APPENDIX B

Gibbsite Dissolution Rate Plots

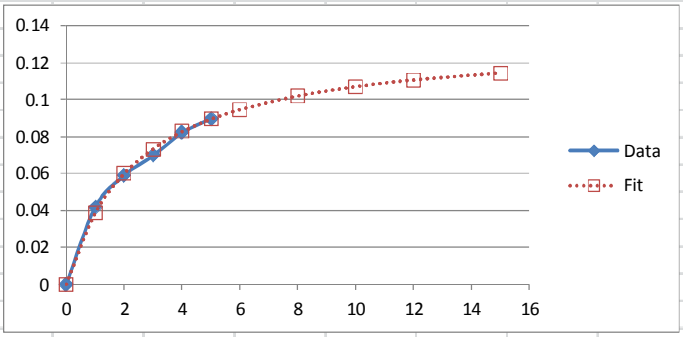
Run 1

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.119	1.695	0.000	0
1	0.047			0.044	9.99E-06
2	0.063			0.065	3.36E-06
3	0.073			0.076	9.20E-06
4	0.083			0.084	7.86E-07
5	0.090			0.089	2.82E-07
6				0.093	2.50E-05
8				0.098	
10				0.102	
12				0.104	
15				0.107	



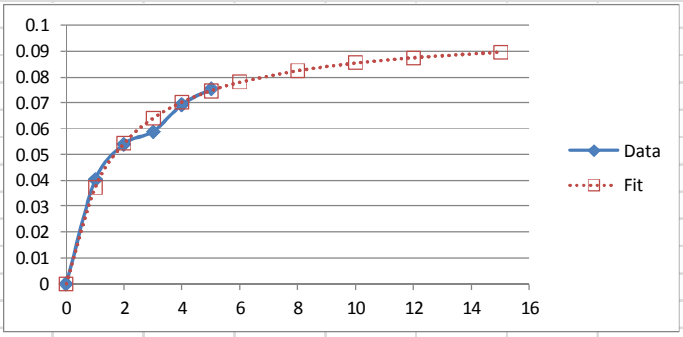
Run 2

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.133	2.454	0.000	0
1	0.042			0.039	1.00E-05
2	0.059			0.060	8.79E-07
3	0.070			0.073	1.29E-05
4	0.082			0.083	3.31E-07
5	0.090			0.089	2.08E-07
6				0.095	2.54E-05
8				0.102	
10				0.107	
12				0.111	
15				0.114	



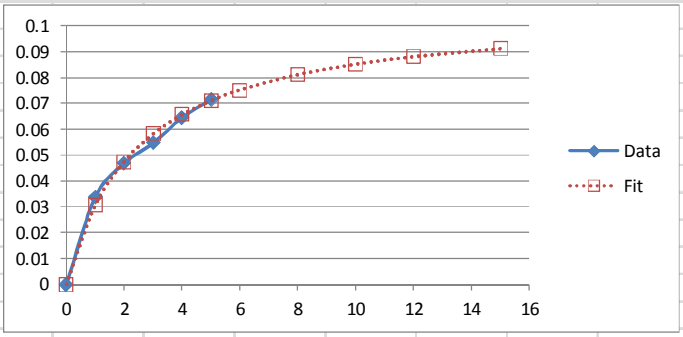
Run 3

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.100	1.662	0.000	0
1	0.040			0.037	8.43E-06
2	0.054			0.054	6.79E-08
3	0.059			0.064	2.60E-05
4	0.069			0.070	8.48E-07
5	0.075			0.075	4.39E-07
6				0.078	3.80E-05
8				0.082	
10				0.085	
12				0.087	
15				0.090	



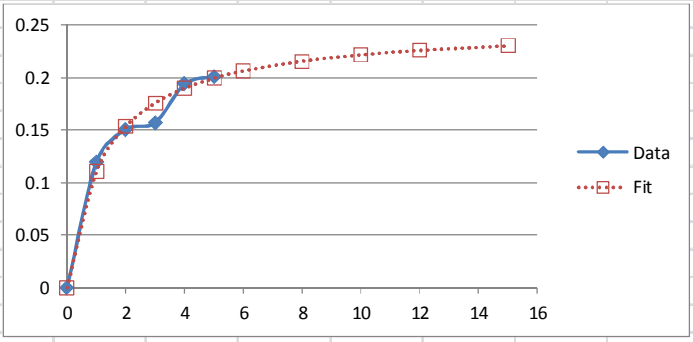
Run 4

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.106	2.471	0.000	0
1	0.034			0.031	9.83E-06
2	0.047			0.047	5.75E-07
3	0.055			0.058	1.21E-05
4	0.064			0.066	1.46E-06
5	0.072			0.071	2.72E-07
6				0.075	2.56E-05
8				0.081	
10				0.085	
12		0.053		0.088	
15	2.5	0.053		0.091	



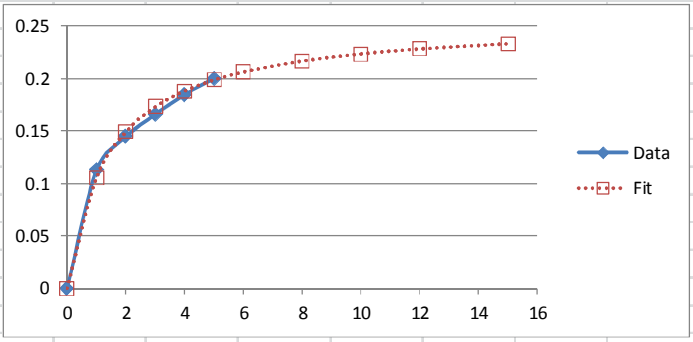
Run 5

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.249	1.256	0.000	0
1	0.119			0.110	8.14E-05
2	0.150			0.153	6.65E-06
3	0.157			0.176	3.51E-04
4	0.194			0.190	1.56E-05
5	0.201			0.199	2.63E-06
6				0.206	4.70E-04
8				0.215	
10				0.221	
12				0.226	
15				0.230	



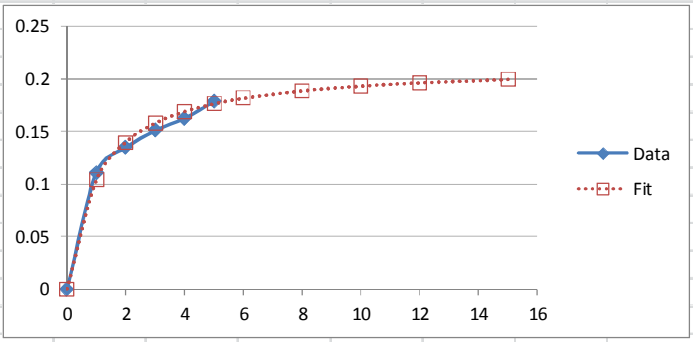
Run 6

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.255	1.426	0.000	0
1	0.112			0.105	5.37E-05
2	0.144			0.149	2.12E-05
3	0.166			0.173	4.89E-05
4	0.184			0.188	1.28E-05
5	0.200			0.198	2.28E-06
6				0.206	1.50E-04
8				0.216	
10				0.223	
12				0.228	
15				0.233	



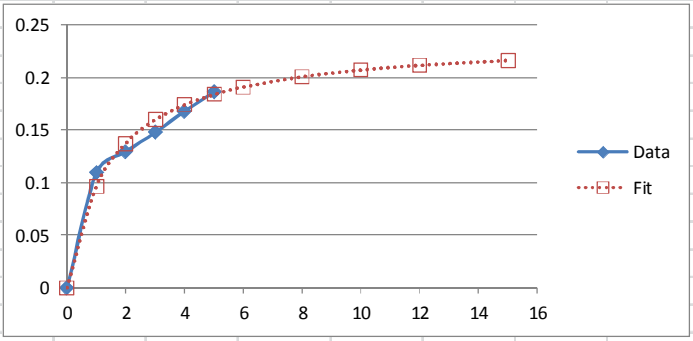
Run 7

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.213	1.054	0.000	0
1	0.111			0.104	5.35E-05
2	0.134			0.140	2.67E-05
3	0.151			0.158	5.08E-05
4	0.162			0.169	4.12E-05
5	0.178			0.176	4.22E-06
6				0.181	1.98E-04
8				0.188	
10				0.193	
12				0.196	
15				0.199	



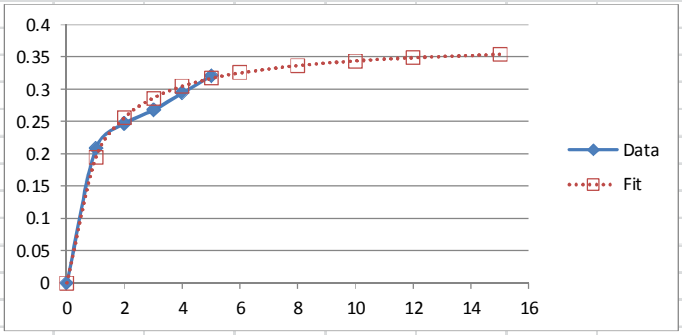
Run 8

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.237	1.450	0.000	0
1	0.109			0.097	1.60E-04
2	0.129			0.137	6.29E-05
3	0.148			0.160	1.43E-04
4	0.168			0.174	3.64E-05
5	0.186			0.184	6.56E-06
6				0.191	4.41E-04
8				0.201	
10				0.207	
12				0.211	
15				0.216	



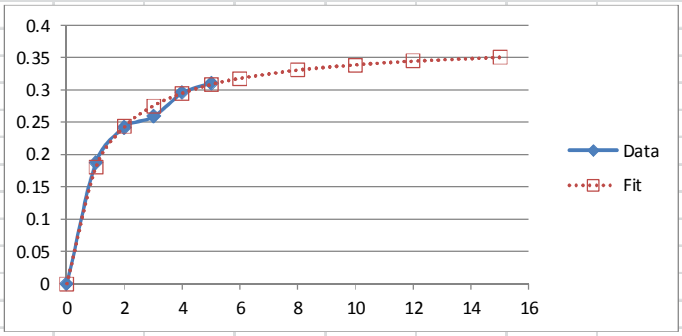
Run 9

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.376	0.938	0.000	0
1	0.209			0.194	2.06E-04
2	0.247			0.256	8.25E-05
3	0.268			0.287	3.46E-04
4	0.294			0.305	1.16E-04
5	0.321			0.317	1.84E-05
6				0.325	8.61E-04
8				0.337	
10				0.344	
12				0.349	
15				0.354	



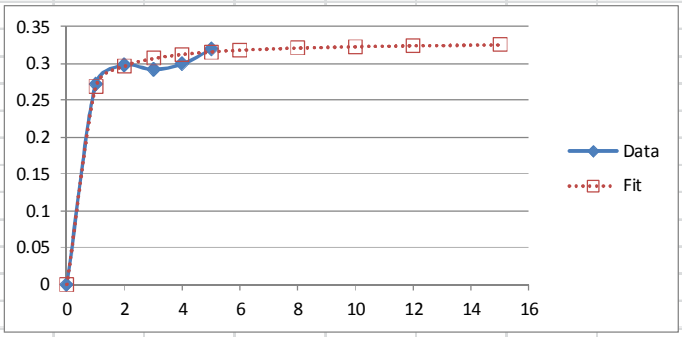
Run 10

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.376	1.093	0.000	0
1	0.187			0.180	5.28E-05
2	0.242			0.243	8.64E-07
3	0.259			0.276	2.89E-04
4	0.296			0.295	7.67E-08
5	0.311			0.309	3.63E-06
6				0.318	3.65E-04
8				0.331	
10				0.339	
12				0.345	
15				0.351	



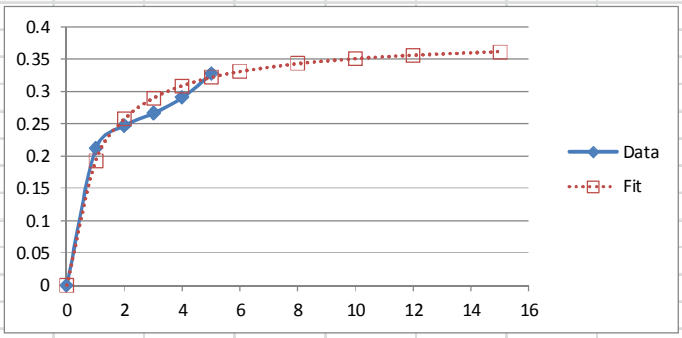
Run 11

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.330	0.229	0.000	0
1	0.272			0.268	1.42E-05
2	0.297			0.296	1.56E-06
3	0.291			0.306	2.24E-04
4	0.299			0.312	1.66E-04
5	0.319			0.315	1.46E-05
6				0.318	4.93E-04
8				0.321	
10				0.322	
12				0.324	
15				0.325	



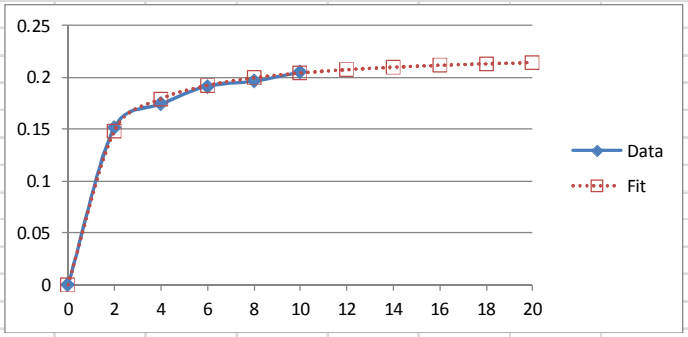
Run 12

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.386	0.993	0.000	0
1	0.212			0.194	3.50E-04
2	0.247			0.258	1.12E-04
3	0.267			0.290	5.40E-04
4	0.290			0.309	3.50E-04
5	0.328			0.322	3.62E-05
6				0.331	1.57E-03
8				0.343	
10				0.351	
12				0.356	
15				0.362	



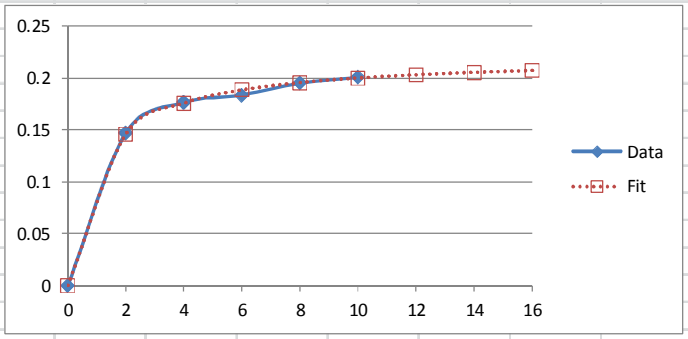
Run 55

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.225	1.033	0.000	0
2	0.152			0.148	1.04E-05
4	0.174			0.179	2.43E-05
6	0.191			0.192	4.65E-07
8	0.196			0.199	9.53E-06
10	0.205			0.204	8.83E-07
12				0.207	5.00E-05
14				0.209	
16				0.211	
18				0.213	
20				0.214	



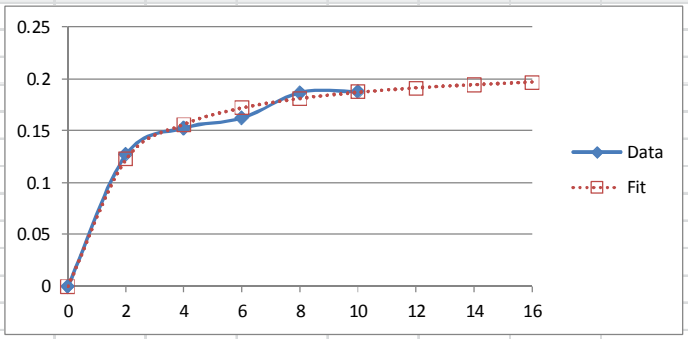
Run 56

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.220	1.013	0.000	0
2	0.147			0.146	1.10E-06
4	0.176			0.176	4.25E-07
6	0.184			0.188	2.35E-05
8	0.195			0.195	3.06E-07
10	0.201			0.200	3.95E-07
12				0.203	2.77E-05
14				0.205	
16				0.207	
18				0.208	
20				0.210	



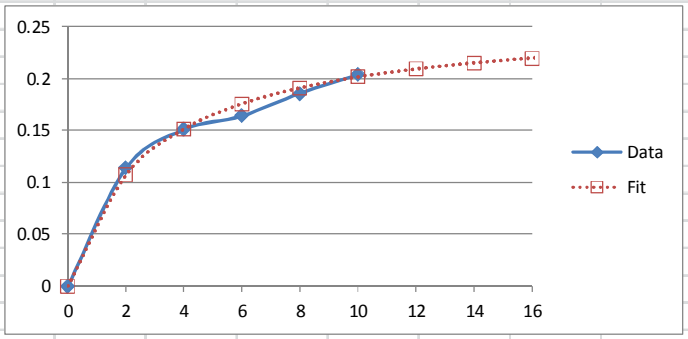
Run 57

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.215	1.525	0.000	0
2	0.127			0.122	2.02E-05
4	0.153			0.156	1.14E-05
6	0.162			0.172	9.61E-05
8	0.187			0.181	3.34E-05
10	0.188			0.187	3.00E-07
12				0.191	1.63E-04
14				0.194	
16				0.197	
18				0.199	
20				0.200	



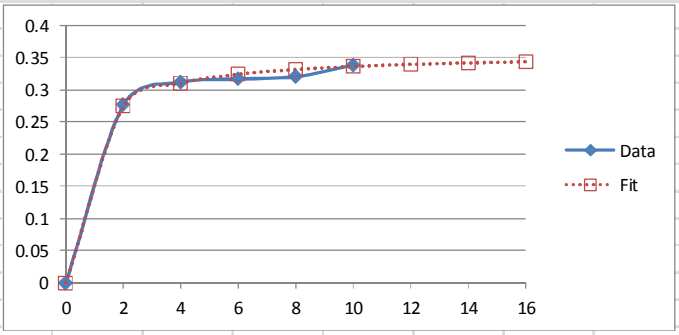
Run 58

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.259	2.839	0.000	0
2	0.114			0.107	4.57E-05
4	0.151			0.151	3.48E-07
6	0.164			0.176	1.37E-04
8	0.186			0.191	2.82E-05
10	0.204			0.202	4.06E-06
12				0.209	2.35E-04
14				0.215	
16				0.220	
18		0.129		0.224	
20	2.8	0.128		0.227	



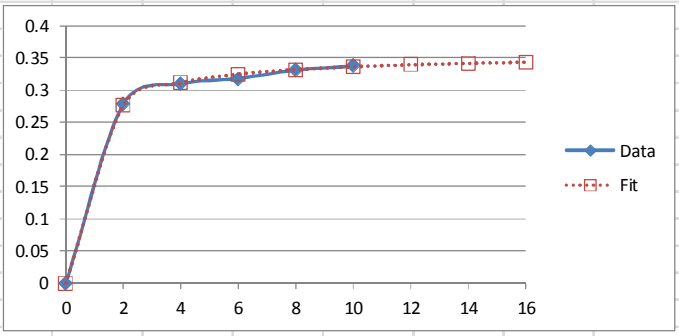
Run 59

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.357	0.599	0.000	0
2	0.276			0.274	3.74E-06
4	0.312			0.310	2.86E-06
6	0.317			0.324	5.51E-05
8	0.321			0.332	1.24E-04
10	0.339			0.337	6.25E-06
12				0.340	2.23E-04
14				0.342	
16				0.344	
18				0.345	
20				0.346	



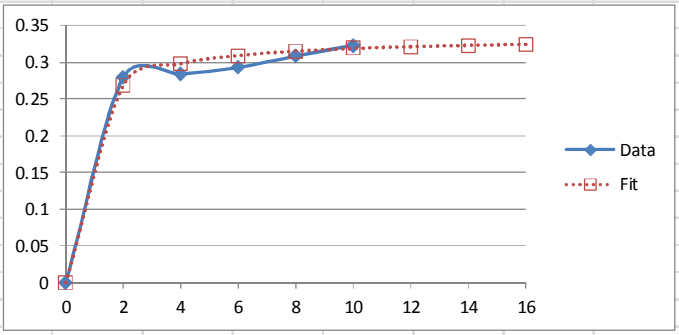
Run 60

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.356	0.572	0.000	0
2	0.279			0.277	5.22E-06
4	0.310			0.311	2.10E-06
6	0.318			0.325	4.37E-05
8	0.331			0.332	7.61E-07
10	0.338			0.337	1.25E-06
12				0.340	5.93E-05
14				0.342	
16				0.344	
18				0.345	
20				0.346	



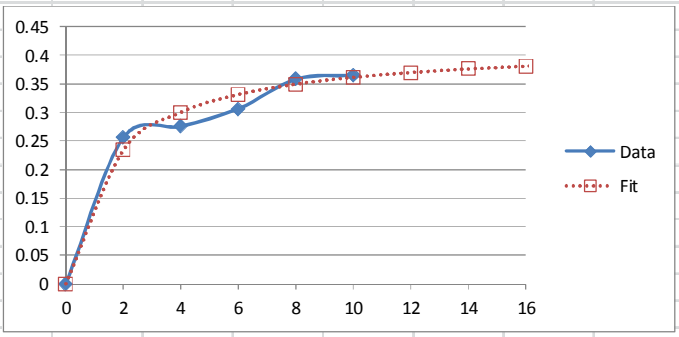
Run 61

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.334	0.487	0.000	0
2	0.279			0.269	1.15E-04
4	0.284			0.298	2.03E-04
6	0.293			0.309	2.66E-04
8	0.308			0.315	4.46E-05
10	0.323			0.319	1.98E-05
12				0.321	7.48E-04
14				0.323	
16				0.324	
18				0.325	
20				0.326	



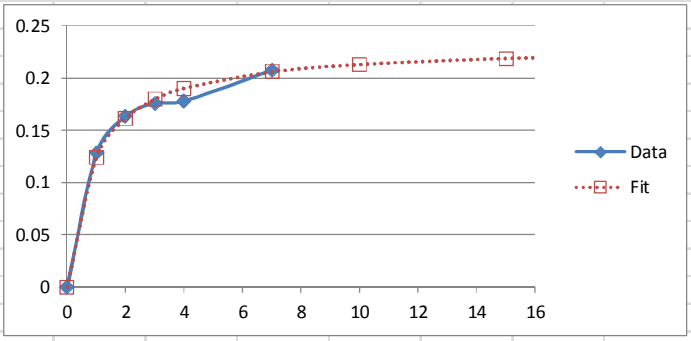
Run 62

x wks	y	a	b	ax/(b+x)	SumSq
0	0	0.418	1.577	0.000	0
2	0.256			0.234	4.93E-04
4	0.276			0.300	6.03E-04
6	0.307			0.331	6.13E-04
8	0.358			0.350	7.75E-05
10	0.365			0.361	1.13E-05
12				0.370	1.85E-03
14				0.376	
16				0.381	
18		0.209		0.385	
20	1.58	0.209		0.388	



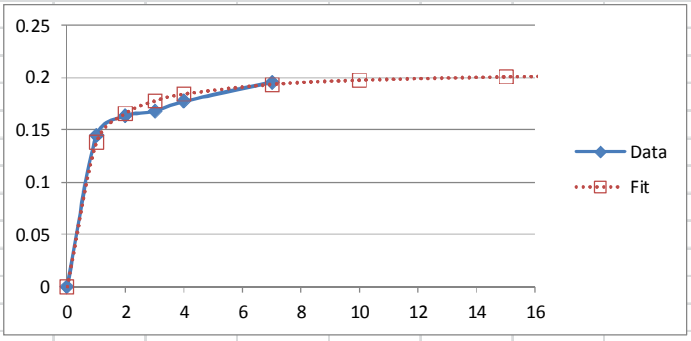
Run 21

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.231	0.866	0.000	0
1	0.128	0.231	0.866	0.124	1.51E-05
2	0.163	0.231	0.866	0.161	3.96E-06
3	0.176	0.231	0.866	0.179	1.29E-05
4	0.178	0.231	0.866	0.190	1.52E-04
7	0.207	0.231	0.866	0.206	3.12E-06
10		0.231	0.866	0.213	2.02E-04
15		0.231	0.866	0.218	
20		0.231	0.866	0.221	
25		0.231	0.866	0.223	
30		0.231	0.866	0.225	



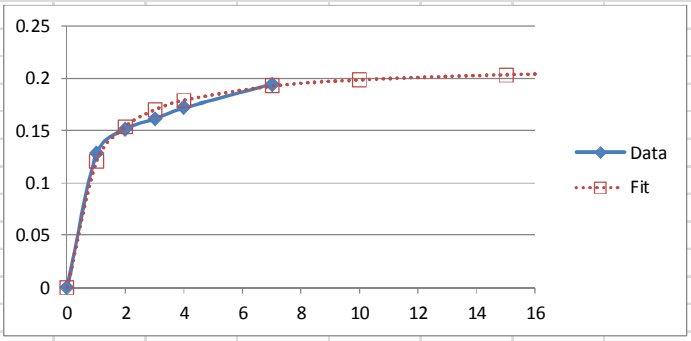
Run 22

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.207	0.503	0.000	0
1	0.145	0.207	0.503	0.138	4.46E-05
2	0.163	0.207	0.503	0.166	6.25E-06
3	0.168	0.207	0.503	0.178	9.52E-05
4	0.177	0.207	0.503	0.184	5.04E-05
7	0.196	0.207	0.503	0.193	4.76E-06
10		0.207	0.503	0.197	2.25E-04
15		0.207	0.503	0.201	
20		0.207	0.503	0.202	
25		0.207	0.503	0.203	
30		0.207	0.503	0.204	



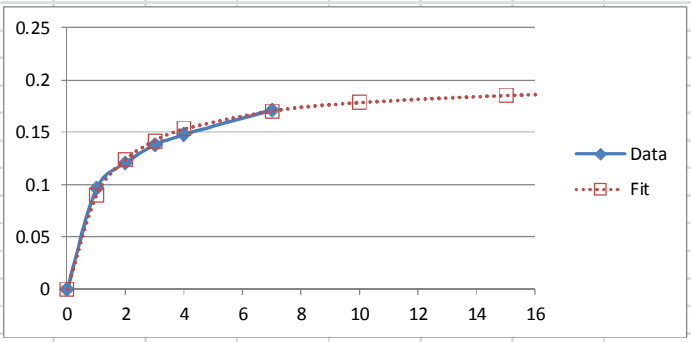
Run 23

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.214	0.780	0.000	0
1	0.128	0.214	0.780	0.120	5.68E-05
2	0.152	0.214	0.780	0.154	5.55E-06
3	0.161	0.214	0.780	0.170	7.57E-05
4	0.172	0.214	0.780	0.179	5.55E-05
7	0.194	0.214	0.780	0.192	3.86E-06
10		0.214	0.780	0.198	2.17E-04
15		0.214	0.780	0.203	
20		0.214	0.780	0.206	
25		0.214	0.780	0.207	
30		0.214	0.780	0.208	



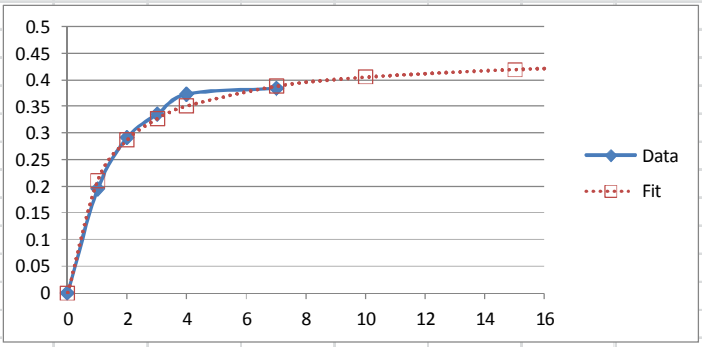
Run 24

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.200	1.234	0.000	0
1	0.096	0.200	1.234	0.090	4.37E-05
2	0.121	0.200	1.234	0.124	9.71E-06
3	0.138	0.200	1.234	0.142	1.53E-05
4	0.148	0.200	1.234	0.153	2.88E-05
7	0.171	0.200	1.234	0.170	1.31E-06
10		0.200	1.234	0.178	1.05E-04
15		0.200	1.234	0.185	
20		0.200	1.234	0.189	
25		0.200	1.234	0.191	
30		0.200	1.234	0.192	



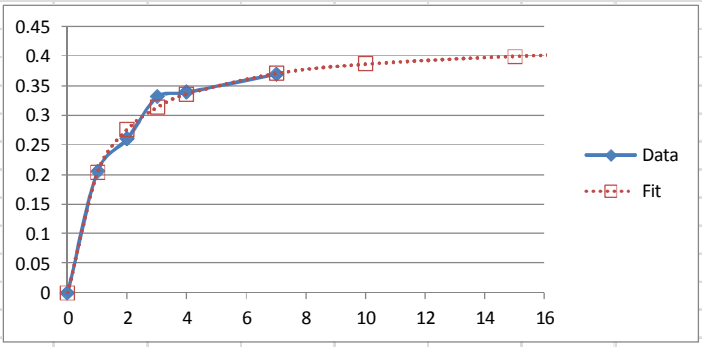
Run 25

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.451	1.142	0.000	0
1	0.194	0.451	1.142	0.211	2.57E-04
2	0.292	0.451	1.142	0.287	2.19E-05
3	0.335	0.451	1.142	0.327	7.67E-05
4	0.373	0.451	1.142	0.351	4.96E-04
7	0.384	0.451	1.142	0.388	1.38E-05
10		0.451	1.142	0.405	9.35E-04
15		0.451	1.142	0.419	
20		0.451	1.142	0.427	
25		0.451	1.142	0.431	
30		0.451	1.142	0.434	



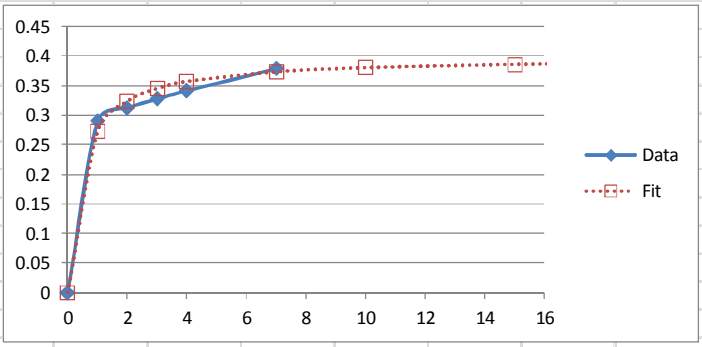
Run 26

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.429	1.109	0.000	0
1	0.205	0.429	1.109	0.203	3.23E-06
2	0.260	0.429	1.109	0.276	2.49E-04
3	0.331	0.429	1.109	0.313	3.13E-04
4	0.339	0.429	1.109	0.336	8.28E-06
7	0.369	0.429	1.109	0.370	1.28E-06
10		0.429	1.109	0.386	5.81E-04
15		0.429	1.109	0.399	
20		0.429	1.109	0.406	
25		0.429	1.109	0.411	
30		0.429	1.109	0.414	



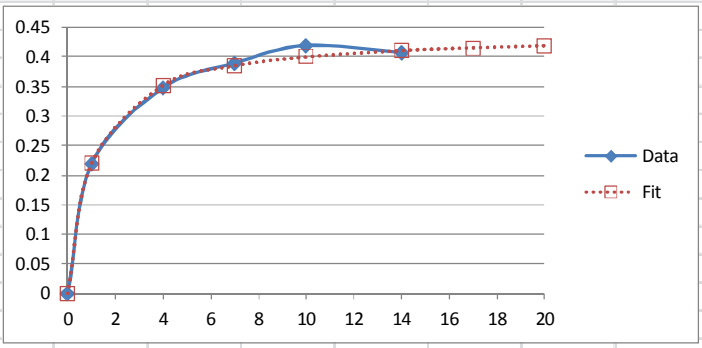
Run 27

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.397	0.457	0.000	0
1	0.289	0.397	0.457	0.273	2.73E-04
2	0.312	0.397	0.457	0.324	1.39E-04
3	0.327	0.397	0.457	0.345	3.09E-04
4	0.341	0.397	0.457	0.357	2.47E-04
7	0.378	0.397	0.457	0.373	2.41E-05
10		0.397	0.457	0.380	1.11E-03
15		0.397	0.457	0.386	
20		0.397	0.457	0.389	
25		0.397	0.457	0.390	
30		0.397	0.457	0.392	



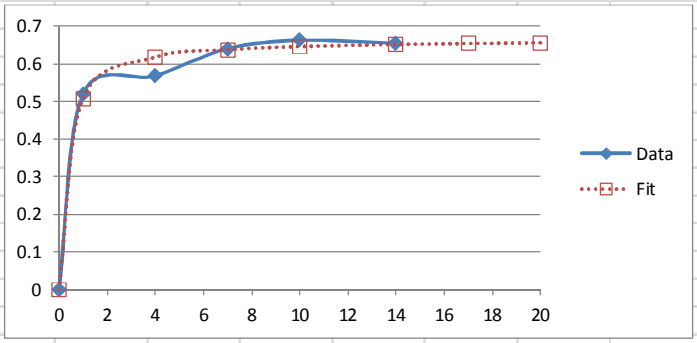
Run 28

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.440	0.998	0.000	0
1	0.219	0.440	0.998	0.220	1.15E-06
4	0.348	0.440	0.998	0.352	1.70E-05
7	0.389	0.440	0.998	0.385	2.27E-05
10	0.419	0.440	0.998	0.400	3.81E-04
14	0.407	0.440	0.998	0.410	1.04E-05
17		0.440	0.998	0.415	4.84E-04
20		0.440	0.998	0.419	
23		0.440	0.998	0.421	
26		0.440	0.998	0.423	
30		0.440	0.998	0.425	



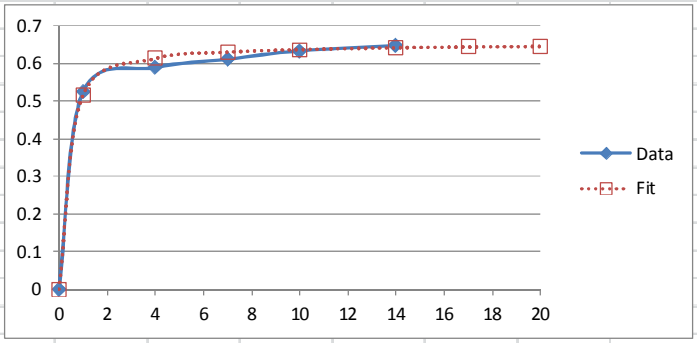
Run 29

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.665	0.312	0.000	0
1	0.520	0.665	0.312	0.507	1.68E-04
4	0.568	0.665	0.312	0.617	2.45E-03
7	0.640	0.665	0.312	0.637	7.08E-06
10	0.662	0.665	0.312	0.645	2.79E-04
14	0.654	0.665	0.312	0.651	8.73E-06
17		0.665	0.312	0.653	2.96E-03
20		0.665	0.312	0.655	
23		0.665	0.312	0.656	
26		0.665	0.312	0.657	
30		0.665	0.312	0.658	



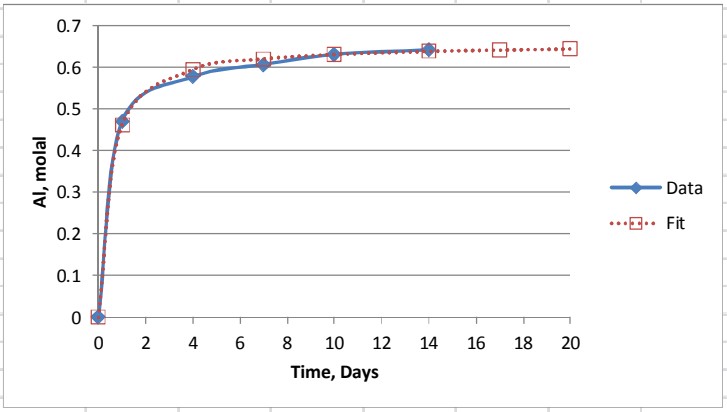
Run 30

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.653	0.267	0.000	0
1	0.524	0.653	0.267	0.516	7.50E-05
4	0.589	0.653	0.267	0.613	5.58E-04
7	0.611	0.653	0.267	0.629	3.36E-04
10	0.633	0.653	0.267	0.636	1.03E-05
14	0.647	0.653	0.267	0.641	3.76E-05
17		0.653	0.267	0.643	1.21E-03
20		0.653	0.267	0.645	
23		0.653	0.267	0.646	
26		0.653	0.267	0.647	
30		0.653	0.267	0.648	



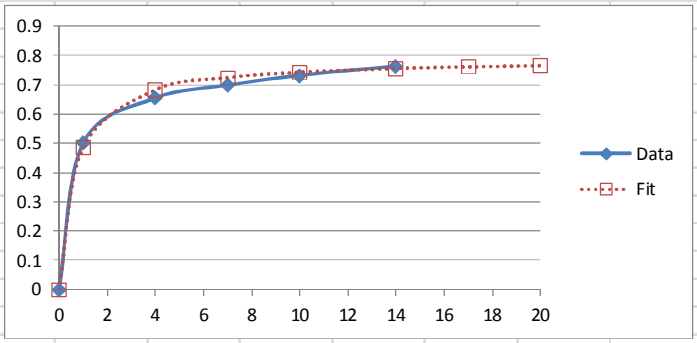
Run 31

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.657	0.422	0.000	0
1	0.469	0.657	0.422	0.462	5.34E-05
4	0.577	0.657	0.422	0.594	3.03E-04
7	0.607	0.657	0.422	0.620	1.66E-04
10	0.631	0.657	0.422	0.630	7.98E-08
14	0.642	0.657	0.422	0.638	1.49E-05
17		0.657	0.422	0.641	6.12E-04
20		0.657	0.422	0.644	
23		0.657	0.422	0.645	
26		0.657	0.422	0.647	
30		0.657	0.422	0.648	



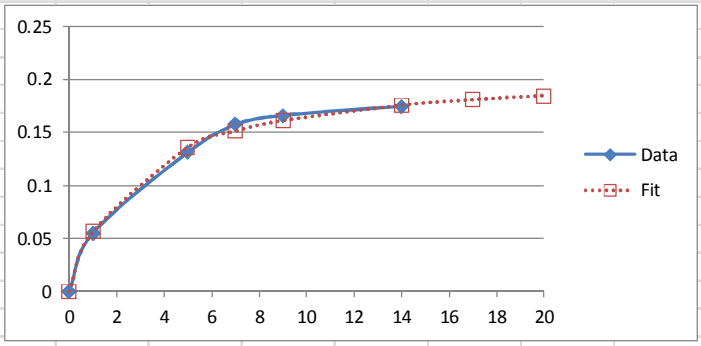
Run 32

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.789	0.626	0.000	0
1	0.501	0.789	0.626	0.485	2.45E-04
4	0.655	0.789	0.626	0.682	7.60E-04
7	0.698	0.789	0.626	0.724	6.66E-04
10	0.732	0.789	0.626	0.742	1.08E-04
14	0.763	0.789	0.626	0.755	6.90E-05
17		0.789	0.626	0.761	2.19E-03
20		0.789	0.626	0.765	
23		0.789	0.626	0.768	
26		0.789	0.626	0.770	
30		0.789	0.626	0.773	



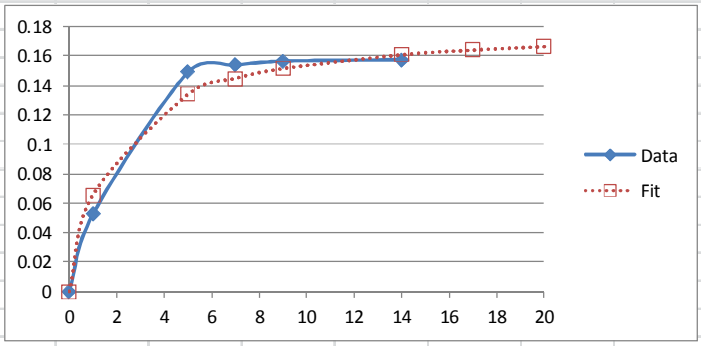
Run 41

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.210	2.713	0.000	0
1	0.055	0.210	2.713	0.056	1.86E-06
5	0.131	0.210	2.713	0.136	2.18E-05
7	0.157	0.210	2.713	0.151	3.84E-05
9	0.166	0.210	2.713	0.161	2.39E-05
14	0.175	0.210	2.713	0.176	9.20E-07
17		0.210	2.713	0.181	9.15E-05
20		0.210	2.713	0.185	
23		0.210	2.713	0.188	
26		0.210	2.713	0.190	
30		0.210	2.713	0.192	



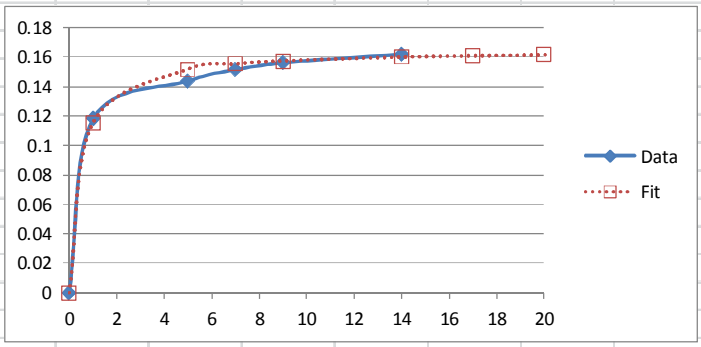
Run 42

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.181	1.749	0.000	0
1	0.053	0.181	1.749	0.066	1.73E-04
5	0.149	0.181	1.749	0.134	2.27E-04
7	0.154	0.181	1.749	0.145	8.10E-05
9	0.156	0.181	1.749	0.151	2.57E-05
14	0.157	0.181	1.749	0.161	1.12E-05
17		0.181	1.749	0.164	5.73E-04
20		0.181	1.749	0.166	
23		0.181	1.749	0.168	
26		0.181	1.749	0.169	
30		0.181	1.749	0.171	



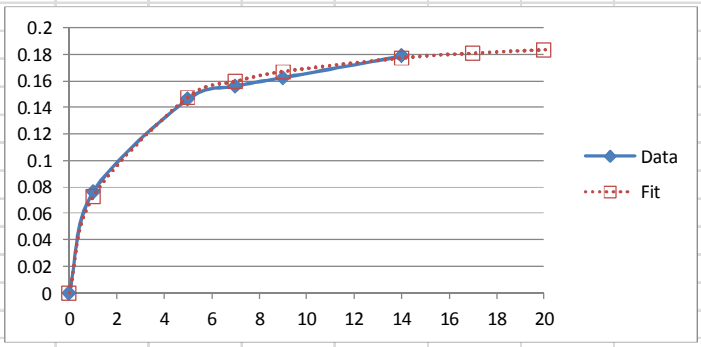
Run 43

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.165	0.429	0.000	0
1	0.118	0.165	0.429	0.115	6.83E-06
5	0.144	0.165	0.429	0.152	6.62E-05
7	0.151	0.165	0.429	0.155	1.62E-05
9	0.156	0.165	0.429	0.157	1.64E-06
14	0.162	0.165	0.429	0.160	3.36E-06
17		0.165	0.429	0.161	1.11E-04
20		0.165	0.429	0.161	
23		0.165	0.429	0.162	
26		0.165	0.429	0.162	
30		0.165	0.429	0.163	



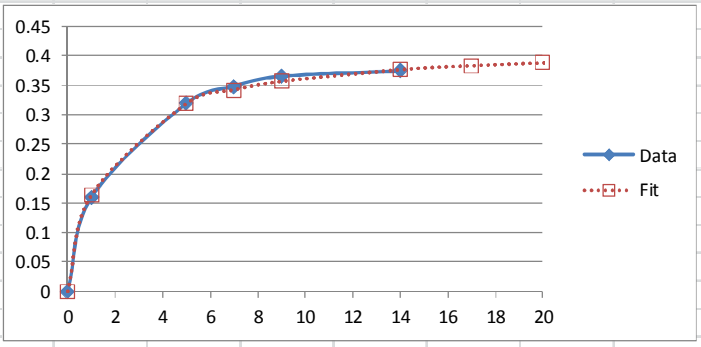
Run 44

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.199	1.748	0.000	0
1	0.076	0.199	1.748	0.073	1.05E-05
5	0.146	0.199	1.748	0.148	2.24E-06
7	0.156	0.199	1.748	0.160	1.31E-05
9	0.162	0.199	1.748	0.167	2.10E-05
14	0.179	0.199	1.748	0.177	1.56E-06
17		0.199	1.748	0.181	5.63E-05
20		0.199	1.748	0.183	
23		0.199	1.748	0.185	
26		0.199	1.748	0.187	
30		0.199	1.748	0.188	



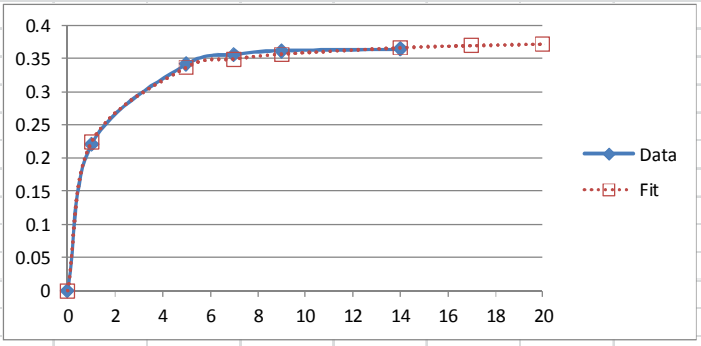
Run 45

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.418	1.554	0.000	0
1	0.160	0.418	1.554	0.164	1.63E-05
5	0.319	0.418	1.554	0.319	1.51E-07
7	0.348	0.418	1.554	0.342	3.79E-05
9	0.365	0.418	1.554	0.356	7.62E-05
14	0.374	0.418	1.554	0.376	4.29E-06
17		0.418	1.554	0.383	1.56E-04
20		0.418	1.554	0.388	
23		0.418	1.554	0.392	
26		0.418	1.554	0.394	
30		0.418	1.554	0.397	



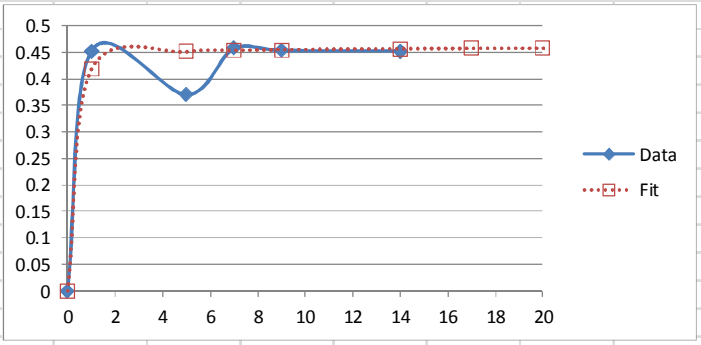
Run 46

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.385	0.716	0.000	0
1	0.221	0.385	0.716	0.225	1.09E-05
5	0.342	0.385	0.716	0.337	2.16E-05
7	0.356	0.385	0.716	0.349	4.67E-05
9	0.362	0.385	0.716	0.357	2.86E-05
14	0.364	0.385	0.716	0.366	5.43E-06
17		0.385	0.716	0.370	1.40E-04
20		0.385	0.716	0.372	
23		0.385	0.716	0.374	
26		0.385	0.716	0.375	
30		0.385	0.716	0.376	



Run 47

x days	y	a	b	ax/(b+x)	SumSq
0	0	0.460	0.100	0.000	0
1	0.453	0.460	0.100	0.418	1.18E-03
5	0.370	0.460	0.100	0.451	6.53E-03
7	0.457	0.460	0.100	0.454	1.48E-05
9	0.453	0.460	0.100	0.455	2.13E-06
14	0.453	0.460	0.100	0.457	1.78E-05
17		0.460	0.100	0.457	7.84E-03
20		0.460	0.100	0.458	did not use
23		0.460	0.100	0.458	
26		0.460	0.100	0.458	
30		0.460	0.100	0.458	



Electronically Approved by:

UserName: Herting, Daniel (h0004821)
Title: APD Chemist
Date: Monday, 13 January 2014, 11:48 AM Pacific Time
Meaning: Approved by the author or delegate
==========

UserName: Reynolds, Jacob (h0046545)
Title:
Date: Wednesday, 15 January 2014, 07:22 AM Pacific Time
Meaning: Approved by the customer or delegate
==========

UserName: Cooke, Gary (h0410221)
Title: APD Chemist
Date: Wednesday, 15 January 2014, 07:36 AM Pacific Time
Meaning: Approved by the Group Manager or delegate
==========

Distribution List

W. B. Barton	S7-90
G. A. Cooke	T6-05
Q. D. Ho	H4-02
H. J. Huber	T6-05
J. K. McCoskey	T6-05
J. S. Page	T6-05
J. A. Pestovich	T6-05
K. L. Pierson	H4-02
J. H. Rasmussen	R2-58
J. G. Reynolds	R2-58
L. M. Sasaki	S7-90
C. M. Seidel	T6-14
J. E. Trechter	T6-05