Technical Letter Report on Evaluation of WCAP Aluminum Hydroxide Surrogate Stability at Elevated pH

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Executive Summary

One acceptable method to the NRC staff for conducting chemical effects head loss testing is to follow the methodology for creating chemical surrogate material as described in WCAP-16530. Many licensees have employed this method. An assumption in WCAP-16530 is that the water used in head loss testing remains close to a neutral pH. However, during head loss testing, materials such as insulation can leach chemicals that may elevate the pH of the water. The NRC staff requested that Argonne National Laboratory (ANL) evaluate the potential impact that elevated pH may have on the chemical surrogates created using the WCAP-16530 methodology.

Bench scale and loop head loss tests[1] for $Al(OH)_3$ precipitates that can potentially form in sump solutions with high levels of dissolved aluminum (Al) have been performed at ANL with aluminum oxyhydroxide (AlOOH) surrogates prepared as described in WCAP-16530.[2] In previous tests, the characteristics of this surrogate were explored only at near neutral water chemistry. The main objective of these tests is to evaluate whether or not AlOOH surrogates generated using the WCAP-16530 procedure are affected by elevated pH.

The stability of the WCAP AlOOH surrogate was evaluated by measuring dissolved aluminum concentration as a function of time at different pH values. The solubility of the WCAP AlOOH surrogate in tap water increased with pH. In samples filtered through a 0.02 micron filter, 2.3 ppm Al was detected at pH=8.7, while at pH=8.0, the Al concentration was less than the detection limit of 0.5 ppm. As the solution pH decreased over test time because of carbon dioxide from air, the dissolved Al concentration decreased. At pH=9 dissolution occurred rapidly with peak values of the dissolved Al found at times less than 4 hours. The dissolution kinetics were somewhat slower at pH=8.5. At pH=9.0, the surrogate appears to have a lower solubility in high purity water than in tap water, presumably because the higher ionic strength of tap water enhances the Al hydroxide solubility.

The surrogates made with tap water followed the reaction-limited-colloid-aggregation theory. Although the WCAP AlOOH surrogate particles made with tap water were larger than those made with high purity water at the same pH and total Al concentration (2.2 g of AlOOH/L), the constituent particle size was smaller than that in high purity water. Reaction-limited-colloid-aggregation theory suggests that although the overall solubility is increased, the higher ionic strength of tap water may enhance the nucleation of Al hydroxide precipitates.

A vertical loop head loss test at room temperature with solution pH=9.0 was performed with WCAP AlOOH surrogate made with tap water. A WCAP AlOOH surrogate addition equivalent to the precipitation of 3 ppm Al from solution caused a 2.5-psi head loss increase. At this pH and temperature, the head loss was very stable over 5 days, even though the bench scale tests suggest that this amount of Al would be soluble under these conditions. In a previous head loss test with the WCAP AlOOH surrogate at neutral pH, a 1.5 ppm Al equivalent addition was enough to plug the bed. This suggests that the efficiency of the surrogate on plugging a bed is less at pH=9.0 than at neutral pH, as would be expected from the variation of solubility with pH. Dissolution of WCAP AlOOH surrogate at an initial solution pH=9.0 to a steady state Al concentration occurs quite rapidly. The steady state concentration is quite stable over time periods on the order of five days. After 5 days the solution pH decreased to 8.91. It was further decreased to 7.60 by addition of nitric acid. The decrease in pH resulted in an increase in head loss of an additional 3 psi for a total head loss of 5.5 psi, but then the head loss gradually decreased and stabilized at 4 psi after 2 days. This decrease in head loss was unexpected because of the decreased solubility of AlOOH at the lower pH. It may be due to the

higher ionic strength induced by the nitric acid addition or the effect of precipitate aging making the precipitates less effective in producing head loss.

WCAP AlOOH Surrogate Stability Test - Bench Top

Experimental

A WCAP AlOOH surrogate solution having 2.2 g of AlOOH per liter was prepared according to the instructions provided in WCAP-16530-NP.[2] Three 1000-mL glass beakers were filled with ANL tap water (pH=7.89 @ 25.0°C) and one 2000-mL glass beaker was filled with a mixed water (75% high-purity water + 25% ANL tap water) intended to represent a tap water with a low concentration of dissolved species. A surrogate addition equivalent to a 25 ppm Al concentration was then added into tap water (or the mixed water). The solutions were stirred gently and the solution pH was adjusted as noted in the test matrix (see Table 1) using NaOH. Solution samples filtered using 0.02 micron filters were obtained at sampling times of 0, 1, 4, 8, and 48 hrs and analyzed by Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP/OES). Reference samples for tap water and mixed water were also taken. Solution pH was measured for each test solution when a sample was taken.

Table 1. Test matrix for the WCAP AlOOH surrogate stability tests; an 'O' symbol denotes that a test was performed and the 'X' symbol denotes that no test was performed at that condition.

	pH=8.0	pH=8.5	pH=9.0
Tap Water (Without Boron)	O	O	O
75% High-Purity Water + 25% Tap Water (Without Boron)	X	X	O

Test Results

Table 2 shows the ICP analyses for samples taken during the AlOOH surrogate stability test. ICP analyses confirmed that ion concentrations in the mixed water were around 25% of those in the tap water. After the surrogate additions, the concentrations of Ca, Mg, and Na appear to gradually decrease with time but the concentration change over 48 hours was usually less than 1 ppm. The uncertainty of the ICP values is ±10 % of reported value. The Si content was almost always less than the ICP detection limit of 0.5 ppm, which suggests that silicates may precipitate at higher pH and are filtered out, or that the Si is present in the tap water as precipitated form, not soluble form. A test for detecting reactive silica could be done using ammonium phosphomolybdate reagent but it was not performed. In Figure 1, the aluminum concentration of the filtered solutions is plotted as a function of time and initial solution pH. The Al concentration is higher at higher solution pH. At pH=9.0 with tap water, initial Al concentration is the highest compared with other solutions, as expected. At pH=8.5 with tap water, the aluminum dissolution kinetics were slower; the measured peak concentration occurred at 10 hours, and after 48 hours the dissolved Al concentration became less and approached the ICP detection limit. At pH=8.0 with tap water, the Al concentration

was always less than the ICP detection limit, 0.5 ppm. The Al concentration of pH=9.0 solution with tap water gradually decreased from t=1 hr and after 48 hours approached the ICP detection limit. At pH=9.0 with mixed water, the initial aluminum concentration was lower than that of pH=9.0 with tap water and rapidly decreased. The Al concentration became less than the detection limit only after 8 hours.

The solution pH variations are shown in Figure 2. Except for the case of pH=8.0, which seems very stable over 48 hours, the pH of the solutions dropped quickly for the first 4 hours and then slowly decreased over the remaining 44 hours. The initial rapid pH decrease and the long term gradual pH decrease are believed to result from two separate phenomena. The long term gradual pH decrease appears to be due to the presence of carbon dioxide in the air, which can dissolve into water and make it more acidic. The initial rapid pH drop appears to be caused by the aluminum hydroxide dissolution according to the dissolution reaction:

$$\begin{aligned} &Al(OH)_3(s) + H_2O \Leftrightarrow Al(OH)_4^- + H^+ \quad \text{or} \\ &Al(OH)_3(s) + OH^- \Leftrightarrow Al(OH)_4^- \end{aligned} \quad . \tag{1}$$

The presence of dissolved Al indicates the dissolution of AlOOH surrogate. However, the dissolution also results in a pH decrease, which leads to a new equilibrium condition between dissolution and precipitation at a new pH condition. The pH decrease over 48 hours can result in precipitation of aluminum hydroxide and reduction of dissolved Al concentration. Other possible explanations are precipitate aging over time, which could cause the precipitate growth and/or amorphous-to-crystalline phase transition resulting in the reduction of dissolved Al concentration.

For the case of the mixed water at pH=9.0, the solution pH variation was similar to that of tap water at the same pH. However, as noted previously, the aluminum concentration in this solution monotonically decreased without increase and became less than the detection limit after 8 hours. This suggests that WCAP AlOOH surrogate solubility at pH=9.0 is less in the higher purity mixed water than in tap water. Usually the solubility of solid precipitates is dependent on the ionic strength of the solution; higher ionic strength induces higher solubility.[3] Therefore, it seems plausible to attribute this observation to the effect of ionic strength.

These results may seem to contradict earlier results with sodium aluminum silicate (SAS) surrogate.[1] Bench top and head loss tests showed the SAS surrogate was more stable in tap water than in high purity water, even though tap water has higher ionic strength. In this case, account may have to be taken of the specific ions in the tap water, in particular Na and Si ions. The presence of these ions can reduce the solubility of the SAS. This effect is referred to as the "common ion effect."[3] The dissolution reaction of SAS and its solubility product are given by Eq. (2) and (3), respectively;

$$Na(AlSi_3O_8) + 4H_2O + H^+ \Leftrightarrow Na^+ + Al^{3+} + 3H_3SiO_4^- , \tag{2}$$

$$K_{sp} = \frac{a_{Na^+} a_{Al^{3+}} a^3_{H_3SiO_4^-}}{a_{Na(AlSi_3O_8)} a_{H^+} a^4_{H_2O}} \approx \frac{\left[Na^+\right]\left[Al^{3+}\right]\left[H_3SiO_4^-\right]^3}{\left[H^+\right]} . \tag{3}$$

In Eq. (3) a_i means the activity of species *i* and the bracketed terms are the molar concentration of species *i*. Because the solubility product K_{sp} is constant, at a given solution pH and temperature, if sodium and silicate ion concentrations are higher in solution, the

dissolved aluminum ion concentration becomes less. Another possible explanation is that when the SAS surrogate is added to tap water, a certain amount of calcium silicate might precipitate, and this precipitation could contribute to the higher head loss than SAS in high purity water.

From the viewpoint of colloid aggregation, higher ionic strength enhances more colloidal particle aggregation by reducing the diffusion layer thickness around charged particles. But higher particle aggregation tendency does not necessarily mean lower solubility. Therefore, the surrogate solubility difference between tap and mixed water for AlOOH is not necessarily contradictory with the behavior observed for the SAS surrogate.

Table 2. Summary of the ICP analyses for samples taken during the WCAP AlOOH surrogate stability test at elevated pH; all samples were filtered using 0.02 micron filters except ALST-01 and -02 (Uncertainty: ±10% of reported value).

Sample #	Description	Concentration by ICP (ppm)					
		Al	Ca	Mg	K	Si	Na
ALST-01	ANL tap water	<0.5	30.6	10.5	1.24	0.93	7.52
ALST-02	Mixed water (75% high-purity water + 25% ANL tap water)	<0.5	7.54	2.57	<0.5	<0.5	1.85
ALST-03	pH=8.0 with tap water, taken at t=0 hr	<0.5	30.7	10.6	1.29	0.55	76.1
ALST-07	pH=8.0 with tap water, taken at t=1 hr	<0.5	30.6	10.5	1.22	<0.5	75.7
ALST-11	pH=8.0 with tap water, taken at t=4 hr	<0.5	30.2	10.4	1.29	<0.5	75.2
ALST-15	pH=8.0 with tap water, taken at t=8 hr	<0.5	29.7	10.4	1.27	<0.5	73.3
ALST-23	pH=8.0 with tap water, taken at t=48 hr	<0.5	29.2	10.2	1.86	<0.5	73.6
ALST-04	pH=8.5 with tap water, taken at t=0 hr	<0.5	29.5	10.2	1.28	<0.5	77.4
ALST-08	pH=8.5 with tap water, taken at t=1 hr	0.99	29.5	10.2	1.25	<0.5	77.6
ALST-12	pH=8.5 with tap water, taken at t=4 hr	0.71	29.7	10.2	1.22	<0.5	78.9
ALST-16	pH=8.5 with tap water, taken at t=8 hr	1.28	28.9	10.1	1.22	<0.5	75.4
ALST-24	pH=8.5 with tap water, taken at t=48 hr	0.60	28.7	9.97	1.31	<0.5	75.0
ALST-05	pH=9.0 with tap water, taken at t=0 hr	2.19	28.9	9.84	1.24	<0.5	84.1
ALST-09	pH=9.0 with tap water, taken at t=1 hr	2.88	29.2	9.90	1.22	<0.5	83.5
ALST-13	pH=9.0 with tap water, taken at t=4 hr	2.34	28.9	9.84	1.19	<0.5	83.1
ALST-17	pH=9.0 with tap water, taken at t=8 hr	2.30	28.0	9.67	1.30	<0.5	80.1
ALST-25	pH=9.0 with tap water, taken at t=48 hr	0.61	29.6	9.58	1.25	<0.5	85.0
ALST-06	pH=9.0 with mixed water, taken at t=0 hr	1.92	8.32	2.65	<0.5	<0.5	75.2
ALST-10	pH=9.0 with mixed water, taken at t=1 hr	1.67	7.52	2.56	<0.5	<0.5	74.5
ALST-14	pH=9.0 with mixed water, taken at t=4 hr	1.09	7.43	2.51	<0.5	<0.5	71.9
ALST-18	pH=9.0 with mixed water, taken at t=8 hr	<0.5	7.70	2.49	<0.5	<0.5	75.0
ALST-26	pH=9.0 with mixed water, taken at t=48 hr	<0.5	7.85	2.34	<0.5	<0.5	73.3

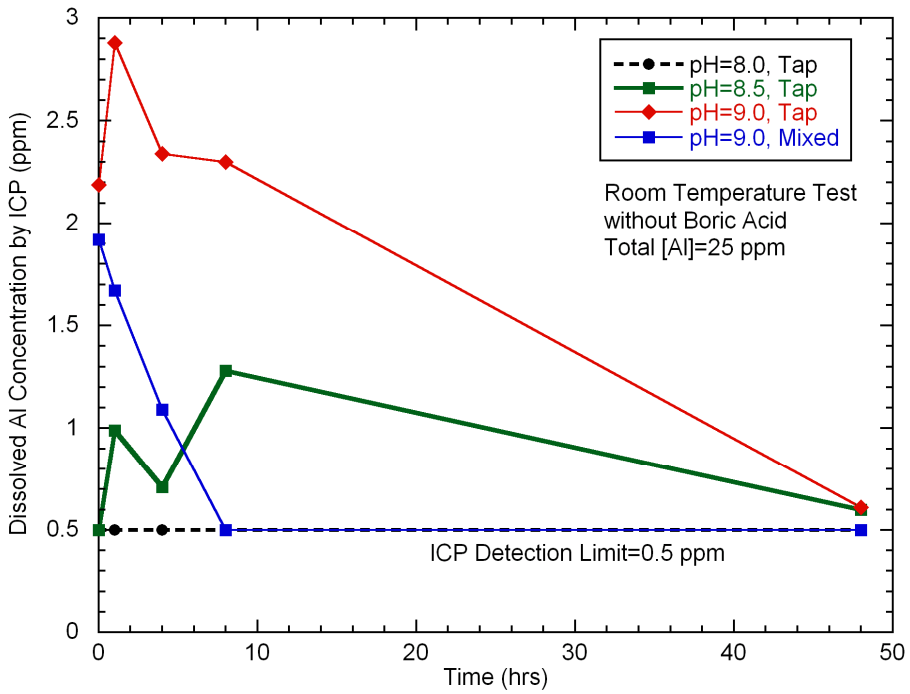


Figure 1. Dissolved Al concentration variations as a function of time and solution pH.

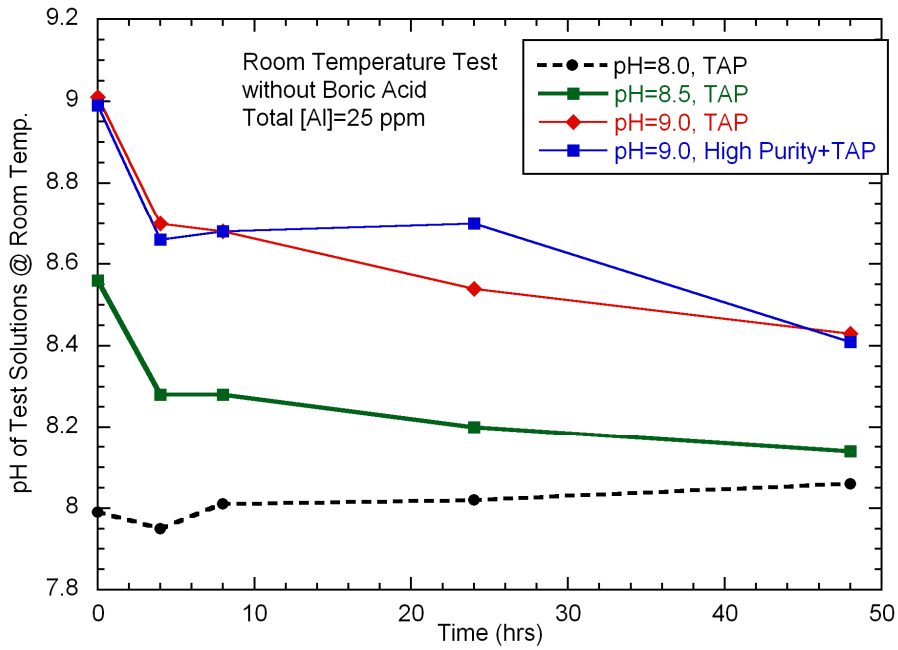


Figure 2. pH variation of test solutions as a function of time.

WCAP AlOOH Surrogate Stability Test - Vertical Loop

A previous vertical loop head loss test with WCAP AlOOH surrogate with high purity water at pH=6.4 showed that an AlOOH surrogate amount equivalent to 1.5 ppm Al was enough to completely plug the NUKON bed.[1] Since the measured Al concentration of AlOOH surrogate was 2.3 ppm at pH=8.7 in bench top tests, at an elevated pH condition like pH=9.0 WCAP AlOOH surrogate might be expected to be dissolved back into solution, and an amount of surrogate equivalent to 1.5 ppm Al might be not enough to completely plug the NUKON bed. A vertical loop head loss test in the ANL vertical head loss test loop was performed at pH=9.0 with tap water to evaluate the effect of pH on the WCAP AlOOH surrogate.

Experimental

A detailed description of the ANL vertical head loss test loop has been provided in a previous NUREG report.[4] The loop was filled with tap water and the pH was raised to 9.0 by adding sodium hydroxide (NaOH) at room temperature. A standard NUKON bed was then made using the procedure described in previous technical letter reports[1,5] and the NUREG report.[4] When the pressure drop stabilized, incremental amounts of WCAP AlOOH surrogate (initial additions were 0.5 ppm Al equivalent) were added attempting to obtain an increase in head loss of about 1 psi. The loop was then run and the head loss was tracked for 1 day to see if there was a significant decrease. If there was a decrease over a day, more surrogate was added and the test continued for another day. After a pressure drop of about 2.5 psi was achieved, the test was continued to test the stability of the head loss over a 5 day period. At the end of this period, small amounts of nitric acid were added in short intervals to determine the effect of lowering the solution pH. The loop water temperature was maintained at 80±3°F over the whole test period.

Test Results

Figure 3 shows the pressure drop across the NUKON bed and approach velocity as a function of time for the vertical loop test. Figure 4 shows the variation of the loop water temperature over the test period. The loop circulation pump was operated at a constant rpm mode. The flow velocity was 0.1 ft/sec initially but was allowed to vary according to the total loop head loss change. As expected, the flow velocity decreased as the head loss increased. The AlOOH surrogate solution was added in increments equivalent to 0.5 ppm Al initially and then in increments of 0.25 ppm Al. After 2.0 ppm Al equivalent had been added, the loop was run over night. The pressure drop during this period (10–24 h) was very stable as shown in Figure 3. The head loss increment produced by each 0.5 ppm Al injection as AlOOH surrogate increased with each addition. After the total Al equivalent addition reached 3.0 ppm, the loop was run for around 4.6 days to determine the stability of the WCAP AlOOH surrogate over a longer time period. The pressure drop appeared to be stable, although small variations due to changes in the loop water temperature were observed. The changes in the loop water temperature appear to be caused by closing a cooling water line over weekend during which the long cooling water pipeline was exposed to a relatively warm laboratory atmosphere. The solution pH change from the beginning of test to the end of the 4.6 day hold time was only 0.15 (from 9.06 to 8.91). The test results suggest that at a 3.0 ppm Al equivalent concentration the WCAP AlOOH surrogate would be stable at pH=9 in tap water for at least 5 days. At a test time of 145 hours, dilute nitric acid was added to lower the loop water pH. A decrease in pH from 8.91 to 8.73 did not cause much increase in head loss. When the solution pH was decreased from 8.73 to 8.10, the head loss rapidly increased, but rapidly decayed and stabilized. This behavior may be attributed to local aluminum hydroxide precipitation near the acid injection

point followed by redissolution of the precipitates as the low pH water near the injection point mixed with the higher pH water in the remainder of the loop. When the overall solution pH decreased from 8.10 to 7.60, the head loss instantaneously increased to near the loop capacity limit. However, over 3 days the head loss gradually decreased and appeared stabilized at the end of the test. The instantaneous increase in head loss at pH=7.60 was expected, but the gradual decrease over 3 days is difficult to explain. Local precipitation and redissolution seems unlikely, because the kinetics of mixing and redissolution would be expected to be on the order of a few hours at most based on the behaviors observed during the pH decrease from 8.73 to 8.10, and in any case, the solubility of aluminum hydroxide at an overall pH=7.6 is negligible. Possible explanations are the effect of ionic strength on solubility, as discussed before, and the effect of precipitate aging. The nitric acid injection increased the solution conductivity by 6% compared with the value before adding nitric acid. But it is not clear that a 6% increase in the ionic strength would be sufficient to cause the solubility change of aluminum hydroxide corresponding to a change of 1-psi in head loss. Assuming that precipitate aging took place over 3 days, during that time period, the precipitate size might change due to the crystalline growth or amorphous-to-crystalline phase transition, which could cause a decrease in pressure drop. However, if precipitate aging were responsible, it is not clear why the precipitate aging did not take place over the 5 days at pH=9.0.

Based on the bench top tests and the previous loop test at a neutral pH, it was expected that an addition of surrogate equivalent to 2.0-2.5 ppm Al would cause a significant increase in head loss, but that the increase would gradually decrease because of dissolution of the surrogate. However, the head losses after either 2.0 or 3.0-ppm Al additions were very stable and at the 3.0 ppm level did not show any significant decrease over 5 days. A 1.5-ppm Al addition produced only a 0.5-psi head loss, which was much lower than that observed in a previous loop test at a neutral pH. The loop test results suggest that some of the WCAP AlOOH surrogate dissolves back into solution at pH=9.0, and that the dissolution is rapid, but limited, because the head loss increases immediately after the surrogate injection, levels off quickly, and remains stable over 6 days. The bench top tests suggest that an amount of the AlOOH surrogate equivalent to around 2.5 ppm Al can be dissolved at pH=9.0. Since the previous loop test showed 1.5 ppm Al was enough to plug the NUKON bed, the estimated surrogate amount to plug the bed at pH=9.0 is 4.0 ppm Al. However, in the test this was not actually confirmed, since we opted to explore the effect of reducing the pH.

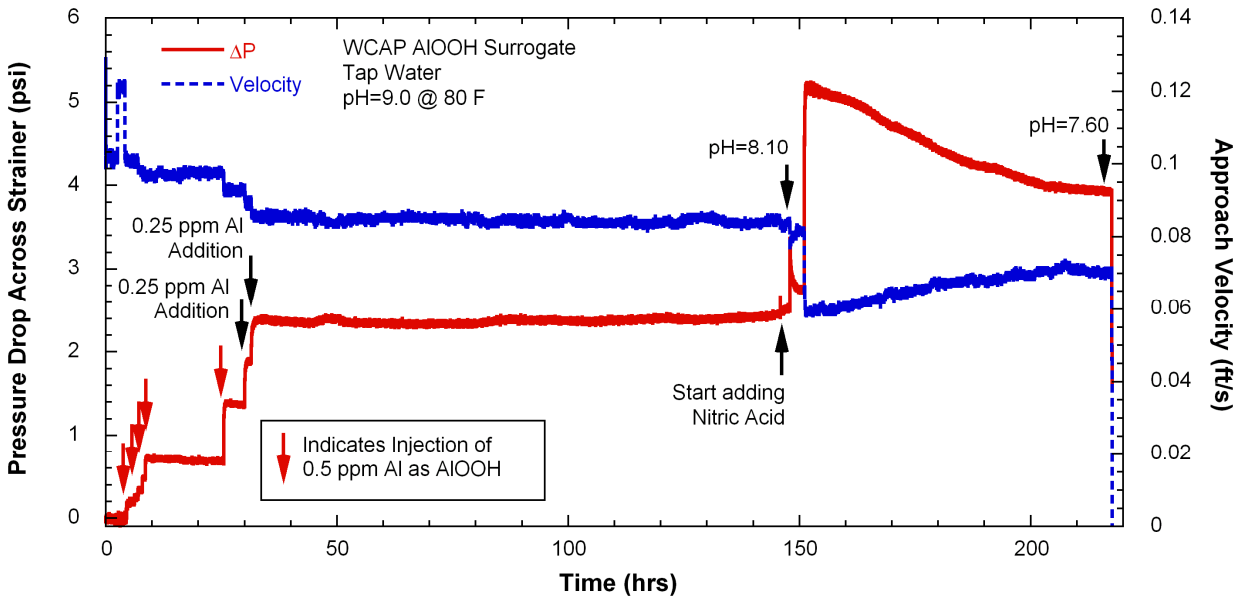


Figure 3. Pressure drop across the NUKON bed and approach velocity as a function of time for a vertical loop head loss test with tap water at initial pH=9.0.

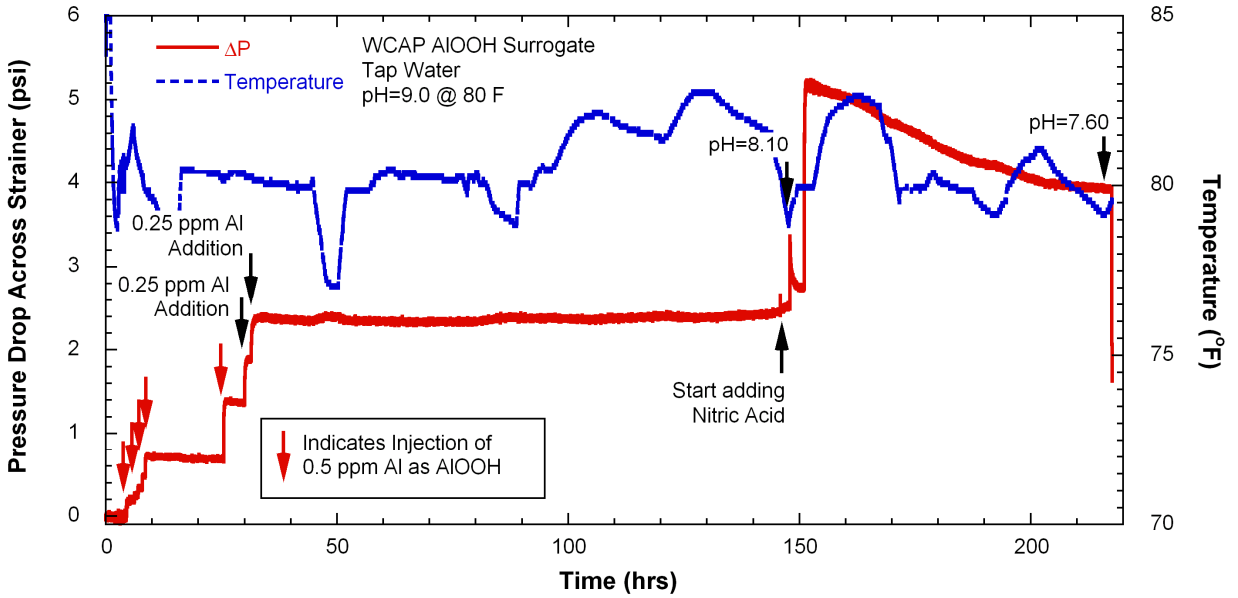


Figure 4. Pressure drop across the NUKON bed and loop water temperature as a function of time for a vertical loop head loss test with tap water at initial pH=9.0.

Discussion

Settling Velocity and Size of Surrogate in Tap Water

To further examine the characteristics of the WCAP AlOOH surrogate in tap water, settling rates and size distributions of the surrogates were measured. A surrogate having 2.2 g of AlOOH per liter was prepared following the WCAP procedure, but the solution pH was adjusted over the range 7.2 to 11.0. This is much larger than the variations observed following the WCAP procedure, in which the final solution pH is typically 8±0.5. The pH variation observed when following the WCAP procedure appears to be attributable to weighing errors for aluminum nitrate and sodium hydroxide powders or in measurement of the total water volume. It could be also caused by the variation in the initial tap water pH or impurities in the aluminum nitrate.

The pH-adjusted surrogate solution was poured into a 250-mL graduated mass cylinder and the distribution of the precipitate particles in the cylinder was tracked as a function of time. The size distribution of the surrogates was measured by a laser light scattering method (CILAS Model 1064 particle size analyzer).

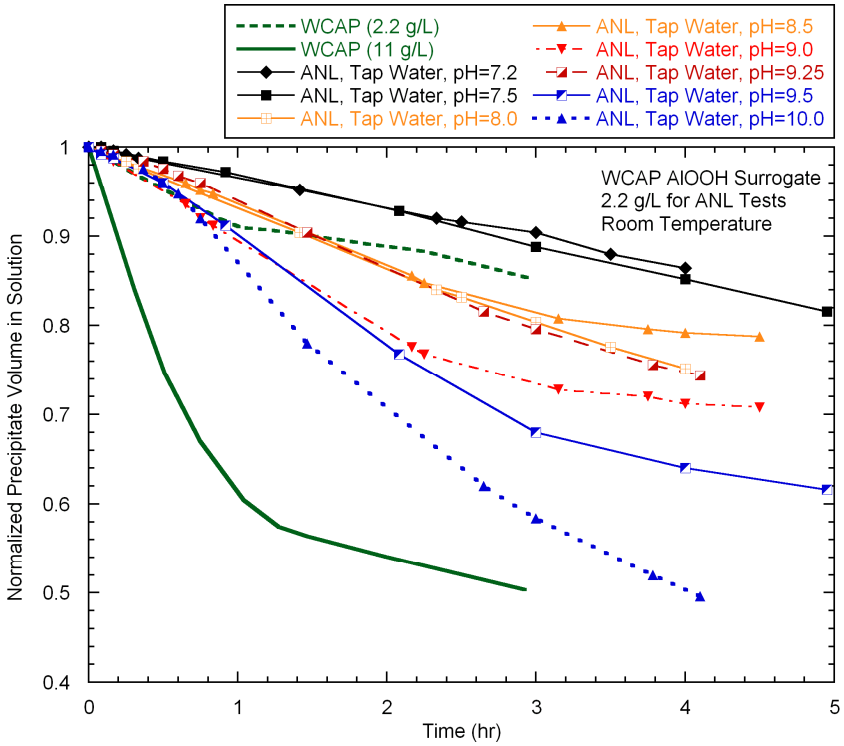
Figure 5 shows the normalized, settled, precipitate volumes of the WCAP AlOOH surrogates made with tap water as a function of solution pH. The settling behavior of the surrogates having a pH of 8.0-8.5 appear to be consistent with those reported for the 2.2 g/L surrogate in the WCAP, as expected. At a pH less than 8.0 the settling velocity was lower and at a pH greater than 8.5 the settling velocity was higher than the velocity reported in the WCAP. When the solution pH was greater than 10.0, the settling velocity became even higher than the velocity of the 11 g/L surrogate reported in the WCAP, as shown in Figure 5(b). As the solution pH increased, the Al fraction in solution increases and, the settled precipitation mass should become less. At pH=10.5 and 11.0 big clusters like cotton-balls were easily visible, which suggests that the higher settling velocities at those pH ranges were associated with the larger flocculated particle size.

The particle size distributions of the surrogates in solutions with pH ranging from 7.2 to 10.0 are plotted in Figure A1. The overall shape of the size distribution is similar to that of the AlOOH surrogate made with high purity water reported in a previous letter report[1], but the median particle size is larger than that of surrogate made with high purity water at the same pH. Based on the colloid aggregation theory,[6] higher ionic strength enhances the colloid aggregation so that the median particle size of the surrogate would be higher in tap water. It is noted that in the pH range of 8.5 and 9.5 the ultrasonic vibration made the surrogate particles not only break into parts leading to a higher broad peak at smaller diameters, but also enhanced aggregation leading to a second peak at a larger diameter. This appears to be attributed to the surface electric potential variation with the solution pH. Since the point-of-zero charge (PZC) of aluminum hydroxide is in between 8.9 and 9.7 depending on its crystal phase,[6] the surface potential (or zeta potential) would be very low at the pH ranging from 8.5 to 9.5, which might help the relatively bigger particles overcome their repulsive inter-particle potential barrier with the given ultrasonic vibration energy. In these tests, it was assumed that only aluminum hydroxide precipitates were formed but, no analyses were performed to determine the actual identity of the precipitated materials in the surrogates with tap water. At pH=10.5 to 11.0, $Ca(OH)_2$, $CaCO_3$, $MgCO_3$ and silicates can begin to precipitate from the tap water. The carbonate precipitates in particular should settle quickly but would appear more crystalline. The “cotton balls” do not seem like crystalline materials but flocculated material which is likely a mixture of several different materials.

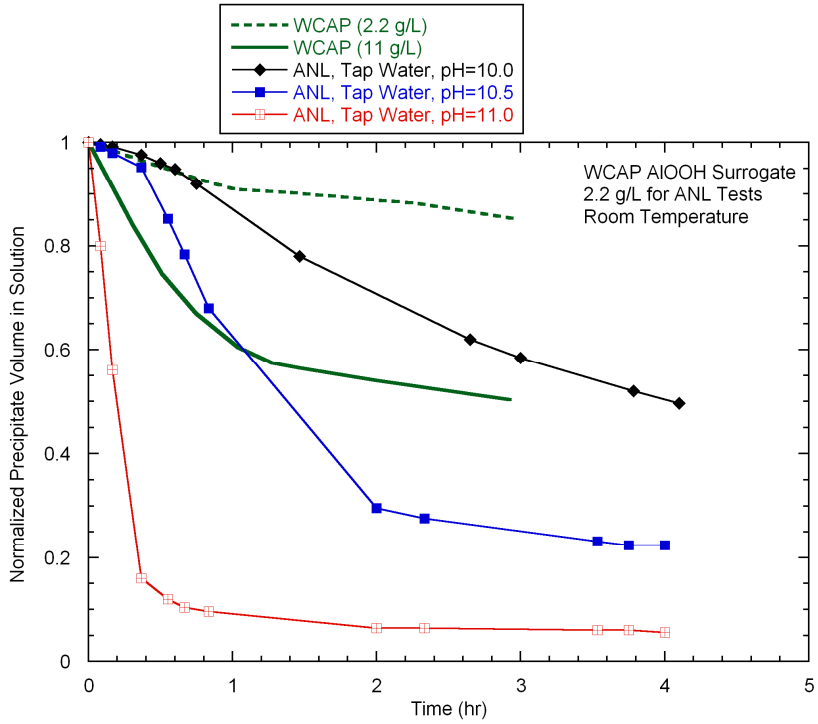
Figure 6 shows median particle size and settling velocity of the WCAP AlOOH surrogate made with tap water as a function of solution pH. The particle size appears to have a peak at around pH=9.0 but the settling velocity is a maximum at the higher pH. However, this conclusion is valid only in the pH range of 7-10. Figure 7 shows the measured settling velocities of the WCAP AlOOH surrogate made with tap water for the first hour as a function of median particle size compared with the WCAP surrogates made with high purity water and theoretically predicted values based on colloid aggregation theory. The data for the surrogates made with high purity water and the theoretical predictions were reproduced from a previous letter report.[1] The settling velocity data for the tap water varies linearly with the median particle size and the slope is consistent with that of the surrogates made with high purity water. One data point measured at pH=10.0 seems to depart from the general trend, which suggests that at higher pH (>10.0) different materials like calcium carbonates began to precipitate as well as aluminum hydroxide. The similar slopes suggests that the WCAP AlOOH surrogate made with tap water also follows colloid aggregation theory, which postulates that colloidal particle aggregation behavior is universal and not dependent on the chemical characteristics of the particles. Although the two data sets have similar slopes, they are offset from each other. At a given agglomerated particle diameter, the surrogate in tap water shows lower settling velocity than the surrogate in high purity water, which means that the constituent particle size (i.e. small particles composing of big particle cluster) in tap water is smaller than that in high purity water. The settling velocity of colloidal clusters limited by reaction limited colloid aggregation theory can be described using the fractal dimension d_f of the clusters and the constituent particle size a;[1]

$$v=\frac{2g}{9\mu}(\rho_a-\rho_o)a^2\left[\frac{R_h}{a}\right]^{d_f-1}, \tag{4}$$

where ρ_a is the density of the constituent particles, ρ_o is the density of water, R_h is the hydrodynamic radius of the cluster, g is gravitational acceleration, and μ is viscosity of solution. The quantity 'd_f-1' is the slope of the plot of the logarithmic velocity as a function of the logarithmic particle size, as shown in Figure 7. The constituent particle size may be related to the nucleation site density when the precipitation starts in supersaturated solution. Therefore, it is conjectured that tap water enhances the nucleation of aluminum hydroxide precipitate, which leads to higher number density but smaller size of the constituent particles, compared with the case of high purity water.



(a) Initial Surrogate Solution pH ranging from 7.2 to 10.0



(b) Initial Surrogate Solution pH ranging from 10.0 to 11.0

Figure 5. Normalized settled precipitate volumes of WCAP AlOOH surrogates made with tap water as a function of solution pH.

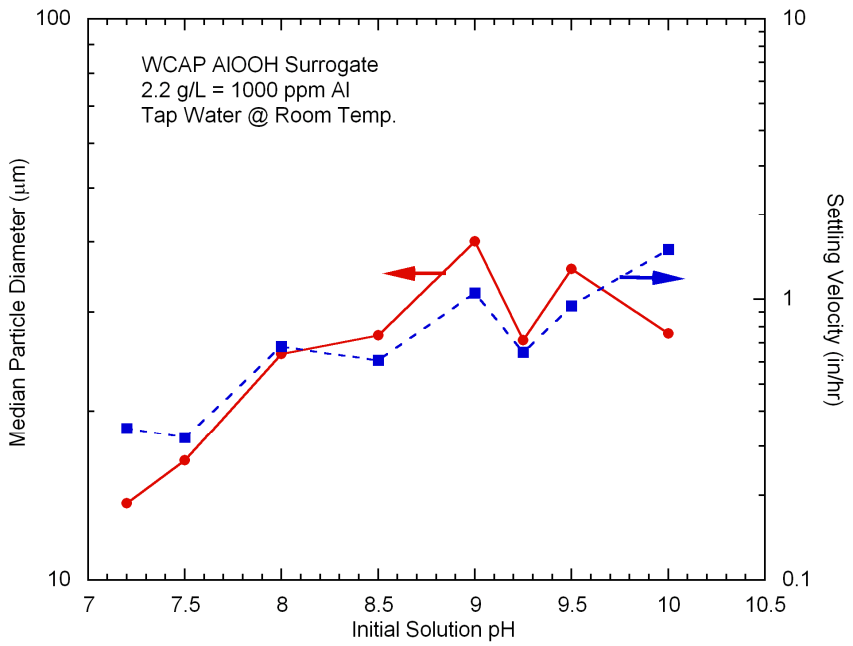


Figure 6.
Median particle diameter and settling velocity of WCAP AlOOH surrogate as a function of initial pH.

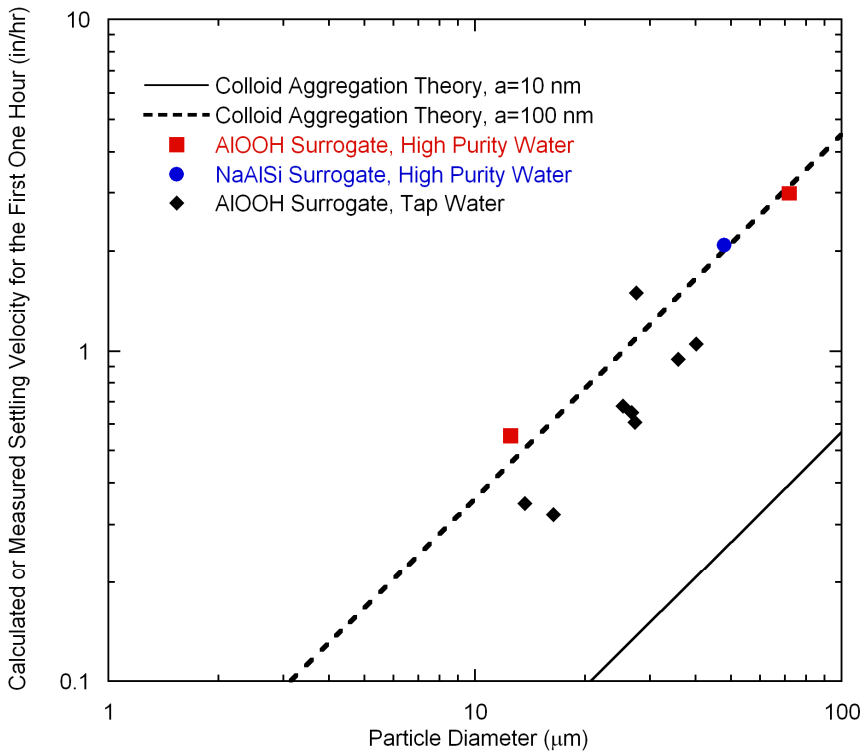


Figure 7.
Measured settling velocity of AlOOH surrogates made with tap water as a function of median particle diameter compared with other surrogates and theoretical results.

Aluminum Hydroxide Solubility

Figure 8 shows Al hydroxide precipitation map in the temperature vs. 'pH+p[Al]$_T$' domain, reproduced from a previous ANL letter report.[5] 'pH+p[Al]$_T$' is related to the supersaturation (Π_j) of aluminate with respect to aluminum hydroxide species, *j*:[7]

$$\Pi_j = \frac{a_{Al(OH)_4^-} \cdot a_{H^+}}{K_{sp,j}}, \tag{5}$$

where a_i and $K_{sp,j}$ denote the activity of ionic species, *i* and solubility product of aluminum hydroxide species, *j*, respectively. There are various crystalline forms for aluminum hydroxide, for example, pseudoboehmite, boehmite, bayerite, and gibbsite. Taking log to the base 10 of Eq. (5) leads to Eq. (6):

$$\begin{aligned} \log \Pi_j &= \log a_{Al(OH)_4^-} + \log a_{H^+} - \log K_{sp,j} \\ pH + p\left[Al\right]_T &= p\Pi_j + pK_{sp,j} \end{aligned} . \tag{6}$$

According to Eq. (6), degree of supersaturation increases with the decrease in 'pH+p[Al]$_T$'. The Al hydroxide precipitation map was developed in such a way that total Al concentration and solution pH was fixed and the solution temperature was decreased from 200°F, which is a similar case to the sump water after a loss-of-coolant accident. Therefore, this map is only valid when the temperature varies at given Al concentration and pH conditions. This map may be applicable when the solution pH or Al concentration varies at a given temperature, but it should be verified experimentally.

In the previous ANL letter report,[5] two Al solubility equations were proposed based on experimental data shown in Figure 8. The room temperature Al solubilities at pH=8.0, 8.5, and 9.0 by Eq. (6) in Ref. 5 are 1, 3, and 10 ppm, respectively. Al solubilities by Eq. (7) in Ref. 5 are 0.5, 1.5, 5 ppm, respectively. The Al solubilities observed in the bench top tests in this report appear to be lower than the estimates from the previous letter report.[5] The effect of boron on aluminum hydroxide solubility is discussed as below.

Van Straten et al.[7] studied the precipitation of aluminum hydroxide from supersaturated potassium aluminate solution at room temperature. It was observed that at high supersaturations the precipitation sequence is amorphous-pseudoboehmite-bayerite and at low supersaturations only bayerite forms. The precipitation boundaries for the amorphous phase and pseudoboehmite as 'pH+p[Al]$_T$' are 12.1 and 12.7, respectively. They also studied the effect of temperature on the precipitation of aluminum hydroxide and found that the boundaries for amorphous and pseudoboehmite phases are insensitive to temperature.[8] In Figure 9, the phase boundaries observed by Van Straten et al. are plotted with the ANL long-term aluminum solubility test data.[6] The solubility of boehmite as a function of temperature by Benezeth et al.[9] is plotted in the same graph. Benezeth et al.[9] also determined solubility as a function of ionic strength; at higher ionic strength, the solubility increases. The solubility line by Benezeth et al. presented in Figure 9 was obtained assuming the total ionic strength is 0.15 M, which corresponds to the value in tests of Van Straten et al.

Van Straten et al. used potassium aluminate and we used sodium aluminate, but this difference does not seem likely to cause significantly different results. The main difference between the ANL solubility tests and tests by Van Straten et al. is the presence of boric acid in test solutions. One possible explanation of the difference in the solubility map is that the presence of boron has shifted the phase boundaries; the pseudo-boehmite boundary at 12.7 as

'pH+p[Al]$_T$' is shifted to 10.2 by boric acid, and the boehmite boundary also shifted. The other possible explanation is that the phase boundary for amorphous Al hydroxide was affected at higher temperature by boron and became dependent on temperature. The first assumption may be supported by the fact that the point of zero charge (PZC) of aluminum hydroxide can be shifted by boric acid. As discussed in a previous letter report,[6] 2500 ppm boron as boric acid lowers the PZC of amorphous aluminum hydroxide by 2.9, which is reasonably close to the apparent phase boundary shift of 2.5 (from 12.7 to 10.2). However, the second assumption can also be rationalized by some experimental observation and prediction by Visual MINTEQ, a thermodynamic chemical equilibrium code.[10] Chen et al.[11] reported that amorphous Al hydroxide precipitates were formed after cooling the test solutions of ICET #1 and #5. We also reported that based on the X-ray diffraction analyses for glass-fiber samples tested in a loop head loss test, Al hydroxide precipitates formed on the glass-fiber sample was more likely amorphous.[5] As shown in Figure 9, the amorphous Al hydroxide solubility line predicted by Visual MINTEQ code is very close to the observed bounding line. It is difficult to determine which assumptions are correct, but it is likely that amorphous Al hydroxide was precipitated regardless of its flocculation tendency and boric acid enhances the solubility of amorphous aluminum hydroxide at higher temperature. The mechanism of boron's effect on the solubility needs to be further explored, but boron may inhibit the nucleation of aluminum hydroxide precipitates from supersaturated state and/or the growth of precipitates due to the adsorption on the aluminum hydroxide precipitates. Since both aluminum and boron are group III elements, it could be possible that aluminum solubility increases because it forms a coordination complex with borate ion. The observed temperature-insensitive boundary at around 10.2 as 'pH+p[Al]$_T$' between flocculation and non-flocculation is more discussed in a following section.

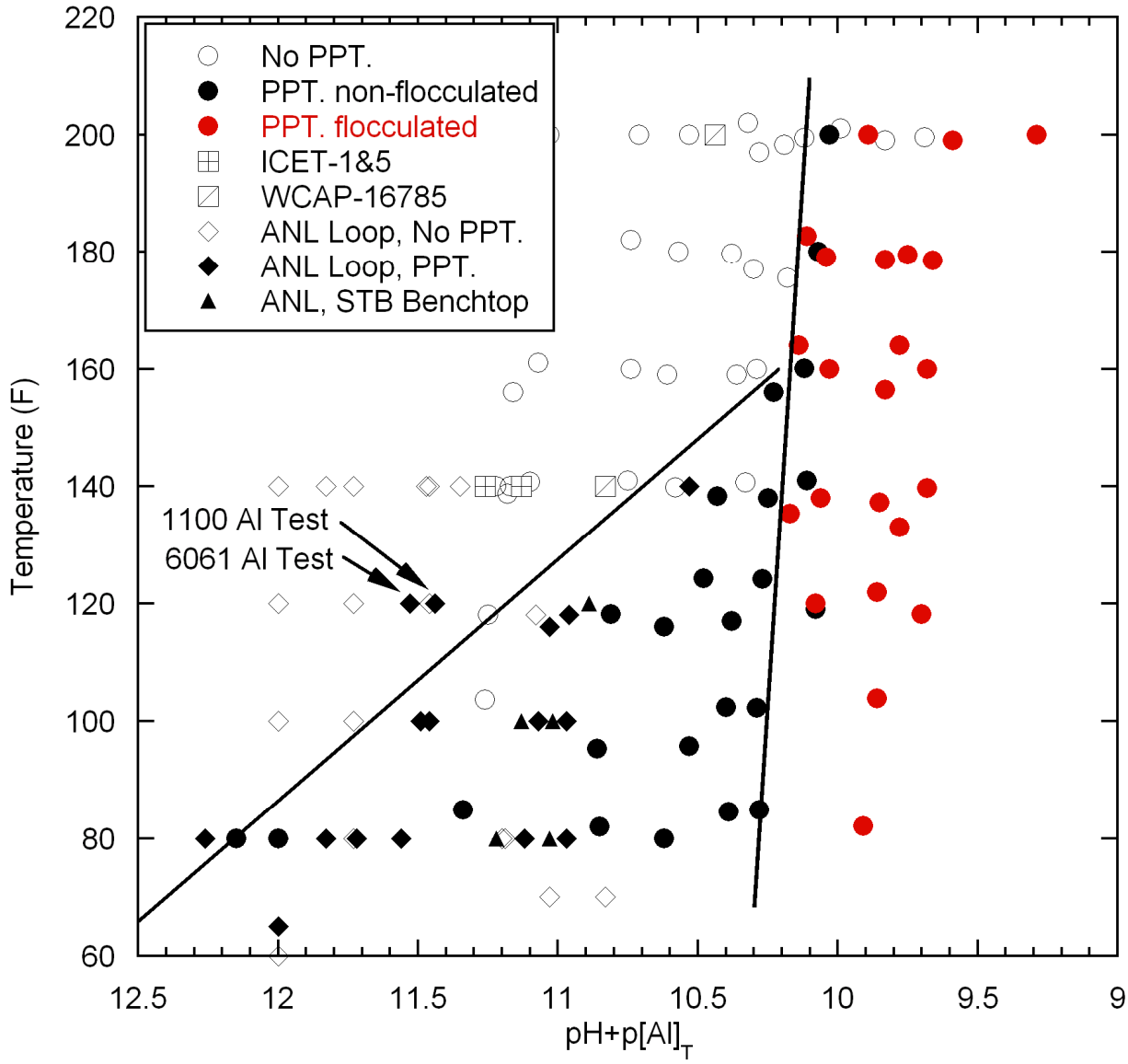


Figure 8. Al stability map in the temperature vs. ‘pH+p[Al]$_T$’ domain; filled and open symbols mean the occurrence of Al hydroxide precipitation and no precipitation, respectively; ‘pH’ and ‘p[Al]$_T$’ mean the solution pH at temperature and the negative log to the base 10 of the total aluminum content as dissolved or precipitated in units of mol/kg (reproduced from Ref. [5])

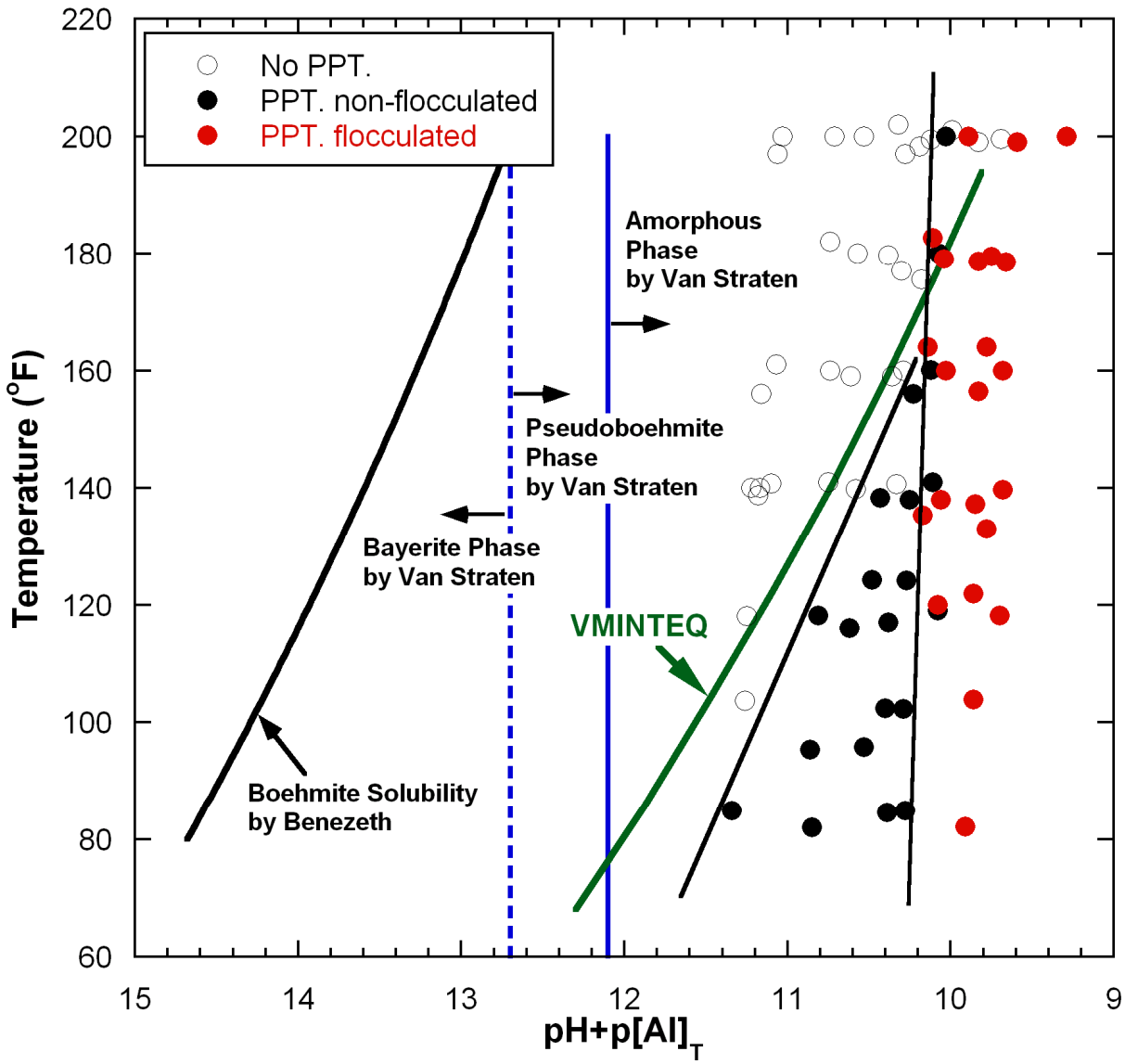


Figure 9. Comparison of the ANL long-term Al solubility test results with literature data for precipitation tests from supersaturated aluminate solutions and amorphous Al hydroxide solubility predicted by Visual MINTEQ designated as 'VMINTEQ'.

Colloid Phase Diagram

Protein solutions are one type of colloidal solutions. Many studies have been performed to determine a phase diagram of colloidal proteins in a temperature vs. concentration domain. Muschol and Rosenberger[12] proposed a generic phase diagram for proteins, in which a cloudy solution region (called "metastable Liquid-Liquid region") and an amorphous gel precipitate region are shown. Modeling results for colloidal systems with short-ranged attractive interactions showed a similar phase diagram.[13] These literature data are qualitatively very similar to that observed in previous Al hydroxide benchtop and loop tests, which are presented in a temperature vs. 'pH+p$[Al]_T$' domain (see Figure 8). Assuming the solution pH is constant, 'pH+p$[Al]_T$' can be considered as total Al concentration. Based on the phase diagram of Muschol and Rosenberger,[12] above a critical temperature and a critical concentration amorphous gel is predominant, which is valid to some extent of temperature, and below the critical concentration there is a phase boundary between cloudy solution region and non-cloudy region, which is temperature-dependent. In Figure 8, the cross-point of phase boundaries located at 160°F and 10.2 as 'pH+p$[Al]_T$' may be considered as a critical point of the Al hydroxide colloidal system in borated solution. However, further experimental study is needed to determine if the Al hydroxide colloidal system is applicable to a phase diagram developed from protein colloidal systems.

It is interesting to note that Muschol and Rosenberger[12] found that thermal cycling through the phase boundary between the cloudy solution region and non-cloudy region enhanced the precipitate nucleation rate, which appears a very similar phenomenon to that observed in the 1100 Al alloy test. In that test, as reported in a previous letter report,[5] rapid Al hydroxide precipitation occurred after increasing loop temperature from 100 to 120°F. The Al hydroxide phase diagram shown in Figure 8 predicts the phase boundary is located at between 100 and 120°F with the pH and Al concentration of the 1100 Al alloy loop test. It is reported that the nucleation rate is enhanced because small precipitates that nucleate upon thermal cycling continue to grow at higher temperature.[12] Therefore, it is likely that the rapid increase in head loss after increasing temperature was caused by thermal cycling through the phase boundary, as well as the effect of intermetallic particles. Although thermal cycling in the long-term solubility test did not cause such a nucleation enhancement, more experimental work would be needed to estimate the possibility of the nucleation enhancement in the coolant of ECCS by recirculating through the heat exchanger and reactor core.

Major Findings and Summary

- Based on the bench top tests, the solubility of WCAP AlOOH surrogate increased with increasing pH in tap water. At pH=8.7, 2.3 ppm Al was detected after filtering a solution sample by a 0.02 micron filter while at pH=8.0, detected Al concentration was less than the detection limit of 0.5 ppm. These solubilities are lower than would be expected in solutions containing significant amounts of boron.
- The dissolution of the WCAP AlOOH surrogate at a given pH level ranging 8.0-9.0 occurs within less than 4 hours.
- The solubility of AlOOH at pH=9.0 is lower in high purity water than in than tap water, presumably because the higher ionic strength of tap water enhances the Al hydroxide solubility.
- WCAP AlOOH surrogates made with tap water have larger particle sizes than those with made high purity water at the same pH. The particle size of the precipitate was a maximum in the range of pH=9.0-9.5 after a three hour aging period. Like the surrogates made with high purity water, the surrogates made with tap water can also be described by a reaction limited colloid aggregation theory. However, the theory predicts that the constituent particle size (i.e. small particles composing of big particle cluster) of the surrogate made with tap water is smaller than those made with high purity water.
- In ANL vertical loop head loss test, the WCAP AlOOH surrogate equivalent to 3.0 ppm Al caused 2.5-psi head loss increase at pH=9.0 and room temperature. The head loss was very stable at that condition over 5 days. This head loss is less than that resulting from a 1.5 ppm Al equivalent addition to a near-neutral pH solution (pH=6.4).
- Dissolution of WCAP AlOOH surrogate at pH=9.0 to a steady state concentration occurs quite rapidly. The steady state concentration is quite stable over time periods on the order of five days.
- The pH decrease from 8.91 to 7.60 caused the increase in head loss of additional 3 psi, but the head loss gradually decreased and stabilized after 2 days. It is conjectured that this may be due to increase in solubility associated with the higher ionic strength induced by adding nitric acid or the effect of precipitate aging.

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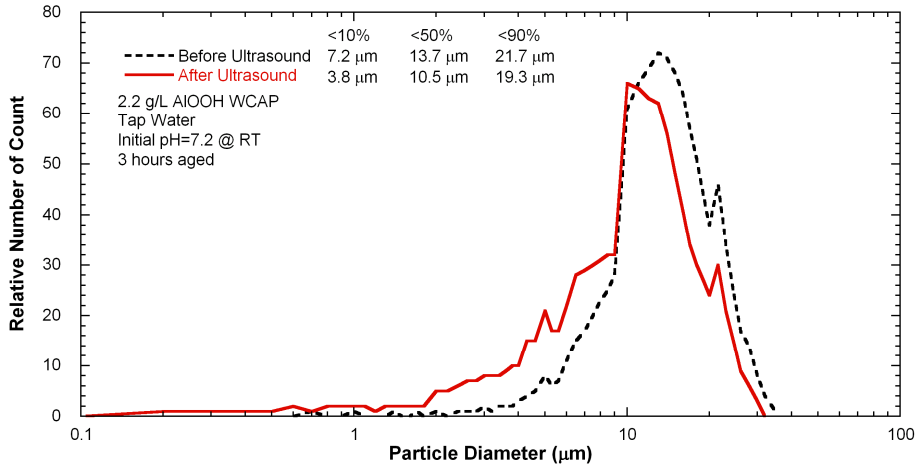
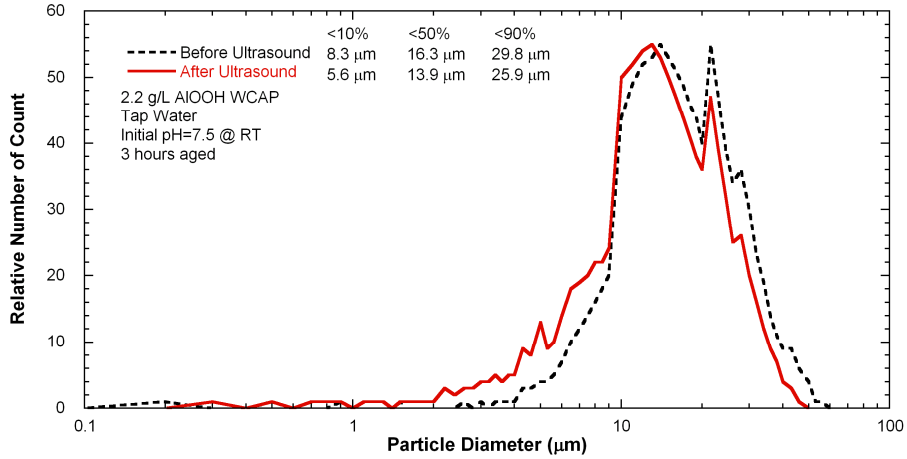
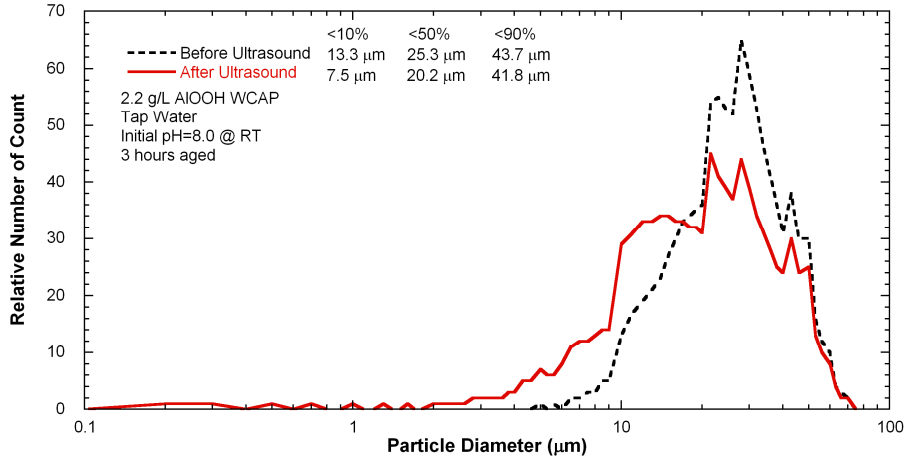
Appendix A: WCAP AlOOH Surrogate Particle Size Distributions.



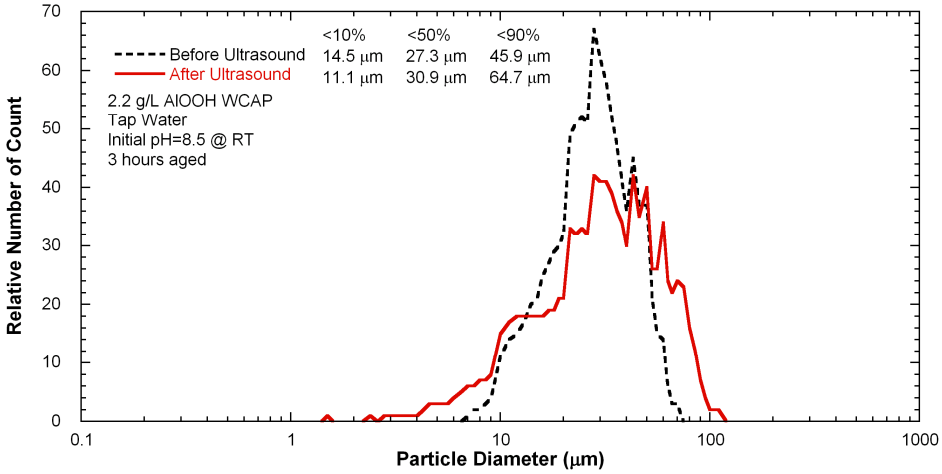
(a) Initial pH=7.2



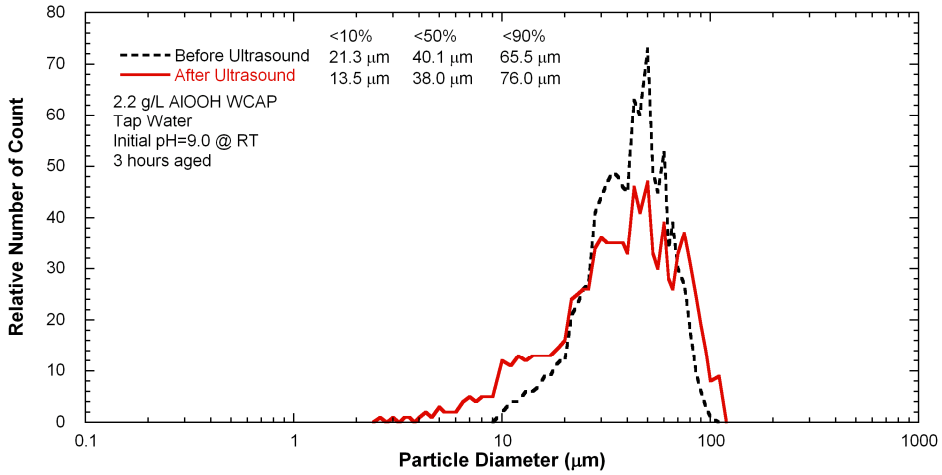
(b) Initial pH=7.5



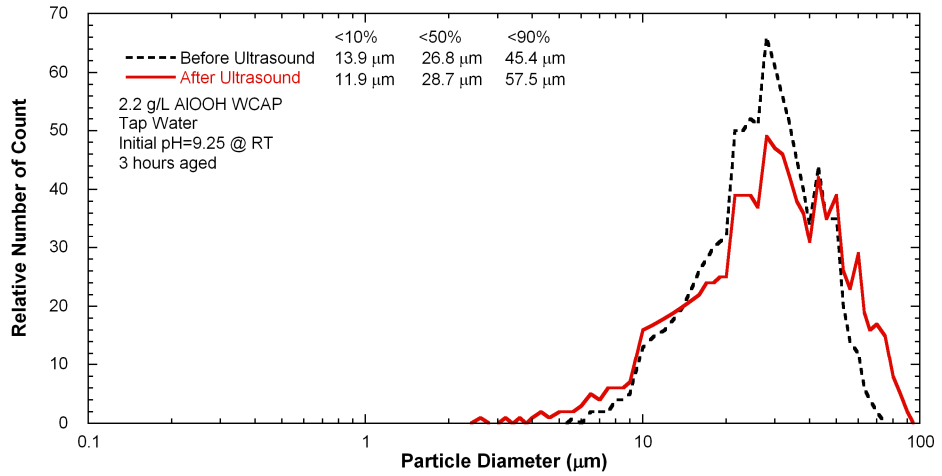
(c) Initial pH=8.0



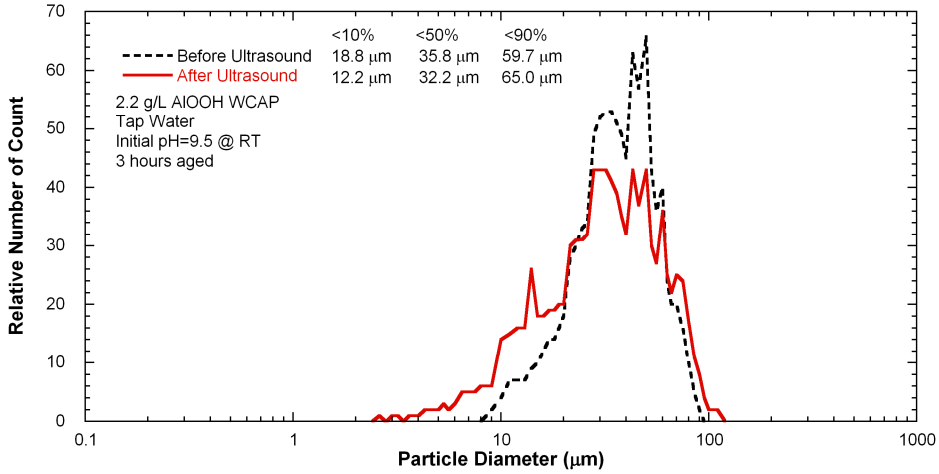
(d) Initial pH=8.5



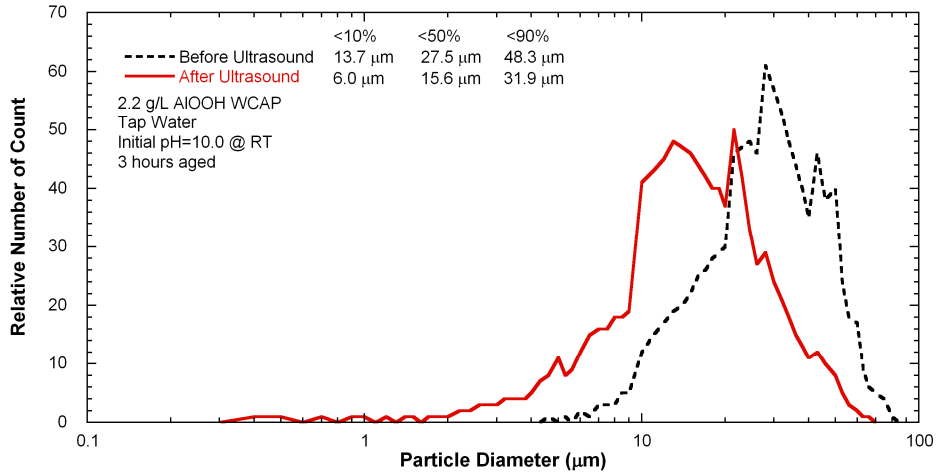
(e) Initial pH=9.0



(f) Initial pH=9.25



(g) Initial pH=9.5



(h) Initial pH=10.0

Figure A1. Particle size distributions of the WCAP AlOOH surrogates made with tap water as a function of initial surrogate solution pH.