Technical Letter Report on Follow–on Studies in Chemical Effects Head-Loss Research; Studies on WCAP Surrogates and Sodium Tetraborate Solutions

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Studies on the WCAP Surrogates

WCAP Surrogate Bench Tests

Westinghouse report WCAP-16530-NP[1] provides a procedure for preparing surrogates for the $Al(OH)_3$* precipitates that can form in sump solutions with high levels of dissolved Al. The procedure recognizes that concentration during the precipitation process affects the size of the precipitate product and places limitations on the maximum concentrations in the reaction vessels. The effect that relatively small changes in the precipitation process can have is illustrated in Fig. 1, which shows surrogate mixtures prepared at Argonne different concentrations. The precipitate in beaker 4 is much denser and more compacted than the other solutions.

In additions to limits on the maximum concentrations of solutions used for the preparation of the surrogates, the procedure also sets limits on the settling speed of the resulting product. The WCAP limitations on the concentrations and settling rates do seem effective at producing fine precipitates. However, no argument or data are available to show that they are in any physical sense equivalent to the suspensions that would be produced under conditions more representative of those that might occur in a sump pool. For example, the concentrations in the mixing vessels are still very high compared to the concentrations expected in the sump, in the ANL 100 ppm loop tests, or ICET–1. The solutions in the ANL 100 ppm loop test were very effective in causing head drop, but produced only barely visible colloidal suspensions after being allowed to settle for a day.

Figure 2 shows x–ray spectra from surrogates similar to those developed by the WCAP process. The pH values for the "B" and "C" surrogates are outside the specifications and these surrogates would not pass the settling test. However, it might be argued that they are chemically and physically similar to the surrogates that are deemed acceptable. The "B" and "C" surrogates are clearly crystalline (bayerite). Because of the small size of the "A" surrogate, no clear diffraction pattern can be obtained, but it appears likely that it too is crystalline. The WCAP does not provide other information such as solubility under changing pH or temperature conditions that might provide information on whether the products are crystalline or amorphous.

Testing on the Westinghouse surrogates was halted after the first head loss test in the ANL loop and reports of the head losses observed by NRC staff during loop tests at Alion. Whatever differences there are between these products and the "real" products are, the surrogate products are very effective in producing head loss. The important question appears to be whether or not the products will form in prototypic environments. If they do form, very small amounts are sufficient to produce very large increases in head loss. In the ANL head loss test discussed in the next section, the amount of surrogate added to the loop corresponded to the precipitation of 5 ppm Al from the loop volume of 119 liters.

Head Loss Test with WCAP Surrogate (ICET–1-W)

A head loss test was conducted using the WCAP surrogate. The test was performed using a perforated plate that has a 40% flow area and 1/8-in. holes with 3/16-in. staggered centers. The plate was mounted in a nominal 6-in. dia. transparent PVC plastic pipe test section.

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*In this report, $Al(OH)_3$ is used a short–hand for a family of aluminum oxyhydroxides that could form in a variety of crystalline and amorphous forms.

(a)

(b)

Figure 1.   (a) Solutions of $Al(NO_4)_3$ and NaOH after initial mixing; (b) Solutions after settling for 20 h.
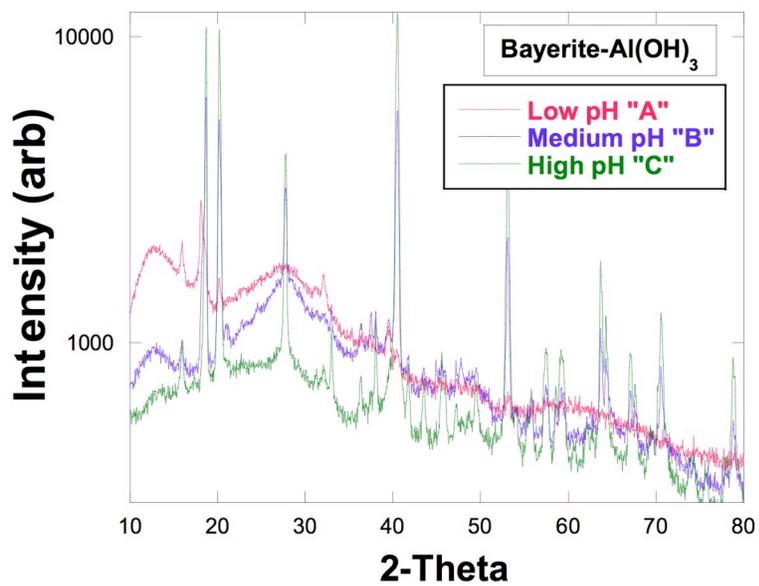
Figure 2.
X-ray diffraction spectra from WCAP like surrogates

The loop was filled with deionized water and heated to 60°C (140°F) and circulated at 2 ft/s for 15 minutes to remove dissolved air. It was kept at about 27°C (80°F) overnight. Before the addition of the surrogate, a NUKON bed was formed on the perforated plate using 11.5 g of NUKON. This amount of material results in a bed of about 12 mm thickness under a screen approach velocity of 0.1 ft/s. The NUKON bed material was coarse shredded NUKON insulation which was then added to 1 liter of loop water and blended for 11 sec in the high-ice crush mode. After processing, another 1500 ml of loop water was added to the blended ingredients in a 3500 ml beaker and the 2500 ml mixture was magnetically stirred for 10 minutes at room temperature. The 2500 ml mixture was added to the loop in < 5 sec while stirring the beaker continuously and then stirring the tee chamber for another 2 minutes. The screen approach velocity was 0.1 ft/s for building the NUKON bed and during all chemical additions after bed building. The Al chemical additions were not started until the pressure drop across the NUKON bed had stabilized and the stabilized bed thickness measured.

The loop water temperature was maintained at 80°F. Surrogate $Al(OH)_3$ product was prepared following the WCAP procedure which limits the concentration of the product to ensure a fine precipitate. The mass of precipitate added to the loop corresponds to the precipitation of 5 ppm Al from the loop volume of 119 liters. The aluminum particulate was suspended and well stirred in 2833 ml of water and added to the loop in multiple consecutive additions consisting of 5% of the total 2833 ml (= 142 ml) through the tee port on the top of the loop.

The pressure velocity time history during the test, ICET–1-W, is shown in Fig. 3.
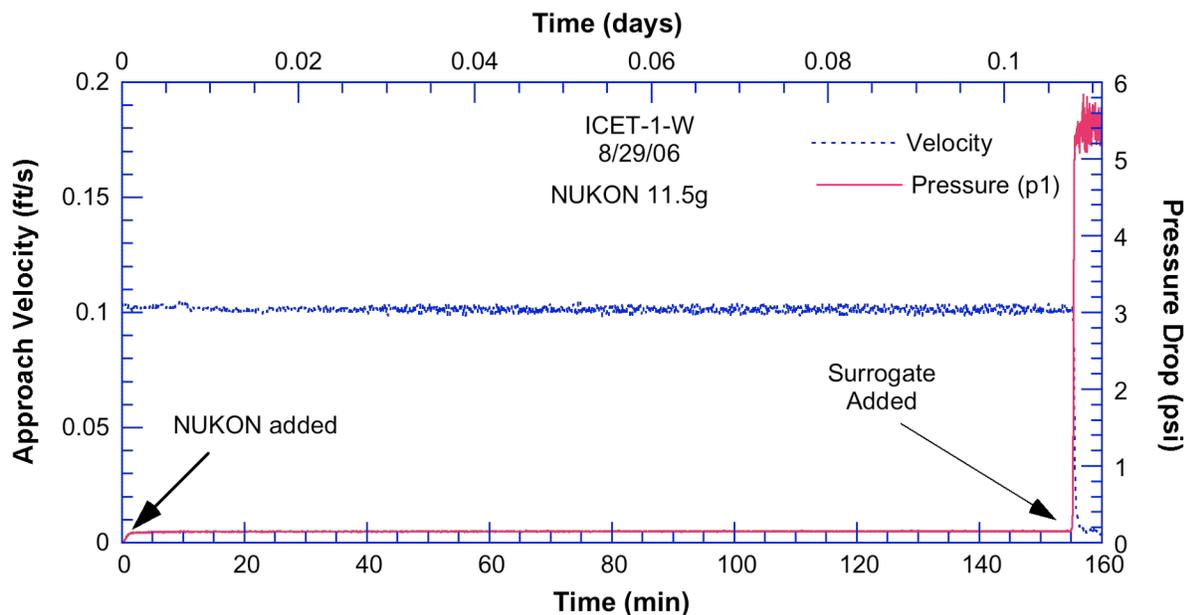
Figure 3.   Pressure/Velocity time history in loop test ICET–1–W using the WCAP $Al(OH)_3$ surrogate.

The pressure increase during the test was extremely rapid, starting just after the few seconds necessary for transport from the mixing tee to the plate with the NUKON bed. The pressure drop capacity of the system was exhausted almost immediately. No precipitate was visible in the water approaching the bed, and no buildup of precipitate was visible on the bed, although the clarity of the PVC test section is considerably inferior to that of a LEXAN test section.
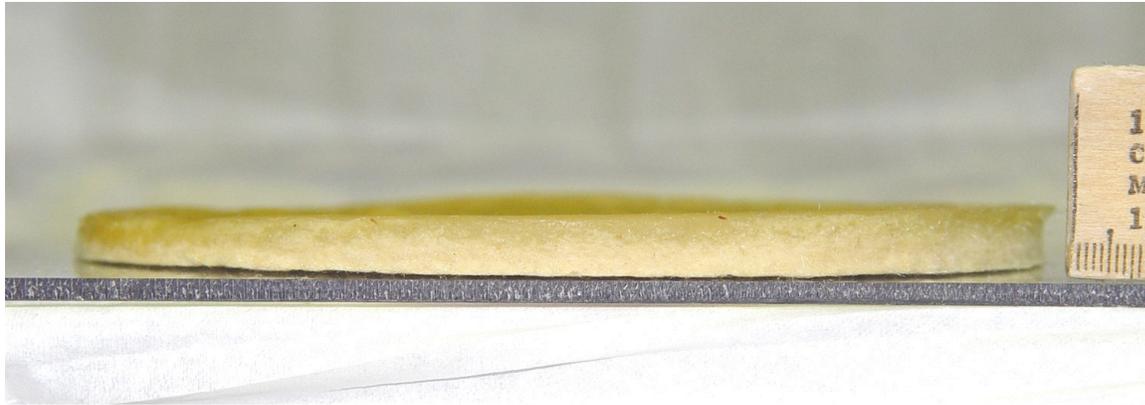
(a)
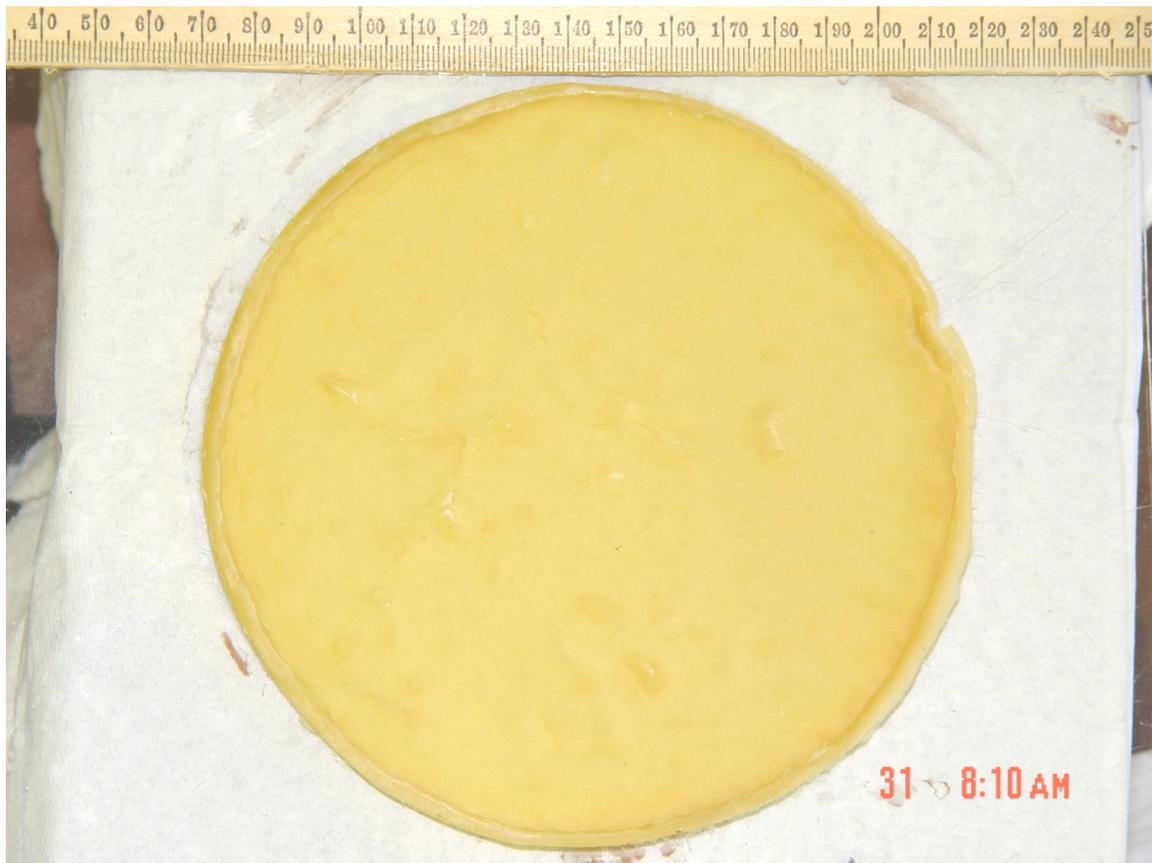
(b)

Figure 4. (a) Side View of NUKON bed with smooth, top–coating; (b) Top View of NUKON bed and coating.

The loop was shut down and allowed to rest overnight. The next day the bed was removed and photographed. Side and top views of the bed are shown in Figs. 4a and 4b.

The coating on the bed is quite different than anything seen in our previous Al/NaOH testing. In the earlier 375 ppm Al test, there was a white, "jello-like" layer on top of the bed. In the 100 ppm Al test, there were no visible deposits. With the Westinghouse surrogate, there was a smooth

layer 1-2 mm thick on top of the bed. It was golden colored and looked like a thick layer of shellac (or butterscotch topping on ice cream). It was impervious. The water above the bed could not drain through the bed and the transducers had to be disconnected so that the water could drain through the transducer ports. The color of the layer of precipitate is presumably somehow associated with the NUKON fiber. A thin layer next to the bed with this color could have been overlooked in the earlier 375 ppm Al test, but as noted the 100 ppm Al test did not have a visible precipitate layer of any color.

Although the layer was smooth when wet, as it dried, it peeled and flaked. Micrographs of the topping taken in a "wet" SEM are shown in Figs. 5a and 5b.

| (a) | (b) |
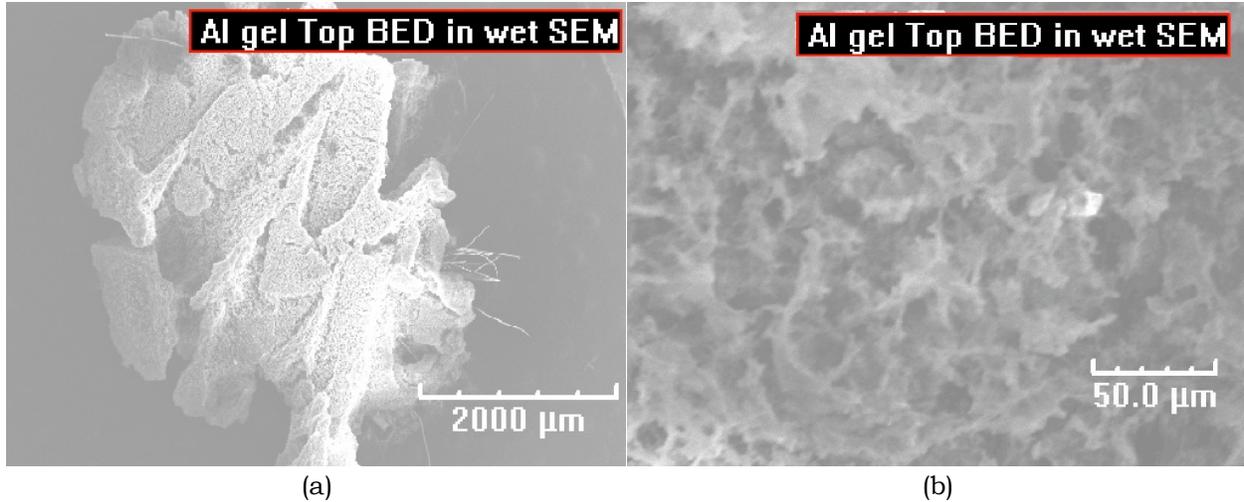
Figure 5.   "Wet" SEM micrographs of the "butterscotch" topping from ICET−1−W (a) low resolution (b) high resolution.
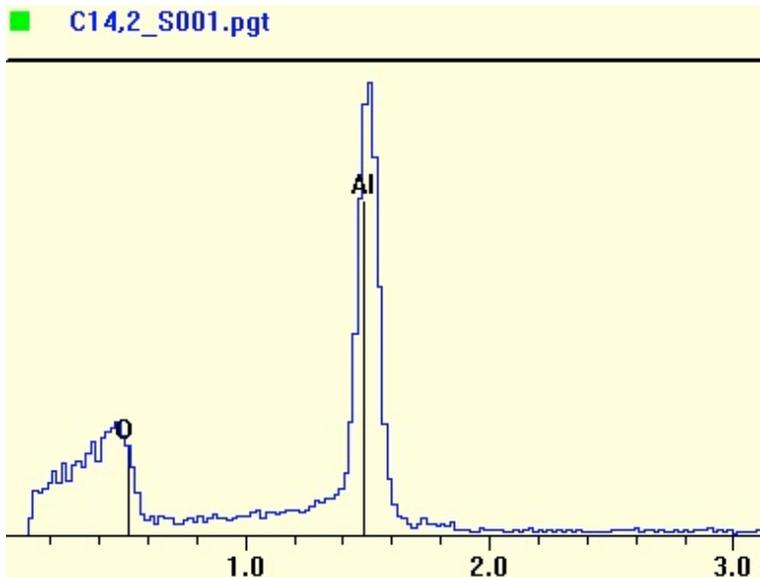
Figure 6.
EDS spectra of topping. High Al and O levels indicate a highly hydrated Al(OH)$_3$.

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
Al	KA1	1.487	0.5788	63.29	50.57	52.56
O	KA1	0.523	0.3246	36.71	49.43	63.32
7-KeV				**100.00**	**100.00**	**48.16**

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Studies with Sodium Tetraborate Buffers

Small–Scale Tests

Two series of small–scale tests were performed. Both started with initial solutions of sodium tetraborate (STB). In the first test series, Al(NO$_3$)$_3$ was added periodically to solutions held at constant temperature resulting in nominal Al concentration ranging from 10 to 90 ppm. The solutions were carefully examined visually for evidence of the formation of precipitates. In the second test series, heavily oversaturated solutions were formed by adding sufficient Al(NO$_3$)$_3$ to produce a nominal Al concentration of 400 ppm. The solutions were then held under isothermal conditions for over 22 days. If the solution is in equilibrium with the precipitate, the dissolved Al concentration will be equal to the solubility of Al(OH)$_3$ under the given conditions.

Solubility of Al in NaOH solutions

The solubility of Al in NaOH solutions has been studied extensively. Although the crystalline forms such as gibbsite have very low solubilities, experience with ICET–1 suggests that over the time frames of interest, the solubility is controlled by the formation of amorphous products.[2] This is also supported by studies in the literature. Van Straten et al.[3] showed that in precipitation of aluminum hydroxides from a basic supersaturated solution the first products to form are the less thermodynamically stable forms and then the product transforms through a series of forms to reach the thermodynamically stable form, gibbsite. The progression suggested by Van Straten et al[3] is amorphous, pseudo boehmite, bayerite, and then gibbsite.

For the pH range of interest the primary solubility product is aluminate, $Al(OH)_4^-$ and the equilibrium reaction with the solid phase is given by:

$$Al(OH)_3 \text{ (solid) } + H_2O = H^+ \text{ (aq) } + Al(OH)_4^- \text{ (aq)} \tag{1}$$
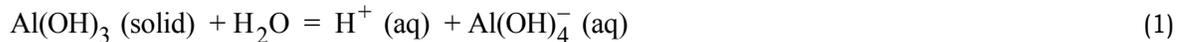
The $Al(OH)_4^-$ concentration at equilibrium is a function of pH:

$$\log Al(OH)_4^- = \log K - \log H^+ = \log K + pH \tag{2}$$

Values of the solubility constant log K are given by Van Straten et al.[3] and Langmuir[4] and can be inferred from experiments by Klasky[2] at LANL and Park at ANL and the ANL loop tests.[5] The available data are summarized in Table 1.

The literature data cited in Van Straten and Langmuir is for simple Al/NaOH systems. The data from Klasky, Park, and the ANL loop tests are for systems with 2800 ppm B and LiOH. Data on the solubility as a function of temperature are given by Benezeth et al.[6]. These suggest that the variation of K with temperature can be expressed as

$$K = K_o \exp(-6969/T)$$

where T is in degrees Kelvin. The "best estimate" value for log K based on experiments in B containing environments is about -12.2.

The LANL ICET–5 test suggests that at a pH of 8.4 the solubility of Al in sodium tetraborate solutions is about 50 ppm at room temperature (70°F). This value is also consistent with the result of ICET-5-1-B2, the initial ANL loop test with STB buffers, in which no head loss was observed with 50 ppm after about 12 days of operation at 70°F. This concentration is much higher than suggested by the literature data ($\approx$ 4 ppm) and this anomaly provides motivation for the current small–scale tests on solubility.

Table 1.   Measured values of the solubility constant K
at 25°C for amorphous $Al(OH)_3$

	log K 25°C
Van Straten	-12.1
	-12.0
	-12.7
	-12.8
Langmuir	-12.1
Klasky	-12.25
	-12.6
Park (bench)	-12.28
ANL loop tests	$\approx$-12.2

Solubility tests – Sodium tetraborate

In the test series examining solubility, Al concentration was increased sequentially from 10 ppm to 90 ppm by adding aluminum nitrate solution. The tests were performed at two temperatures, 80 and 100°F (27 and 38°C). The precipitation kinetics studies, in which an amount of Al equivalent to a concentration of 400-ppm was added to STB buffer solution, were performed at three temperatures, 80, 100, and 120°F (27, 38, and 49°C).

Three mineral oil baths (two 3.5-liters Pyrex beakers and one 1-liter Pyrex beaker) with magnetic stirrers in each bath were used to minimize the temperature variations of the test solutions. Three hot plate/stirrers were used to heat up the mineral oil. A total of five test flasks, which have an open port for a cooling condenser, and an open port for sampling/pH probe insertion, were used as test solution containers. Each flask has its own magnetic stirring bar.

Figure 7 shows the test system configuration for the tests at 80 and 100°F. In Figure 7, each mineral oil bath contains two test flasks.

The Al solubility tests were designated as NRR 80 and NRR 100 corresponding to temperatures of 80 and 100°F, respectively. The three precipitation kinetics tests were designated as ANL 80, ANL 100, and ANL 120 corresponding to temperatures of 80, 100, and 120°F. Therefore, NRR 80 and ANL 80 were placed in the same mineral oil bath and NRR 100 and ANL 100 were placed in the same mineral oil bath. ANL 120 has its own oil bath as shown in Figure 8.

Table 2 shows the test conditions for each test. Enough base solution was prepared for all 5-tests. The initial solutions were all identical with a pH (RT) of 8.6 resulting from the boric acid and the STB additions. The pH was not adjusted because it was expected that the aluminum nitrate additions would decrease the pH.

The necessary amount of $Al(NO_3)_3$ for the each incremental addition in the solubility tests is too small to be accurately measured as a solid for such small-scale tests. A 100-ppm Al reference solution was prepared. An increase of 10-ppm-Al corresponds to an addition of 0.67-mL of the reference Al solution for NRR 80 (125-mL flask) and to 1.33-mL for NRR 100 (250-mL flask).

Figure 7.   Small-scale test system configuration for tests conducted at 80 F (left) and 100 F (right).
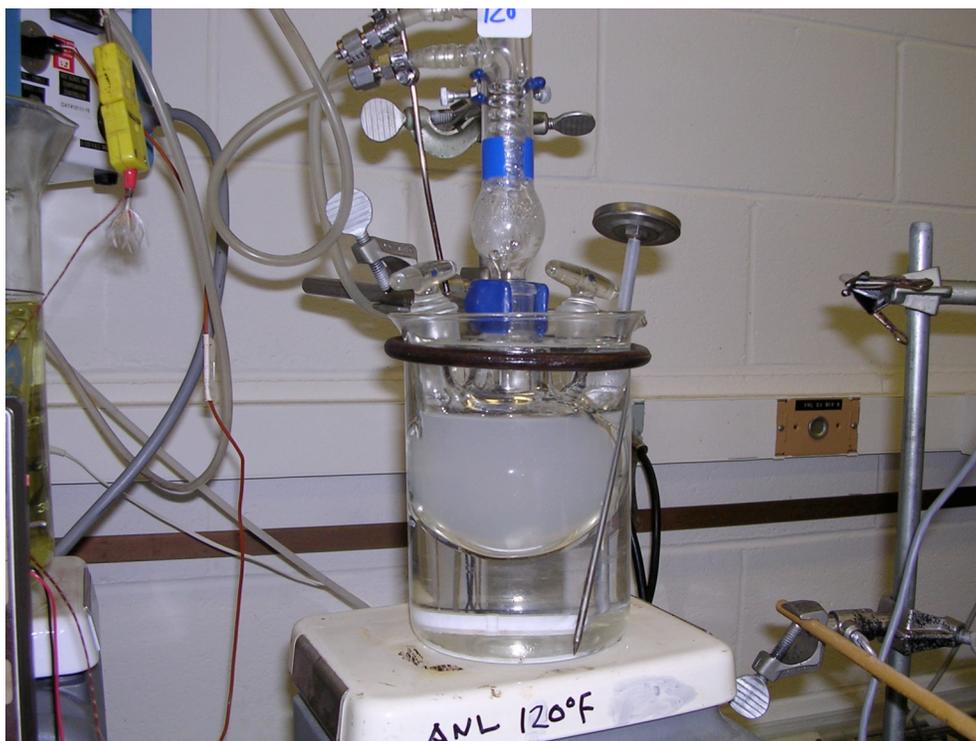
Figure 8.   Small-scale test system configuration conducted at 120 F.

For NRR 80, the added 100-ppm Al solution did not mix uniformly with the solution in the flask presumably due to high local concentrations. Even with stirring, tiny particles formed and could be seen moving around as the solution was stirred. All the particles were dissolved out within 2 hours. For NRR 100, probably because of higher temperature and faster kinetics, the added 100-ppm Al solution mixed more uniformly and any particles that formed dissolved very quickly.

Very small, translucent, precipitate particles were observed in the NRR 80 solution when the nominal Al concentration was increased from 50 to 55 ppm. Tiny particles were formed on the surfaces of the flask and the number of particles increased as Al level was increased. It appears that the flask surface provides nucleation sites for $Al(OH)_3$ precipitation. Even after the Al level was increased up to the nominal value of 90 ppm, the overall solution still looked transparent. For NRR 100, precipitate particles were observed at the bottom of the flask when the nominal Al concentration reached 85 ppm.

Table 3 shows the ICP analysis results for Al for solution samples from NRR 80 and NRR 100. More complete results are given in Appendix A. All samples were filtered using 0.02 μm or 0.22 μm filters (Whatman® Anotop 25). In the case of NRR 80, the measured Al concentrations are about 10 ppm higher than the nominal values, which can't be correct. In Table 3, NRR 80 4 and NRR 80 5 were analyzed at different labs, and both labs reported values higher than the nominal values. The Argonne Analytical Chemistry Laboratory performed most of the measurements reported here. They estimate the uncertainty in their measurements of dissolved Al at the concentrations of interest at about ±5%. This estimate is consistent with the results we have obtained on benchmark solutions that we sent them for blind testing. The most obvious source of errors in the nominal concentrations in these tests are uncertainties in the injection volumes as the concentrations are increased, but those increments seem to accurately reflected in the ICP measurements. The largest apparent error is in the initial concentration for which measurement errors would seem less likely. One possible source of error is the assumption that the $Al(NO_3)_3$ is hydrated with $9H_2O$. Different hydration levels could affect the amount of Al actually added, but the amount of hydration necessary to account for this discrepancy seems unrealistically high.

There seems to a systematic trend to the differences between the nominal values and the measured ICP results. The NRR 80 ICP results for aluminum are always greater than the nominal value while the NRR ICP 100 results are close to or less than the nominal value. Both samples were prepared at the same time by the same individual using the same aluminum nitrate stock solution and the same procedure. No reason for the apparent systematic difference between nominal and measured values in the two samples has been identified.

Two approaches towards "correcting" values were considered. In the first, the nominal concentrations under baseline conditions are considered the benchmark and a scaling factor was calculated to apply to the ICP results to match the benchmark. The scaling approach uses a different scaling factor for each set of samples, which is difficult to justify. In the second, the difference between the ICP result and the nominal baseline concentration was used to compute an additive adjustment to the nominal concentration. Table 4 shows corrected values using both approaches. In the first approach, the nominal values are compared with the normalized ICP results; in the second approach, the adjusted nominal values are compared with the reported ICP values. Both approaches give similar qualitative results.

For NRR 80 visual observation suggests that precipitation began to occur at the lowest reported levels, 55–66 ppm of Al. The amount of precipitate at these levels was very small and difficult to observe. At levels of 80 ppm and greater, the precipitate was easy to see and clearly evident. For NRR 100, visual observation of precipitation was observed at a concentration of 77–

80 ppm. For NRR 80, the amount of $Al(OH)_3$ precipitation is small or the particle sizes of the precipitates were less than 0.22 μm. For NRR 100, the differences between the measured and nominal concentrations were significantly larger than in the case of NRR 80, a somewhat surprising result because solubility would be expected to increase at the higher temperature.

Table 2.   Test conditions for the small-scale tests

Test ID	Temperature (F)	Al Conc. (ppm)	Base Solution	Initial pH
NRR 80	80	10→90	Boric Acid+STB	8.60
NRR 100	100	10→90	Boric Acid+STB	8.60
ANL 80	80	400	Boric Acid+STB	8.30
ANL 100	100	400	Boric Acid+STB	8.30
ANL 120	120	400	Boric Acid+STB	8.30

Table 3.   ICP analysis results for Al concentrations in solution samples from NRR 80 and NRR 100.

Sample ID	Elapsed Time (days)	Nominal Al (ppm)	ICP Analysis Results (ppm)
NRR 80 4[a]	19.0	55	66±3
NRR 80 5	22.2	55	65±3
NRR 80 6	23.1	60	72±4
NRR 80 7	25.9	65	75±4
NRR 80 8	27.8	70	80±4
NRR 80 9	28.9	75	85±4
NRR 80 10	29.9	80	91±5
NRR 80 11[b]	32.9	85	96±5
NRR 80 12[b]	34.1	90	102±5
NRR 100 5	22.2	55	57±3
NRR 100 11[b]	32.9	85	80±4
NRR 100 12[b]	34.1	90	82±4

[a]This sample was analyzed by University of Minnesota; all other samples were analyzed by ACL at Argonne.

[b]This sample was filtered using a 0.22 μm filter.

Table 4.   "Corrected" concentration values for solution samples from NRR 80 and NRR 100.

Sample ID	Elapsed Time (day)	Nominal Al (ppm)	Normalized ICP (ppm)		Adjusted Nominal Al (ppm)	ICP Analysis Results (ppm)
NRR 80 4[a]	19.0	55	55		66	66±3
NRR 80 5	22.2	55	55		66	65±3
NRR 80 6	23.1	60	60		71	72±4
NRR 80 7	25.9	65	63		76	75±4
NRR 80 8	27.8	70	67		81	80±4
NRR 80 9	28.9	75	71		86	85±4
NRR 80 10	29.9	80	77		91	91±5
NRR 80 11[c]	32.9	85	80		96	96±5
NRR 80 12[c]	34.1	90	86		101	102±5
NRR 100 5	22.2	55	55		57	57±3
NRR 100 11[c]	32.9	85	77		87	80±4
NRR 100 12[c]	34.1	90	79		92	82±4

[a]This sample was analyzed by University of Minnesota; all other samples were analyzed by ACL at Argonne.

[b]This sample was filtered using a 0.22 μm filter.

In the precipitation kinetics tests, ANL 80, ANL 100, and ANL 120, all test solutions were cloudy at the beginning of the tests, as shown in Figures 7 and 8. But ANL 120 looked less cloudy than ANL 80 and ANL 100. After 9 days, the sediment in ANL 80 and ANL 100 had largely settled, but ANL 120 was still cloudy with no sedimentation. ANL 120 did not show visible sedimentation until 20 days after the test started. The solution pH was 8.3-8.4 for ANL 80, ANL 100, and ANL 120. Table 5 shows the ICP analysis results for solution samples from ANL 80, ANL 100 and ANL 120. After 22 days the solution have not reached an equilibrium concentration. The tests were shut down after ≈104 days, but unfortunately the last samples were taken at 22 days. Because room temperature is not too different from the test temperature for the 80°F test, a sample was taken at 134 days from this solution. The decrease from the initial 400 ppm, then increase, then decrease in concentration level in the ANL 80 test is difficult to explain, but the changes are too large to be explained by uncertainty in the measurements.

Since long–time data were not available, the long–time concentrations at 100° and 120°F were estimated assuming an exponential decrease in the supernate concentrations. The measured values of the Al concentration at 134 days for ANL 80, the measured values at 22 days for ANL 100 and 120, and the extrapolated long–time data for ANL 100 and 120 are plotted as a function of temperature in Fig. 9. The predicted Al solubility based on literature data reviewed in this report is also plotted in the Fig. 9. The measured results are much higher than the predicted results.

The reasons for this difference are not clear. One possibility is a change in solubility due to the higher ionic strength of the test solutions compared to the simpler solutions used in most of the literature results. Eq. (2) is strictly valid only for dilute solutions. More generally, the equilibrium constant K is given by:

$$K = a_{Al(OH)_4^-} a_{H^+} = m_{Al(OH)_4^-} m_{H^+} \gamma_{Al(OH)_4^-} \gamma_{H^+} \tag{3}$$

where m indicates molal concentration and γ indicates the molal activity coefficient for each ion in the saturated solution. The activity coefficient will decrease with the increase in ionic strength due to the high boron and sodium ion concentrations. The data necessary to calculate γ as a function of ionic strength and temperature are not available. Rough estimates suggest that the effect of the ionic strength cannot account for the apparent difference in solubilities. It should also be noted that Klasky[2] and Park[5] determined solubilities for boric acid and NaOH solutions that are in reasonable agreement with the literature values. These are reasonably high ionic strength solutions. The previous small-scale test with $NaAlO_2$ and NaOH with boric acid at the pH ranges of 9.5-10.0, as described in Appendix C of Reference (5) indicated a good agreement with the predicted Al solubility data.

The predicted results show a monotonic increase of Al solubility with increasing temperature, but the measured Al concentrations in the supernates after 22 days showed the highest concentration at the lowest temperature. The NRR 80 and NRR 100 solutions also seem to indicate a higher solubility at 80°F than at 100°F. However, rather than a difference in solubilities, it may be that the STB solutions can be highly supersaturated at 80°F because the precipitation kinetics are slow. For the 100°F solutions, the kinetics would be faster so that the observed Al concentration in the supernate could be lower than that of ANL 80. At 120°F, the higher temperature would enhance kinetics and dissolution. The processes could also be made more complex by changes in the kinetics of the transformation of the precipitates from their initial amorphous form to crystalline forms.

Because of the slow kinetics, longer–term tests would be needed to get better quantitative estimates of Al solubility by this approach.

Table 5.   ICP analysis results for solution samples from ANL 80, ANL 100, and ANL 120.

Sample ID[a]	Elapsed Time (day)	ICP Analysis Results (ppm)						
		Al	B	Na	Ca	K	Si	P
ANL 80 1	5.0	78.4	4500	3580	NM[c]	NM[c]	NM[c]	NM[c]
ANL 80 2	9.0	79.7	4540	3480	NM[c]	NM[c]	NM[c]	NM[c]
ANL 80 3	14.0	82.0	4500	3390	NM[c]	NM[c]	NM[c]	NM[c]
ANL 80 4[b]	19.0	98.5	4510	3810	2.4	11.2	1.5	<0.35
ANL 80 5	22.2	92.9	4290	3470	NM[c]	<2.5	<2.5	<2.5
ANL 80 6[d]	134.1	50.7	4600	3610	NM[c]	NM[c]	NM[c]	NM[c]
ANL 100 4[b]	19.0	72.6	4600	3830	3.2	17.7	0.4	3.4
ANL 100 5	22.2	64.6	4340	3600	NM[c]	<2.5	<2.5	3.78
ANL 120 4[b]	19.0	78.6	4790	3955	2.1	21.2	1.1	<0.35
ANL 120 5	22.2	74.9	4450	3670	NM[c]	<2.5	<2.5	<2.5

[a]All samples were filtered by using 0.22 µm filter.

[b]This sample was analyzed by University of Minnesota and all other samples were analyzed by ACL in Argonne National Lab.

[c]Not measured

[d]Actual sample temperature was 80°F for ≈104 days; ≈70°F for ≈30 days.
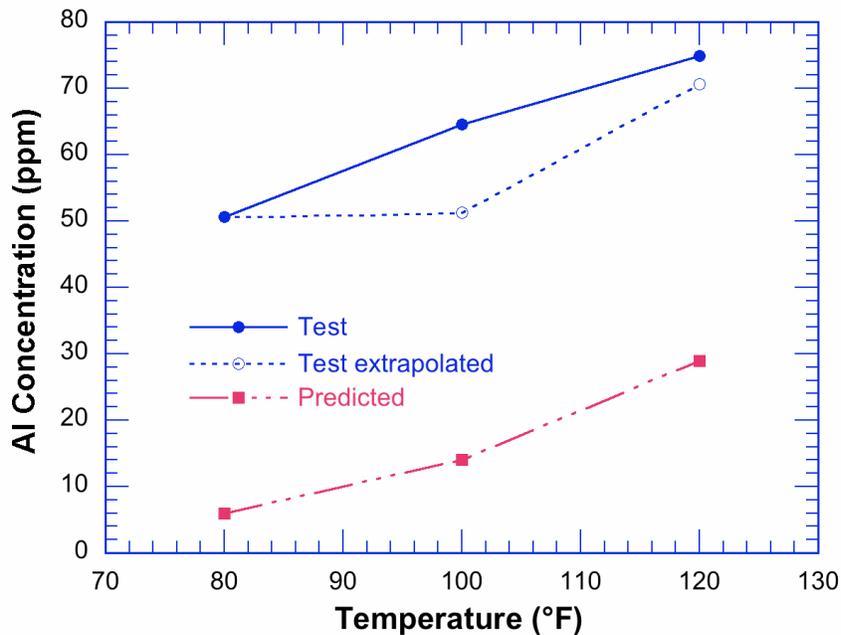
Figure 9.
Measured Al concentrations in the supernate from ANL 80, ANL 100, and ANL 120 as a function of temperature, extrapolated long–time values, and predicted solubility.

Head Loss Test with STB Buffer (ICET–5–2–B2)

The loop was filled with deionized water and heated to 60°C (140°F) and circulated at 2 ft/s for 15 minutes to remove dissolved air. It was kept at about 27°C (80°F) overnight. Boric acid in powder form was slowly added to the loop and circulated until it was dissolved. The LiOH was added as a solution. Sodium tetraborate was added to get a pH of 8.3. The loop was operated at 1 ft/s for 15 minutes to mix the chemicals. After the chemical solution was prepared, the physical debris bed was built by adding a slurry containing 11.5 g NUKON to the loop with the loop flow at 0.1 ft/s. The bed was about 12 mm thick. The flow velocity was maintained at 0.1 ft/s for the whole test.

After the bed had formed and the pressure drop stabilized, the temperature was raised to 60°C (140°F) and the $Al(NO_3)_3$ solution was added. The concentration of the solution was chosen so that the concentration in the loop was 50 ppm after all the solution was added. The temperature was then decreased to ≈ 80°F and held there for ≈ 21 days. The temperature and pressure history during the test is shown in Fig. 10. No significant increase in pressure drop in was observed in the initial ≈ 21 days of testing.

After ≈21 days, the temperature was increase to 120°F and $Al(NO_3)_3$ added to increase the nominal dissolved Al concentration to 60 ppm. The temperature was decreased to 80°F and the test continued for about a day. The temperature was then increased to 120°F and additional $Al(NO_3)_3$ added to increase the nominal dissolved Al concentration to 70 ppm. The addition of $Al(NO_3)_3$ alters the pH. Nitric acid additions were made as necessary to keep the pH roughly constant (in the range 8.35–8.40), as shown in Table 6, which gives a detailed history of the chemistry changes over the course of the test. With a nominal 70 ppm dissolved Al, a notable pressure increase occurred even at 120°F. The pressure drops increased as the temperature was dropped to 100°F and then 80°F. The jump in pressure drop between 120 and 80°F with 60 ppm is consistent with that expected due to the change in viscosity (≈50%). The initial jump in

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pressure drop between 120 and 100°F with 70 ppm (≈20%) is also consistent with the change in viscosity (≈20%). However, the continued increase in pressure drop with time at 100°F and 70 ppm is indicative of precipitate formation. The jump in pressure drop as the temperature is decreased from 100 to 80°F (≈30%) is consistent with that expected from viscosity alone (≈30%). The growth in pressure drop with time at 120°F with a nominal 80 ppm Al is clearly faster than with a nominal 70 ppm Al. The jump in pressure drop as the temperature is decreased from 120 to 100°F with a nominal 80 ppm Al (≈40%) is somewhat greater than would be expected from viscosity alone (≈20%). The jump in pressure drop as the temperature is decreased from 100 to 80°F with a nominal 80 ppm Al (≈40%) is again somewhat greater than would be expected from viscosity alone (≈30%).

The pressure drop increased from ≈0.2 psi at 80°F with a nominal 50 ppm Al to 1.3 psi with 80 ppm Al and the difference was still increasing when the test was terminated.
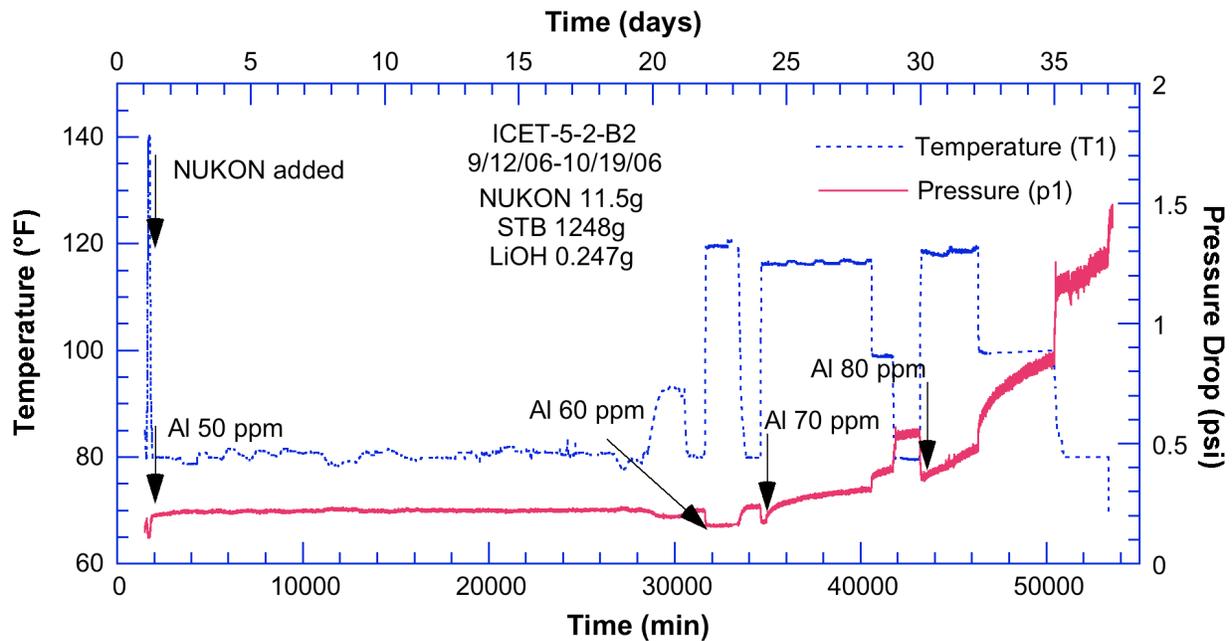
Figure 10. Pressure/Temperature time history during loop test ICET–5–2–B2

The values for the Al concentration in Fig. 10 are nominal values based on the $Al(NO_3)_3$ additions that were made during the test. Tables 6 and 7 give the ICP results. The ICP results are lower than the nominal values even at the 50 ppm level. The reason for this is not clear. With the NUKON bed present, there is the potential for the formation of a sodium aluminum silicate coating on the NUKON that would reduce the amount of Al in solution even with no formation of $Al(OH)_3$. The formation of such a coating has been postulated as the explanation for the relatively low levels of Si seen in the ICET tests. In Table 7 both the possibility that nominal values should be reduced to reflect loss to the NUKON bed and the possibility that the ICP results need to normalized to get a more accurate quantitative match have been considered. Both approaches suggest that at a nominal test level corresponding to 70 ppm there is a decrease in the Al concentration solution. This is consistent with the observation of increasing head loss at this point in the test. At a nominal test level of 80 ppm Al, the estimates of Al removed from the solution range from 3–7 ppm. The lower estimate is reasonably consistent with the surrogate test suggesting that a precipitation product corresponding to 5 ppm of Al should cause complete

plugging of the system. The higher estimate suggests that the surrogate product is somewhat conservative in terms of the amount of head loss produced.

Discussion

The ICET–5–2–B2 test confirms the results from the WCAP surrogate test, ICET–1-W, that relatively small amounts of dissolved Al have to precipitate to produce a significant increase in head loss. Because of the uncertainties in the ICP measurements, a precise quantitative comparison can't be made, but in the ICET–5–2–B2 test, precipitation of 3–7 ppm of the dissolved Al produced a large increase in head loss, which seems reasonably consistent with the result of the surrogate test where the addition of a product equivalent to that formed by 5 ppm of dissolved Al was sufficient to plug the bed.

The visual observations in the small–scale solubility tests, the long–term concentration measurements in the precipitation kinetics tests, and the two long–term loop tests all suggest that a concentration of 50 ppm Al can be maintained in STB and boric acid solutions with pH 8.4 at 70–80°F for periods of at least 20 days without the formation of significant amounts of precipitate product. The true solubility of $Al(OH)_3$ may be less than 50 ppm; the current estimate is from the precipitation kinetics test that showed 51 ppm of Al in solution after 134 days. Although the true solubility may be < 50 ppm, the precipitation kinetics are slow and at nominal levels of 85–90 ppm both the small–scale solubility tests and the loop tests suggest that only 3–10 ppm of Al is actually removed from solution (at least in terms of precipitate particles > 0.22μm) over a time scale of 1–2 days.

The apparent solubility of $Al(OH)_3$ at pH 8.4 is much higher than would be expected from literature data on $Al(OH)_3$ in $Al(NO_3)_3$/NaOH solutions or from the tests of Klasky et al.[2] and Park[5] in solutions with $Al(NO_3)_3$, boric acid, and NaOH. Again, we have not fully determined whether this is a true difference in solubility or whether it reflects extremely sluggish precipitation kinetics. Klasky[2] has suggested that boron complexing could affect the solubility of Al. The apparent solubility in $Al(NO_3)_3$, boric acid, and NaOH solution seems similar to that in $Al(NO_3)_3$ and NaOH solutions, but perhaps STB solutions are different. It should be noted that the corrosion rate of Al in STB solutions also seems different from that in boric acid/NaOH solutions with similar pH. The corrosion rate in ICET–5 over day 1–11 was 5.1 mg/m²·min. The predicted corrosion rate[*] based on tests in boric acid/NaOH solutions is 14.4 mg/m²·min.

The results in the current tests also do not appear to be fully consistent with the ICET–5 test. The Al concentration during ICET–5 is shown in Fig. 11. In this test at 140°F the peak concentration of Al is ≈ 55 ppm on day 12; the concentration then averages ≈ 45 ppm. In ICET–5, beginning with the Day 2 water sample, white precipitates were observed after the samples had been at room temperature for several days. These precipitates settled to the bottom of the sample bottles. When the bottles were gently turned upside down, the precipitates formed wispy patterns in the solution. They were re-suspended when the bottles were shaken and could not be seen. It takes 2–3 days for the precipitates to settle again in the sample bottles. The precipitate was not concentrated enough to allow samples to be obtained for analysis.

These precipitates apparently are forming at very low Al levels. It is possible that they are sodium aluminum silicates formed before the NUKON was sufficiently coated to become effectively inert and simply remain in suspension and become visible only when allowed to settle. The decrease in Al concentration from Day 12 onward is more difficult to rationalize.

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[*]Determined from the WCAP -16530-NP Rev. 0 Eq. (6–1) with coefficients corrected as per the Technical Letter Report on WCAP-16530-NP by W. J. Shack, Sept. 2006.

Table 6. Chemical control history during ICET–5–2–B2

Date	Time (h:min)	ElapsedTime (days)	Sample Designation or Activity	Cond (mS)	pH	Temp (C)	Temp (F)	Nominal Al conc (ppm)	ICP Results (ppm)
9/11	10:00	0.00	#5-1	1.33 µS	5.78	57	135	0	
9/11	10:00	0.00	Add BA, STB, LiOH						
9/12	8:30	0.93	#5-2	3.63	8.50	28	82	0	
9/12	9:40	0.98	Add NUKON						
9/12	11:45	1.07	#5-3	3.67	8.49	27	80	0	
9/12	13:50	1.16	Add AN (50 ppm Al)						
9/12	14:10	1.17	#5-4	3.94	8.22	60	139	50	
9/12	16:30	1.27	#5-5	?	8.38	27	81	50	
9/13	15:00	2.21	#5-6	3.88	8.42	24	76	50	
9/14	15:25	3.22	#5-7	3.88	8.40	27	80	50	
9/15	8:20	3.93	#5-8	3.85	8.39	27	81	50	
9/18	10:30	7.02	#5-9	3.89	8.38	27	80	50	42.2
9/19	11:10	8.05	#5-10	3.85	8.39	27	81	50	
9/20	9:05	8.96	#5-11	3.86	8.37	27	80	50	
9/21	10:00	10.00	#5-12	3.86	8.36	29	84	50	
9/22	16:50	11.28	#5-13 (missing)	3.87	8.40	27	81	50	
9/25	13:15	14.13	#5-14	3.88	8.36	27	81	50	41.2
9/26	10:15	15.01	#5-15	3.86	8.40	27	81	50	
9/27	15:20	16.22	#5-16	3.85	8.41	27	80	50	
9/28	17:15	17.30	#5-17	3.84	8.41	27	81	50	
9/29	16:06	18.25	#5-18	3.81	8.41	27	80	50	40.6
10/3	15:30	22.23	#5-19	3.97	8.31	48	119	50	
10/3	15:32	22.23	Add 1st batch of AN						
10/4	8:35	22.94	#5-20	4.11	8.32	49	119	53	
10/4	10:10	23.00	Add 2nd batch of AN						
10/4	13:05	23.13	#5-21	4.20	8.33	48	118	57	
10/4	13:58	23.16	Add 3rd batch of AN (60 ppm Al)						
10/4	14:15	23.17	#5-22	4.28	8.35	48	118	60	50.2
10/5	9:30	23.98	#5-23	4.15	8.46	27	80	60	49.4
10/5	13:24	24.14		4.30	8.33	46	115	60	
10/5	13:27	24.14	Add 1st batch of AN						
10/5	13:58	24.16		4.38	8.37	47	116	63	
10/5	14:00	24.16	Add 2nd batch of AN						
10/5	14:25	24.18		4.46	8.39	47	116	67	
10/5	14:30	24.18	Add 3rd batch of AN (70 ppm Al)						
10/5	15:25	24.22		4.55	8.39	47	116	70	
10/5	15:30	24.23	Add Nitric acid						
10/5	16:37	24.27		4.56	8.35	47	116	70	
10/5	17:10	24.30	Add Nitric acid						
10/5	17:18	24.30		4.58	8.33	47	116	70	
10/6	8:30	24.93		4.58	8.37	47	116	70	
10/6	13:20	25.14		4.58	8.36	47	116	70	
10/6	15:33	25.23	#5-24	4.59	8.35	47	117	70	
10/9	13:15	28.13	#5-25-1F: 0.22 um filter	4.59	8.37	47	117	70	56.8
			#5-25-2: 2 cc samples						56.9
			#5-25-3: 2 cc samples						56.1
			#5-25-4: 2 cc samples						56.4
			#5-25-5 & 6: 100 cc samples						
10/9	17:05	28.29	#5-26	4.53	8.41	37	99	70	

Date	Time (h:min)	ElapsedTime (days)	Sample Designation or Activity	Cond (mS)	pH	Temp (C)	Temp (F)	Nominal Al conc (ppm)	ICP Results (ppm)
10/10	8:40	28.94	#5-27	4.52	8.41	37	98	70	
10/10	16:45	29.28	#5-28	4.46	8.48	27	80	70	
10/11	8:45	29.94	#5-29	4.44	8.46	26	80	70	
10/11	11:50	30.07	#5-30	4.59	8.34	48	118	70	
10/11	12:00	30.08	Add 1st batch of AN						
10/11	13:15	30.13	#5-31	4.66	8.33	48	119	73	
10/11	13:20	30.14	Add 2nd batch of AN						
10/11	14:03	30.17	#5-32	4.75	8.32	48	118	77	
10/11	14:10	30.17	Add 3rd batch of AN (80 ppm Al)						
10/11	15:45	30.24	#5-33	4.83	8.37	48	118	80	
10/12	8:27	30.93	#5-34	4.80	8.38	48	118	80	66.1
10/12	10:20	31.01	Add Nitric acid (3:1 dilution)						
10/12	10:40	31.02		4.89	8.36	48	118	80	
10/12	11:00	31.04		4.90	8.36	48	118	80	
10/12	11:10	31.05	Add Nitric acid (3:1 dilution)						
10/12	11:39	31.07		4.91	8.35	48	118	80	
10/12	11:42	31.07	Add Nitric acid (3:1 dilution)						
10/12	15:47	31.24	#5-35	4.94	8.34	48	119	80	
10/12	16:20	31.26	Add Nitric acid (3:1 dilution)						
10/12	17:10	31.30	#5-36	4.95	8.35	48	118	80	
10/13	8:55	31.95	#5-37	4.95	8.36	48	118	80	
10/13	9:25	31.97	Add Nitric acid (3:1 dilution)						
10/13	13:13	32.13	#5-38	4.97	8.33	48	119	80	65.1
10/13	16:27	32.27	#5-39	4.89	8.40	38	100	80	
10/16	9:10	34.96	#5-40	4.88	8.39	38	100	80	64.3
10/16	17:30	35.31	#5-41	4.82	8.46	26	80	80	
10/17	8:50	35.95	#5-42	4.83	8.45	27	80	80	
10/17	9:30	35.98	Add Nitric acid (30 mL, 3:1 dilution)						
10/17	10:45	36.03		4.86	8.43	27	80	80	
10/17	11:00	36.04	Add Nitric acid (30 mL, 3:1 dilution)						
10/17	11:30	36.06	#5-43	4.91	8.41	27	80	80	
10/17	13:15	36.13		4.89	8.41	27	80	80	
10/17	13:20	36.14	Add Nitric acid (30 mL, 3:1 dilution)						
10/17	14:00	36.16	#5-44	4.93	8.39	27	80	80	64
10/17	14:10	36.17	Add Nitric acid (30 mL, 3:1 dilution)						
10/17	14:30	36.18	#5-45	4.99	8.37	27	80	80	
10/17	14:55	36.20	Add Nitric acid (30 mL, 3:1 dilution)						
10/17	15:10	36.21	#5-46	5.03	8.34	27	80	80	
10/17	15:20	36.22	Add Nitric acid (45 mL, 3:1 dilution)						
10/17	15:40	36.23	#5-47	5.09	8.31	27	81	80	
10/17	16:20	36.26	Add Nitric acid (90 mL, 3:1 dilution)						
10/17	16:35	36.27	#5-48	5.24	8.23	27	80	80	
10/18	8:40	36.94	#5-49-1F (0.22 um filter)	5.23	8.21	27	80	80	61.2
			#5-49-2						64.3
			#5-49-3						64.5
			#5-49-4						

Table 7. "Corrected" concentration values for the ICET–5–2–B2 test

Elapsed Time (days)	Sample Designation or Activity	Cond (mS)	pH	Temp (°F)	Nominal Al conc (ppm)	Normalized ICP		Adjusted Nominal	ICP Results (ppm)
7.02	#5-9	3.89	8.38	80.06	50	51.0		41.3	42.2
14.14	#5-14	3.88	8.36	81.14	50	49.8		41.3	41.2
18.25	#5-18	3.81	8.41	80.24	50	49.1		41.3	40.6
23.18	#5-22	4.28	8.35	118.04	60	60.7		51.3	50.2
23.98	#5-23	4.15	8.46	79.7	60	59.8		51.3	49.4
28.14	#5-25-1F					68.7		61.3	56.8
	#5-25-2	4.59	8.37	116.6	70	68.8		61.3	56.9
	#5-25-3					67.9		61.3	56.1
	#5-25-4					68.2		61.3	56.4
30.94	#5-34	4.80	8.38	117.5	80	80.0		71.3	66.1
32.13	#5-38	4.97	8.33	118.94	80	78.8		71.3	65.1
34.97	#5-40	4.88	8.39	99.5	80	77.8		71.3	64.3
36.17	#5-44	4.93	8.39	79.88	80	77.4		71.3	64
36.94	#5-49-1F					74.0		71.3	61.2
	#5-49-2	5.23	8.21	79.88	80	77.8		71.3	64.3
	#5-49-3					78.0		71.3	64.5
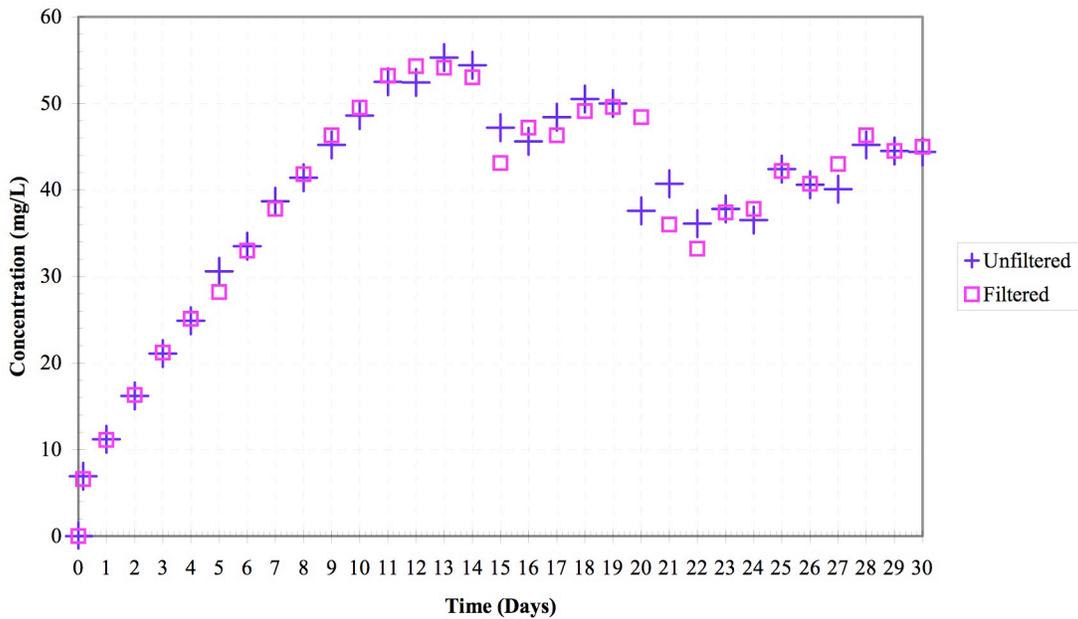
Figure 11. Al concentrations in the ICET–5 test[7]

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Appendix A

Table A1.   Complete ICP analysis results for solution samples from NRR 80 and NRR 100.

Sample ID	Elapsed Time (day	Nominal Al (ppm	ICP Analysis Results (ppm						
			Al	B	Na	Ca	K	Si	P
NRR 80 4[a]	19.0	55	66.0	4540	3660	2.0	14.4	1.1	0.4
NRR 80 5	22.2	55	65.1	4580	3630	NM[b]	<2.5	<2.5	<2.5
NRR 80 6	23.1	60	71.7	4620	3640	NM[b]	<2.5	<2.5	<2.5
NRR 80 7	25.9	65	75.4	4630	3620	NM[b]	<2.5	<2.5	<2.5
NRR 80 8	27.8	70	80.2	4470	3550	NM[b]	<2.5	<2.5	<2.5
NRR 80 9	28.9	75	85.0	4360	3480	NM[b]	<2.5	<2.5	<2.5
NRR 80 10	29.9	80	91.3	4510	3470	NM[b]	<2.5	<2.5	<2.5
NRR 80 11[c]	32.9	85	95.5	4600	3500	NM[b]	<2.5	<2.5	<2.5
NRR 80 12[c]	34.1	90	102.0	4480	3540	NM[b]	<2.5	<2.5	<2.5
NRR 100 5	22.2	55	57.1	4470	3610	NM[b]	<2.5	2.62	<2.5
NRR 100 11[c]	32.9	85	80.4	4700	3680	NM[b]	<2.5	2.82	<2.5
NRR 100 12[c]	34.1	90	82.0	4520	3580	NM[b]	<2.5	2.91	<2.5

[a]This sample was analyzed by University of Minnesota and all other samples were analyzed by ACL in Argonne National Lab.

[b]Not measured

[c]This sample was filtered by using 0.22 μm filter and other samples were filtered by 0.02 μm filter