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Desilication from DWPF Recycle Using Ferric Flocculation

W. R. Wilmarth, J. T. Mills, and V. H. Dukes
Westinghouse Savannah River Company
Aiken, SC 29808

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Summary

The presence of silicate and glass-forming frit in the recycle waste from the Defense Waste Processing Facility produces wastes that when combined with the traditional aluminate-bearing wastes stored in H-tank farm can produce insoluble sodium aluminosilicates. Treatment to remove the silicon has been proposed to allow greater flexibility for processing these wastes in the Site�s evaporators. The use of a ferric precipitation (flocculation) to remove the silicon has been tested using waste simulants. The experimental results indicate the following conclusions.

- Ferric precipitation following ferric nitrate addition to two DWPF recycle waste simulants was effective at removing silicon to levels below concern for processing in the 2F or 3H Evaporators.
- Removal of silicon was rapid with test durations less than 2 hours and elevated temperatures were not required.
- Capacities of the resultant iron flocculent were ~ 0.1 g of silicon per gram of iron at a final silicon concentration of 50 mg/L.
- The silicon removal obeys a classical Freundlich adsorption isotherm.

Keywords: DWPF Recycle, Precipitation, Freundlich Isotherm

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 concentrated 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.

In the late 1990's, 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, currently slated for Yucca Mountain, NV. 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.[1,2]

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.[3]

Studies have also examined silicon treatment options. A literature review by Lahoda[4] 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) along with the possible treatment inside DWPF at the point of origin of the silicon-containing waste (the recycle collection tank (RCT)).[5]

One identified treatment option is the use of the addition of ferric ion to the alkaline waste resulting in the formation of an iron flocculant. This treatment technology[6] removes silicon by co-precipitation and/or silicon absorption onto the iron precipitate. This treatment technology has been well established for municipal wastewater operations[7] but has not been tested with either simulated nuclear wastes or actual waste from the tank farm. Additionally, formation of the ferric precipitate and it�s filtration performance are needed to assess the technology for nuclear application. Therefore, initial testing for silicon removal by ferric flocculation was performed on simulated wastes from the tanks containing stored DWPF recycle (termed Tank 20 simulant) and from a projected composition of the alkaline contents of the recycle collection tank.

Experimental Details

Laboratory tests were performed on the 50 mL scale using the simulated wastes with the compositions shown in Table 1. As generated the DWPF recycle is slightly acidic. The stream is neutralized prior to discharge in accordance with the tank farm�s Waste Acceptance Criteria (WAC). This produces the RCT stream shown in Table 1. Additionally, the DWPF Recycle that was discharged to the tank farm during the outage of the 2H Evaporator also contained elevated silicon concentrations. The composition of this stream, the Tank 20 simulant, is also in Table 1. The simulants were prepared from reagent grade chemicals. Silicon was added as the hydrated sodium meta-silicate salt.

The ferric precipitation agent was prepared from reagent-grade ferric nitrate and dissolved in de-ionized water to a 1M $Fe(NO_3)_3$ concentration. Following procedures used for other ferric flocculent applications[8] tests were conducted at ambient and elevated (50�C) temperatures. The silicon-bearing solutions were added to the 100 mL reaction vessel, heated to reaction temperature in a water bath, and stirred using a magnetic stir bar for at least 2 hours. Afterward, the ferric slurry was filtered through a 0.45 μ m filter. Mass measurements were performed initially and at the end of the experiment to correct measured concentrations for evaporation.

Table 1. DWPF Recycle Compositions

Analyte	Units	Acidic DWPF Recycle	Neutralized DWPF Recycle in RCT	DWPF Recycle in TF
Na	M	0.35	1.25	1
Nitrate	M	0.08	0.05	0.06
Nitrite	M	0.24	0.2	0.25
Free OH	M	Slightly acidic	1	0.5
Carbonate	M	*	*	0.075
Al	mg/L	270	250	*
Si	mg/L	620	600	56
Fe	mg/L	590	*	*
Formate	mg/L	21	*	*
			*None added	

The stock solution and resulting filtrate solutions were analyzed for silicon using Inductively Coupled Plasma-Emission Spectrometer (ICP-ES). The ferric flocculant was dried at ambient temperature and characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) for elemental profiling.

Results and Discussion

Tank 20 Simulant (DWPF Recycle in Tank Farm)

As previously mentioned, the DWPF recycle that was generated during the period when the 2H evaporator operation was curtailed is stored in the H-Area Tanks 21, 22, and 24. The volume, nearly 3 million gallons, will eventually be concentrated in the 2H Evaporator. However, the recycle that is currently being generated represents ~ 70 � 80% of the 2H Evaporator utility. Therefore, it is potentially desirable to remove the silicon and concentrate with the other site evaporators. A simulant with the composition previously discussed was tested for silicon removal by ferric flocculation. Shown in Figure 1is a dosage curve for the addition of iron and the subsequent removal of silicon for a Tank 20 simulant with a 200 mg/L starting silicon concentration. The curve appears linear until ~ 70% of the silicon is removed and hen flattens out with higher addition of iron.

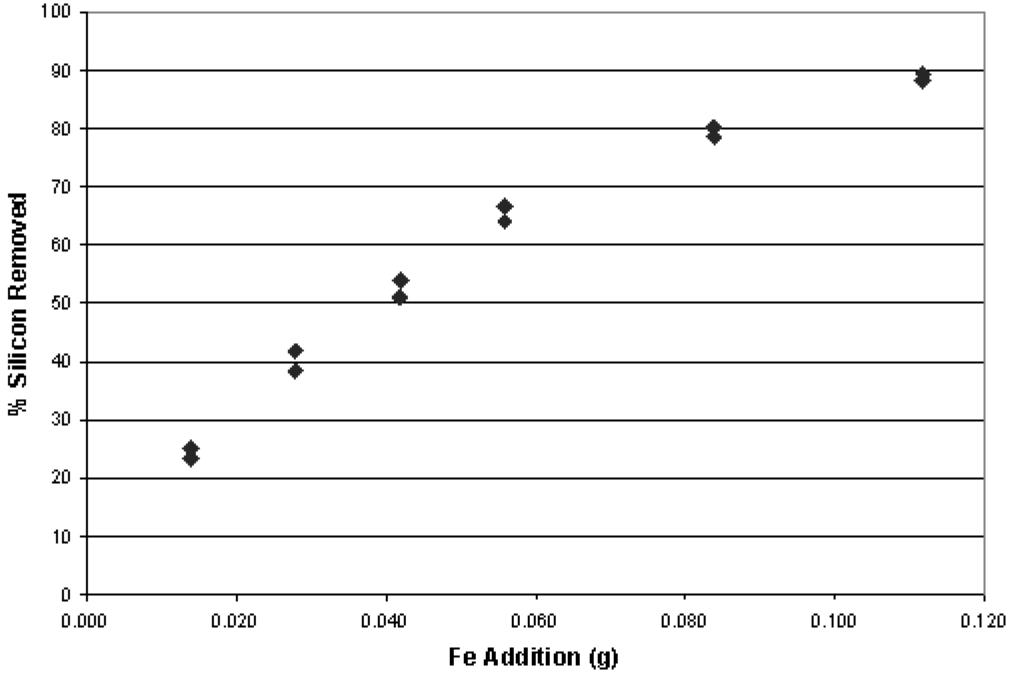


Figure 1. Silicon Removal via Iron Addition

Figure 2 shows the measured capacity of the ferric flocculent for silicon removal as a function of the measured final silicon concentration. The data is located in the Appendix. Tests were initially conducted at ambient laboratory temperature and 50°C. The targeted silicon concentration that would allow the treated Tank 20 material to be processed in other site evaporators is less than 50 mg/L. The data shown in Figure 1at a final silicon concentration below 50 mg/L did not indicate a difference between performing the tests at ambient or elevated temperature. Therefore, additional testing was conducted at ambient temperature.

The plot in Figure 2 shows silicon capacities on the order of 0.1 g of silicon /g of iron added to reach a final silicon concentration of 50 mg/L and 0.15 g Si/g Fe at 150 mg/L final silicon concentration. These capacities are higher than ferric flocculent capacity report in wastewater treatment.[7] This is most likely do to silicon being in the form of silicate ions in the caustic solution as compared to the species in pH 7 waters. At the capacities measured in the Tank 20 simulant, ferric flocculation will remove silicon to levels allowing processing in either the 2F or 3H Evaporators.

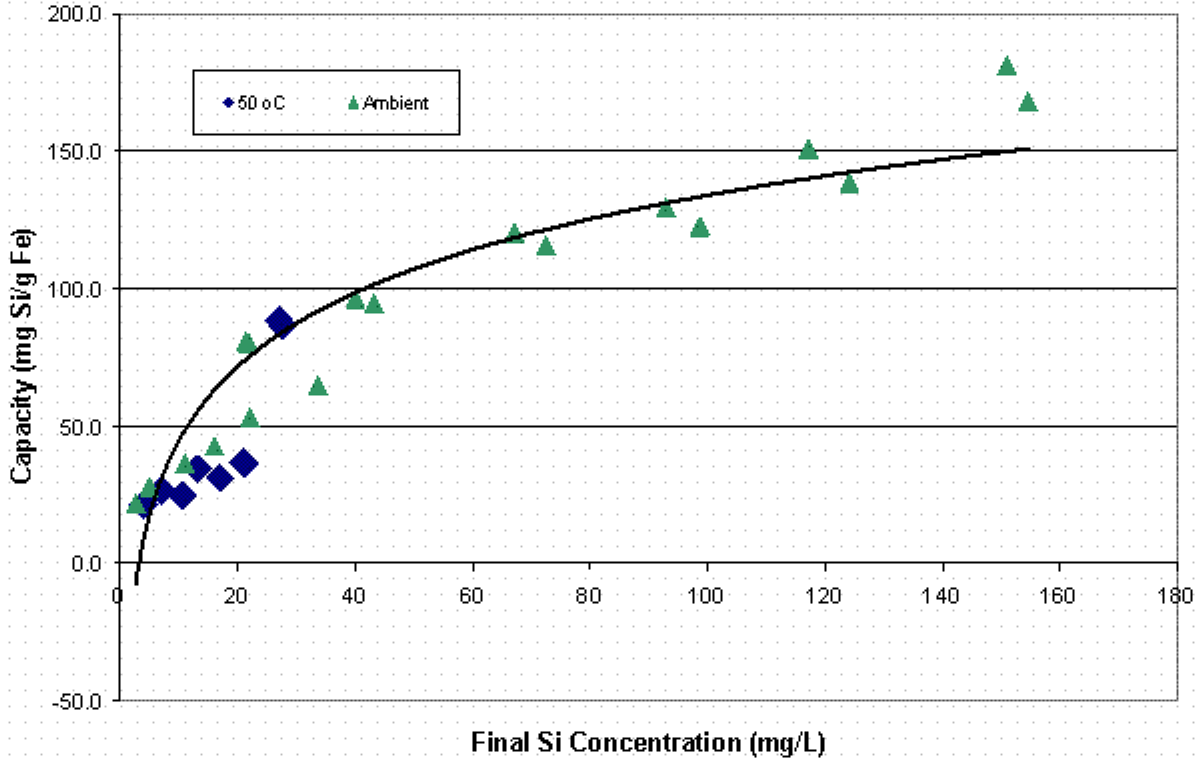


Figure 2. Si Adsorption Isotherm

Adsorption onto solids has been studied for decades. There are two adsorption models that are traditionally used to describe the process. The Freundlich isotherm model was one of the first proposed to correlate the amount of a substance absorbed to he concentration of material in solution. Equation 1 shows the Freundlich expression where m is the number of grams absorbed per gram of absorbent and c is the sorbate concentration with k and n as constants.

$$M = kc^{1/n}$$

Equation 1. Freundlich Isotherm

The other adsorption model is the Langmuir isotherm and is very useful if only a monolayer of adsorption occurs. The data from the ambient temperature tests performed using the Tank 20 simulant was plotted using the Freundlich and Langmuir expressions. The regression of the data revealed that the adsorption of silicon on ferric flocculent did not obey the Langmuir model but did obey the Freundlich model as shown in Figure 3. The fit of the data to the Freundlich isotherm was very good with a correlation coefficient of 0.95. There does appear to be some aspects to a sinusoidal curve to the lower final silicon concentrations. Potentially other absorption models would better explain this portion of the data.

Neutralized DWPF Recycle in the Recycle Collection Tank (RCT)

Recycle water is accumulated in the recycle collection tank and neutralized prior to discharge to tank farm. Though no samples of the water have been analyzed due to the difficulty in retrieving a sample, the estimated composition is provided in Table 1. The silicon concentration in the neutralized recycle is high ~ 600 mg/L. Therefore a wider silicon concentration range was used in ferric flocculation testing. Figure 4 shows the measured silicon isotherm for the ferric flocculent produced in the tests with neutralized DWPF recycle.

The capacity for silicon removal at a targeted 50 mg/L final concentration is approximately the same (0.1 g Si/g Fe) for the neutralized recycle as the capacity measured in the Tank 20 simulant. The data was analyzed using the Freundich isotherm model and the results are shown in Figure 5. The fit for the Freundlich model is very good ($R^2 = 0.93$). The silicon removal efficiency using the ferric flocculation technique appears to not vary much with small changes in solution composition. Most likely indicating the same silicon species is being removed.

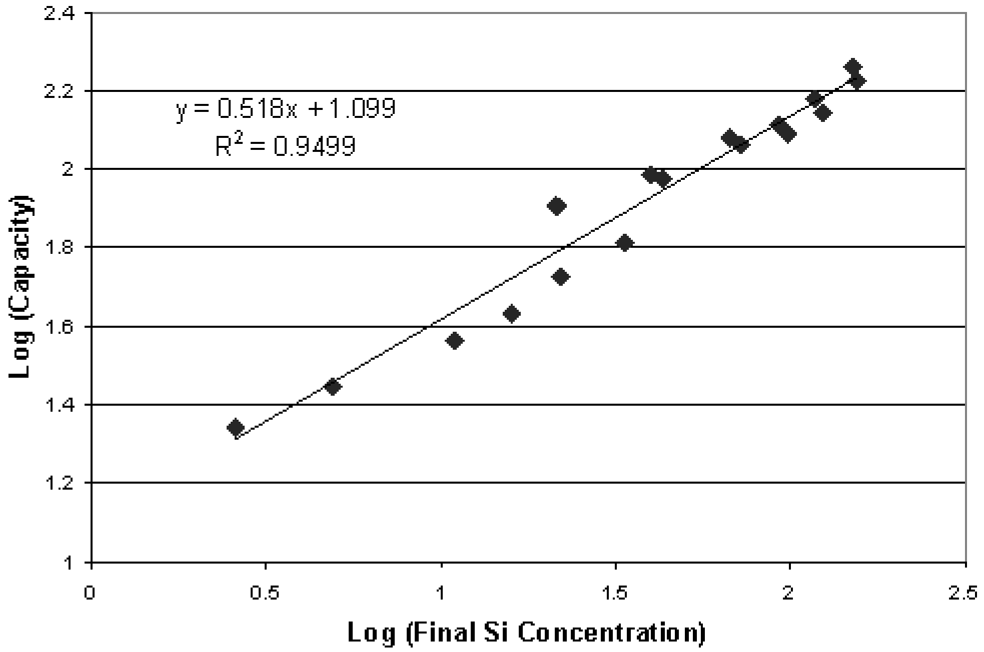


Figure 3. Freundlich Plot of Silicon Adsorption

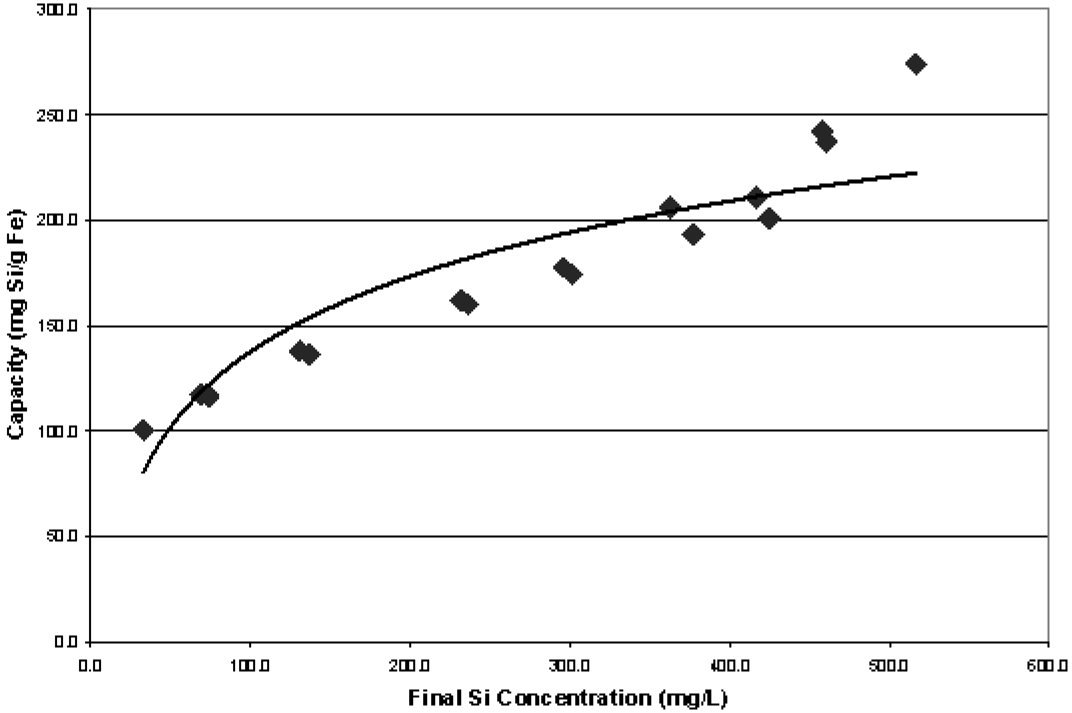


Figure 4. Silicon Removal from Neutralized DWPF Recycle

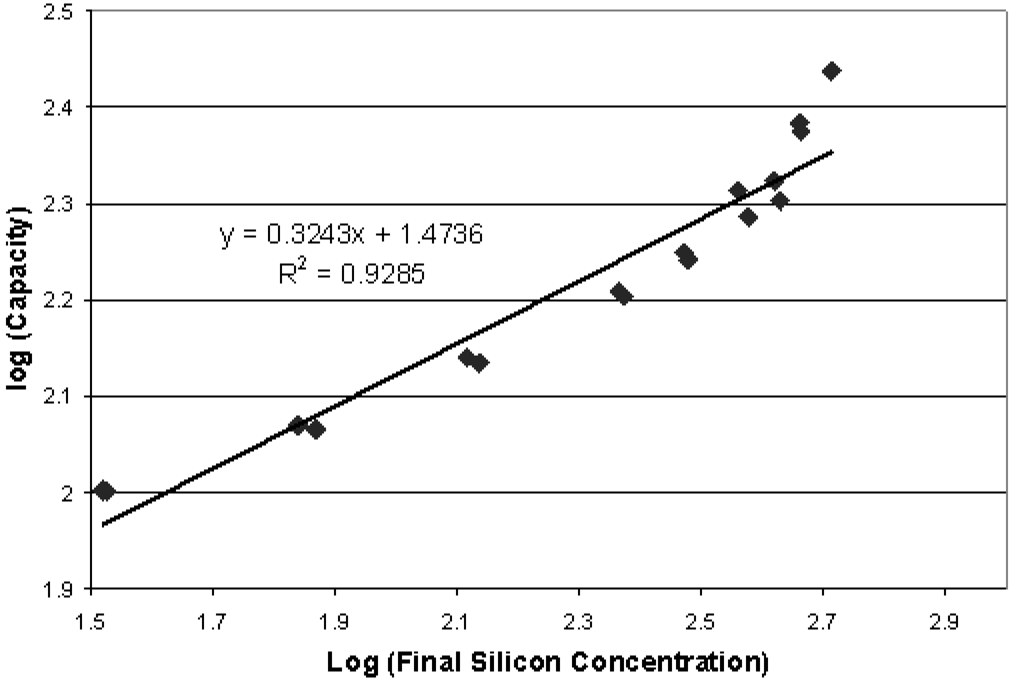
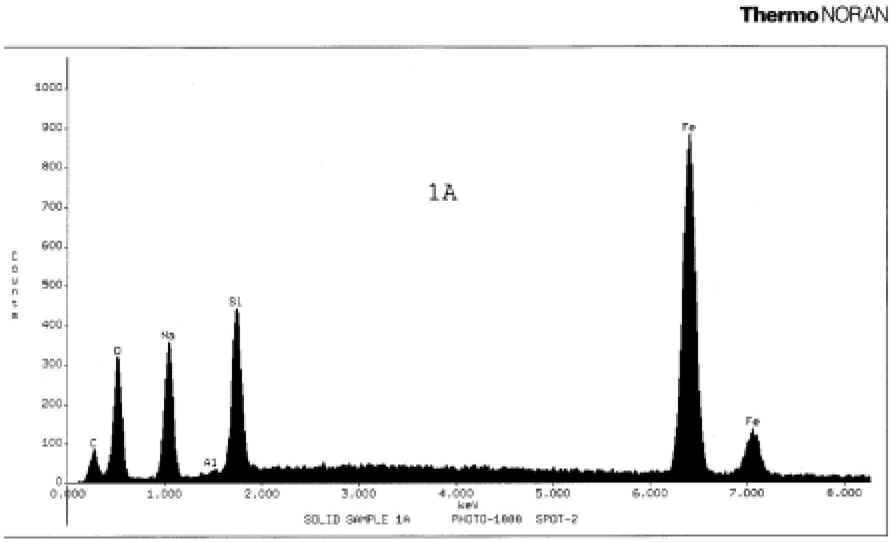


Figure 5. Freundlich Isotherm for Neutralized DWPF Recycle

Samples from a previous scoping test in which the mother solution was spiked with very high silicon concentrations (8 g/L) were submitted for analysis by X-ray diffraction and scanning electron microscopy. The samples were rinsed once with inhibited water. The X-ray diffraction data did not show diffraction peaks from crystalline iron oxides/oxyhydroxide. Only the broad band from the amorphous component of the precipitate was observed. The energy dispersive spectra obtain during the scanning electron imaging is shown in Figure 6. The spectra contain peaks for iron and silicon as expected along with sodium from salt solution.



SOLID SAMPLE 1A PHOTO-1888 SPOT-2

Accelerating Voltage: 25KeV Take Off Angle: 24.2354° Live Time: 24.81 seconds Dead Time: 6.749 seconds

Figure 6. Energy Dispersive Spectra of Silicon-bearing Iron Precipitate

Potential Silicon Removal in DWPF

The treatment of DWPF recycle for removing silicon has received substantial review.[4] Initially, an acid-side evaporator was proposed that would return the silicon-containing frit within DWPF and send only a small fraction of the volume and silicon to the tank farm. However, a review[9] of the possible options showed the cost and schedule considerations would suggest a more promising treatment would include acid-side filtration. Figure 7 shows a potential process involving treating recycle water inside DWPF. The proposed process would involve the collection of the recycle constituents filtering the insoluble frit using crossflow filtration for which a task has been identified to measure the filterability of that DWPF recycle slurry.[10] The soluble component of silicon would be minimized due to the low solubility of silicon under these acidic pH ranges. The filtered frit would be returned to the Slurry Mix Evaporator. The acidic filtrate would be neutralized to a minimal pH. Ferric nitrate would then be added to remove the soluble silicon to concentrations below concern. The caustic slurry containing the iron flocculent would be transferred to the tank farm and incorporated into the sludge for processing in the DWPF or recycled into the Slurry Adjustment and Receipt tank.

Conclusions

The presence of silicon in the DWPF recycle stream represents a waste instability when mixed with the more traditional aluminum-bearing waste produced in the Separation canyons. This instability eventually fouled the 2H Evaporator pot and curtailed operation for an extended duration. The results of these tests aimed at removing silicon from wastes currently stored in the tank farm and for newly generated wastes in the DWPF have shown that ferric flocculation will produce a ferric precipitate, not unlike sludge, that removes soluble silicon.

The adsorption of silicon onto the ferric precipitates is classical and follows a Freundlich isotherm. The capacity of the ferric precipitate is higher than anticipated based on the use of ferric flocculation in municipal wastewater treatment and is ~ 0.1 g of silicon per gram of iron added when targeting a final silicon concentration of 50 mg/L. Optimization of the process for implementation would need to determine the target silicon concentration and the impact of the added iron. The process was effective at removing silicon from both simulant compositions tested. Additionally, ambient and elevated temperature tests indicated that heating the reaction vessel was not necessary.

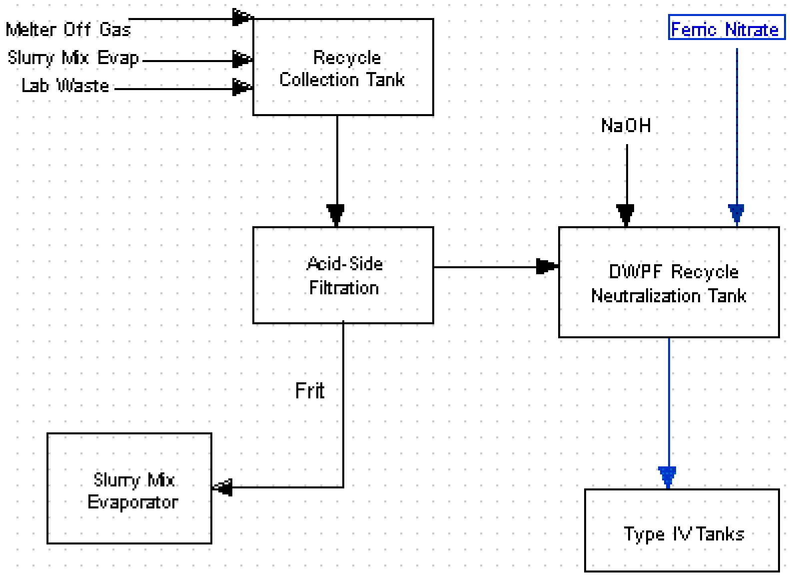


Figure 7. Potential Process for Treating DWPF Recycle

Appendix

Data for Tank 20 Simulant Tests

Temp	Initial Vol	Initial Si	Final Si	Amt Fe Added	Mass Si sorbed	Si Capacity
oC	mL	mg/L	mg/L	g	mg	mg Si/g Fe
		51.8	51.8	0.000		
50	50	51.8	27.048	0.014	1.24	88.6
50	50	51.8	20.904	0.042	1.54	36.9
50	50	51.8	13.2	0.056	1.93	34.6
50	50	51.8	6.9696	0.084	2.24	26.8
50	50	51.8	3.9192	0.112	2.39	21.4
50	50	51.8	27.602	0.014	1.21	86.7
50	50	51.8	21.296	0.042	1.53	36.4
50	50	51.8	16.884	0.056	1.75	31.3
50	50	51.8	10.5	0.084	2.07	24.6
50	50	51.8	3.9512	0.112	2.39	21.4
Ambient	50	51.8	33.666	0.014	0.91	64.9
Ambient	50	51.8	22.08	0.028	1.49	53.2
Ambient	50	51.8	16.008	0.042	1.79	42.7
Ambient	50	51.8	10.974	0.056	2.04	36.5
Ambient	50	51.8	4.922	0.084	2.34	28.0
Ambient	50	51.8	2.585	0.112	2.46	22.0
Ambient	50	201.5	154.56	0.014	2.35	168.1
Ambient	50	201.5	124.08	0.028	3.87	138.6
Ambient	50	201.5	98.7	0.042	5.14	122.7
Ambient	50	201.5	72.404	0.056	6.45	115.6
Ambient	50	201.5	39.949	0.084	8.08	96.4
Ambient	50	201.5	21.344	0.112	9.01	80.6
Ambient	50	201.5	150.88	0.014	2.53	181.3
Ambient	50	201.5	117.18	0.028	4.22	151.0
Ambient	50	201.5	92.92	0.042	5.43	129.6
Ambient	50	201.5	67.05	0.056	6.72	120.4
Ambient	50	201.5	43.152	0.084	7.92	94.5
Ambient	50	201.5	21.712	0.112	8.99	80.5

Data for Neutralized RCT Tests

Initial Vol	Initial Si	Final Si	Amt Fe Added	Mass Si sorbed	Si Capacity
mL	mg/L	mg/L	g	mg	mg Si/g Fe
50	593	516	0.014	3.8	274.0
50	593	461	0.028	6.6	237.1
50	593	425	0.042	8.4	200.7
50	593	363	0.056	11.5	206.1
50	593	296	0.084	14.9	177.5
50	593	236	0.112	17.8	159.7
50	593	131	0.168	23.1	138.0
50	593	69	0.223	26.2	117.3
50	593	33	0.279	28.0	100.2
50	593	458	0.028	6.8	241.9
50	593	416	0.042	8.8	210.8
50	593	377	0.056	10.8	193.2
50	593	301	0.084	14.6	174.2
50	593	232	0.112	18.1	161.7
50	593	137	0.168	22.8	136.1
50	593	74	0.223	26.0	116.2
50	593	33	0.279	28.0	100.3
50	593	9	0.419	29.2	69.8
50	593	8	0.419	29.2	69.8
50	593	3	0.559	29.5	52.9
50	593	2	0.559	29.6	52.9

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