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Desilication Study of DWPF Recycle Stored in Type IV Tanks

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Summary

Batch desilication tests were performed with a simulant of DWPF recycle tank that was developed from sample analysis of recycle stored in the Type IV tanks in H-area. The objective of this work was to examine the use of a controlled reaction of added soluble aluminate ion with the soluble silicate ion from DWPF recycle. Following desilication the liquid waste would meet processing requirements for any of the Site's High Level Waste Evaporators. Results from these tests show the following

- Desilication of wastes with both 200 and 400 mg/L added silicate was accomplished within 368 hours at elevated temperature (60°C) by the addition of aluminate ion at a concentration of 2 g/L.
- Seeding the waste liquor with nitrated-sodalite greatly increased (2X) the rate of desilication.

Introduction

High Level Waste is stored at the Savannah River Site. This liquid waste was made alkaline prior to discharge from the F-and H-Canyon facilities. During storage, the liquid waste is typically evaporated to concentrate the supernate and maintain storage volume. These operations have been performed for many decades during plutonium production. The high level waste is typically several molar in sodium ion with large amounts of free hydroxide, nitrate, nitrite and aluminate concentrations.

The Defense Waste Processing Facility (DWPF) was commissioned to begin transforming the sludge and supernate components of the High Level waste into a vitrified product that would be interned at the federal repository. The DWPF returns a recycle water stream from condenser and other process operations to the tank farm. This stream is currently the largest volume source of influent to the tank farm. The DWPF recycle stream is very dilute (~1M sodium ion concentration) and would be appropriate feed for evaporation. Unfortunately, the DWPF recycle stream contains silicon in the form of soluble silicates and insoluble glass-forming frit. The mixture of soluble aluminate in the historical canyon waste and the silicon from DWPF recycle led to the formation of insoluble sodium aluminosilicates in the 2H Evaporator.'

Operation of the High Level Waste evaporators are vital to maintain tank space to meet site mission requirements as well as regulatory commitments for closing the High Level Waste tanks. Since the aluminosilicate deposits were discovered in the 2H Evaporator pot, research into understanding the reaction kinetics for formation and aluminosilicate product solubilities has been performed. The results have shown that the mixture of the two tank farm streams produced waste supersaturated in aluminosilicate. The aluminosilicate can readily form and precipitate under evaporator conditions.

Studies have also examined silicon treatment options. A literature review by Lahoda showed

several potential treatment options. Current waste handling processes in the tank farm segregate the high aluminate streams from the silicon-containing streams to prevent aluminosilicate formation. However, operational flexibility is hampered by this segregation approach. Therefore, funding was received to examine silicon treatments for use with existing stored DWPF recycle in the tank farm (Tanks 21, 22 and 24).

Experimental

Aluminosilicate formation tests were conducted in Tank 38H waste simulants. These tests were performed on a nominal 100-mL scale at 50°C in Teflon bottles. Periodically, liquid samples were removed by syringe and filtered through 0.02 m m pore sized filters. Thereafter, the liquid samples were submitted for elemental analysis using Inductively Coupled Plasma – Emission Spectroscopy. In order to measure the desilication kinetics accurately, silicon, in the form of sodium metasilicate, was added to the simulant at three levels and the reactant aluminum was added at two levels as shown in Table 1.

Table 1. Simulant Composition and Test Matrix

Analyte	Units	Concentration
Sodium	M	1
Nitrate	M	0.06
Nitrate	M	0.25
Free OH	M	0.5
Carbonate	M	0.075

Test No	Temp (oC)	Seed Level	Si Conc.	Al Conc.
1	50	None	200	2000
2	50	None	400	2000
3	30	0.1 g	200	2000
4	30	0.1 g	400	2000
5	50	0.1 g	200	2000
6	50	0.1 g	400	2000
7	60	0.1 g	200	2000
8	60	0.1 g	400	2000

Laboratory notebooks contain data obtained during these tests and the procedures used. Personnel used routine analytical protocol for the samples in this report. Each test was performed in duplicate and the averaged analytical results from each test are shown in Table 2. Further data analysis was performed on the average of either the silicon or aluminum concentrations for each test.

Table 2. Measured Silicon Concentration (mg/L) versus Time (h)

Time (min)	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
0	116	140.5	101.5	132	103	133	111	149.5
480	71.9	73.55	64.35	69.25	62.9	71.9	69.64	74.6
1440	65.8	68.5	56.5	61.4	58.7	64.6	62.2	66.7
2880	62.7	66.15	52.25	56.7	56	59.35	48.9	60
4320	59.8	63.3	47.4	53.3	44	57	32.45	56.8
13020	58	58.45	46.3	51.4	16.8	49.5	6.25	7.45
21600	51.9	55.2	45.05	51.15	7.4	13.8	5.2	6.9

Results and Discussion

The hydrothermal formation of sodium aluminosilicate under the highly caustic condition of the Tank 20 simulant is thermodynamically favored. At elevated temperature (> 80°C), our experience is the chemical reaction shown in Equation 1 is rapid. However, the work of Mattus using high level waste simulants studied the formation of sodium aluminosilicate from highly supersaturated systems. Tank 20 simulant, on the other hand, is slightly supersaturated if one wished to add aluminate ion to deplete the silicon supersaturation. The tests reported herein examined small aluminate ion additions to two Tank 20 simulant solutions with relatively low silicon concentrations

$6\ AlO_4^- + 6\ SiO_3^{2-} + 2\ NO_3^- + 8\ Na^+$ ® $Na_8Al_6Si_6O_{24}(NO_3)_2$ Eq. 1

Shown in Figure 1 and Figure 2 are the plots of desilication in each of the tests. The supersaturation index, s , is defined as $s = (C_t - C_{eq})/C_{eq}$ where C_t is the silicon concentration at time t and C_{eq} is the equilibrium silicon solubility. The equilibrium silicon solubility was the lowest silicon concentration measured in each of the types of solution; i.e. final measured silicon concentration in test 7 and 8. The degrees of supersaturation shown in these figures are averages of duplicate tests.

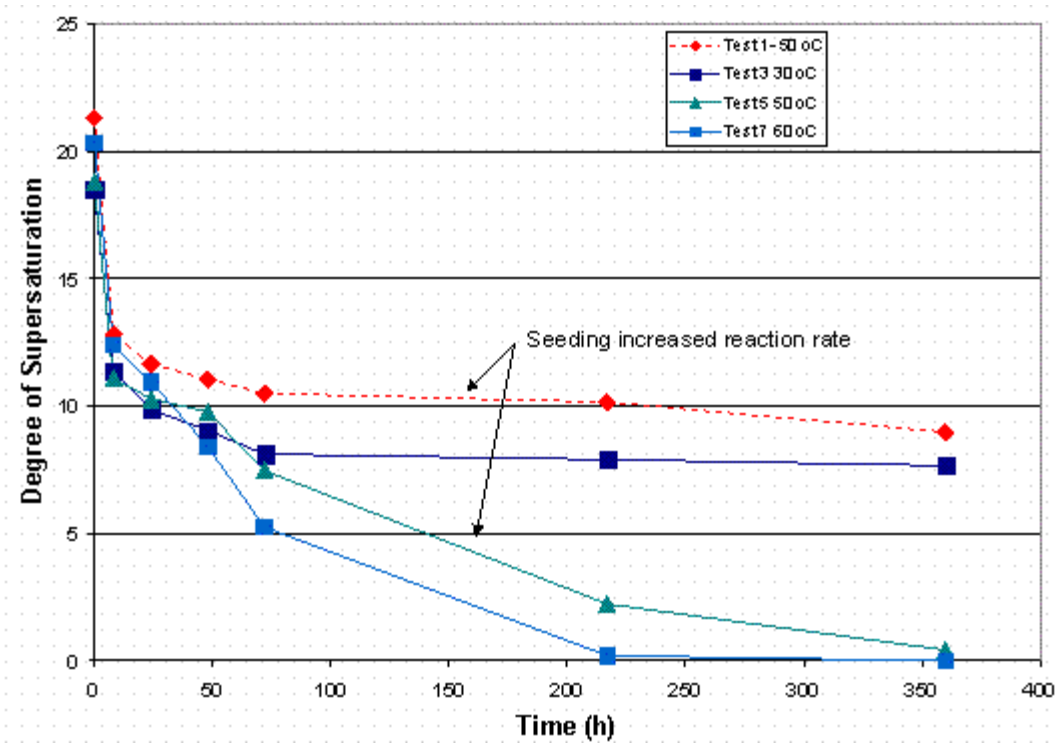

Figure 1. Desilication Curve for Low Silicon Tests

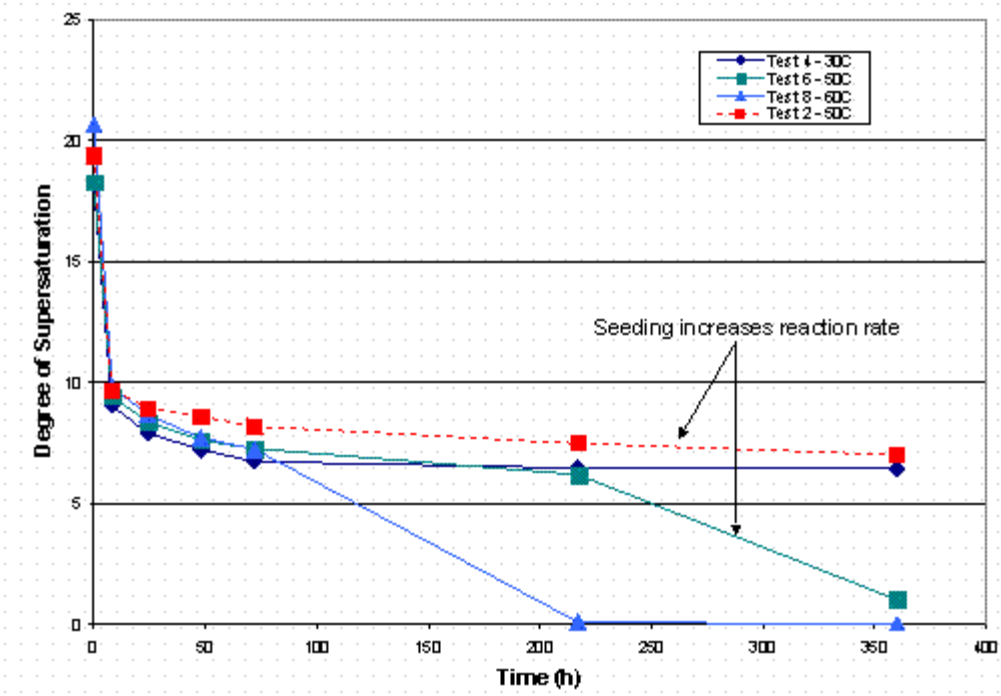

Figure 2. Desilication Curve for High Silicon Tests

In these tests, several variables were examined. For example in the low silicon tests (numbered 1, 3, 5, and 7), the effects of temperature and seeding the liquor with sodalite were examined. The reaction temperatures were 30, 50, and 60°C for tests 3, 5, and 7 respectively. Under these conditions, bulk nucleation, secondary nucleation and heterogeneous crystal growth on the sodalite seeds are occurring simultaneously. The data shows the expected trend of higher reaction temperature and faster desilication. The 60°C reaction is complete, i.e., the silicon concentration has reached equilibrium, by the 220 h sampling and the 50°C reaches equilibrium after 350 hours. The 30°C reaction had not reached the equilibrium and appears that the reaction was slowing down at the last sampling point after 365 hours.

Mattus had previously examined the use of seeding to increase reaction rate in a Tank 43H simulant and found the seeds were effective. In these tests in the Tank 20 simulant, the same effect is observed. In Figure 1, Tests 1 and 5 were performed at 50°C with Test 5 containing 0.1 g of sodalite seeds. The aluminosilicate formation reaction proceeded to completion in Test 5 but did not in the test without seeds (Test 1). The data from test 1 shows the degree of supersaturation was slightly below 10 at the conclusion of the test (368 h).

The tests with higher levels of silicon several reaction attributes were revealed. The starting silicon concentration was targeted to be 400 mg/L. After addition of the sodium metasilicate solution, the sodalite seeds, and mixing for ~ 0.5 h, the measured silicon concentration was only 130 – 150 mg/L, just slightly higher than the low silicon tests. The amount of silicon added was verified. Additionally, the starting soluble aluminum concentration was lower and averaged 1790 mg/L for the high silicon tests compared to 1895 for the low silicon tests. Figure 2 shows the reaction kinetics observed for these four tests with higher added silicon. The initial measured degree of supersaturation is nearly identical to the low silicon test data. The same general trend is observed that increasing the temperature (50°C) drives the reaction to completion in about 200 hours.

The effect of seeding is not as pronounced in these tests with higher seeding. The reason is that in the tests without sodalite seeds the addition of 400 mg/L silicon produced aluminosilicate particles that acted as seeds. Therefore, the test without sodalite seeds really had a lower seed loading and reacted only slightly slower than the seed test.

Conclusions

Using a controlled reaction between soluble aluminate ion and the soluble silicate ion found in the DWPF recycle water stored in the Type IV tanks (Tanks 21H, 22H, and 24H) has been shown as a possible method to remove silicon from solution. For typical silicon concentrations in the stored supernate, addition of aluminate to a concentration of 2 g/L would be effective if the contents of the tank could be heated to 60°C for a period of 3 weeks. Addition of sodalite seeds could accelerate the desilication. The silicon removal step would allow for processing these liquid wastes in any of the Site's evaporators.

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