Impact of Alkali Source on Vitrification of SRS High Level Waste

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The Defense Waste Processing Facility (DWPF) Savannah River Site is currently immobilizing high level nuclear waste sludge by vitrification in borosilicate glass. The processing strategy involves blending a large batch of sludge into a feed tank, washing the sludge to reduce the amount of soluble species, then processing the large "sludge batch" through the DWPF. Each sludge batch is tested by the Savannah River National Laboratory (SRNL) using simulants and tests with samples of the radioactive waste to "qualify" the batch prior to processing in the DWPF.

The DWPF pretreats the sludge by first acidifying the sludge with nitric and formic acid. The ratio of nitric to formic acid is adjusted as required to target a final glass composition that is slightly reducing (the target is for ~20% of the iron to have a valence of two in the glass). The formic acid reduces the mercury in the feed to elemental mercury which is steam stripped from the feed. After a concentration step, the glass former (glass frit) is added as a 50 wt% slurry and the batch is concentrated to approximately 50 wt% solids. The feed slurry is then fed to a joule heated melter maintained at 1150° C. The glass must meet both processing (e.g., viscosity and liquidus temperature) and product performance (e.g., durability) constraints

The alkali content of the final waste glass is a critical parameter that affects key glass properties (such as durability) as well as the processing characteristics of the waste sludge during the pretreatment and vitrification processes[1]. Increasing the alkali content of the glass has been shown to improve the production rate of the DWPF, but the total alkali in the final glass is limited by constraints on glass durability and viscosity. Two sources of alkali contribute to the final alkali content of the glass: sodium salts in the waste supernate and sodium and lithium oxides in the glass frit added during pretreatment processes. Sodium salts in the waste supernate can be reduced significantly by washing the solids to remove soluble species. The "washing strategy" for future sludge batches can be controlled to limit the soluble sodium remaining in the waste stream while balancing the alkali content of the frit to maintain acceptable glass properties as well as improve melter processing characteristics.

Tests were performed to determine if the melt rate of the process would be higher with less washing and alkali-poor glass frit or more washing and alkali-rich glass frits. The tests were designated as "Source of Alkali" (SOA) tests and utilized nonradioactive simulants based on the composition Sludge Batch 3 (SB3)[2]. Varying washing strategies were applied to the baseline SB3 composition and the composition of the frits were varied so that the final glass from all tests would have the same composition, as shown in Table 1, Table 2, and Table 3[3]. The designation given to each batch tested was based on the amount of sodium oxide contained in the glass frit to be used during each test (for example: 4% frit is prepared with 4% Na_2O). The waste loading is defined as the percentage of oxides from the waste sludge contained in the final glass product, as shown in Table 2. The waste loading was adjusted during the testing to maintain a constant glass composition during the testing.

Table 1. Measured Composition for the SOA Simulants

wt% (solids basis)	0% Frit	4% Frit	8% Frit - Baseline	12 % Frit	16% Frit
Al	8.265	8.98	9.865	10.7	11.7
Ba	0.1145	0.122	0.1305	0.145	0.157
Ca	2.03	2.19	2.145	2.64	2.93
Cr	0.1315	0.137	0.167	0.165	0.184
Cu	0.1265	0.146	0.153	0.1765	0.1865
Fe	26.05	27.65	29.7	32.45	35.8
K	0.056	0.1005	0.116	0.1345	0.162
Mg	2.68	2.825	2.945	3.285	3.905
Mn	3.48	3.82	4.26	4.53	4.955
Gd	0.06	0.062	0.0725	0.075	0.092
Na	18.75	16.8	14.9	8.77	3.065
Ni	0.919	1.005	0.964	1.175	1.31
P	0.0295	0.0315	0.045	0.034	0.037
Pb			0.005	0.027	0.02
S	0.3585	0.37	0.393	0.439	0.446
Si	0.9215	0.975	1.16	1.165	1.24
Zn	0.2865	0.305	0.336	0.343	0.3425
Zr	0.3145	0.3555	0.404	0.4015	0.39
mg/kg	0% Frit	4% Frit	8% Frit - Baseline	12 % Frit	16% Frit
NO2	31800	25150	18550	10700	766
NO3	23000	18500	14550	8680	2155
SO4	2010	2075	2120	2135	2195
C2O4	1904	1948	2000	2060	2126
TIC (calc)	1650	1500	1324	1125	901
Total Solids, wt %	25.49	24.37	22.71	20.60	16.29
Calcined Solids, wt %	17.97	17.47	16.34	15.51	12.90
Density, g/mL	1.21	1.20	1.15	1.16	1.11
pH	13.2	13.4	13.4	13.2	12.9
g Calcine Solids/g Dry Solids	0.705	0.717	0.720	0.753	0.792

Table 2. Nominal Compositions of the SOA Frits and Targeted Waste Loadings

Wt% Oxide	0%	4%	Baseline	12%	16%
B_2O_3	8.69	8.35	8.00	7.66	7.32
Li_2O	8.69	8.35	8.00	7.66	7.32
Na_2O	0.05	4.02	8.00	11.95	15.80
SiO_2	82.57	79.29	76.00	72.73	69.55
Waste Loading %	40.17	37.69	35	32.08	28.97

Table 3. Projected Glass Composition

Oxide	Target Composition	Projected Glass Compositions (wt% oxide)				
		0% Na	4% Na	8% Na*	12% Na	16% Na
Al_2O_3	5.991	6.133	6.143	6.303	6.152	6.02
B_2O_3	5.200	5.152	5.297	4.846	5.361	5.474
BaO	0.00	0.036	0.036	0.038	0.036	0.035
CaO	1.291	0.969	0.935	0.977	0.911	0.88
CdO	0.050	LTD	LTD	LTD	LTD	LTD
Cr_2O_3	0.082	0.096	0.091	0.085	0.082	0.093
CuO	0.068	0.075	0.066	0.072	0.074	0.083
Fe_2O_3	14.6	14.5	14.3	13.7	14.3	14.3
K_2O	0.015	0.061	0.059	0.073	0.060	0.067
MgO	1.500	1.645	1.575	1.622	1.562	1.726
MnO	2.283	1.883	1.864	1.845	1.864	1.812
Gd_2O_3	0.027	0.024	0.024	0.025	0.025	0.026
Li_2O	5.200	5.526	5.923	5.633	5.751	5.880
Na_2O	12.5	12.9	13.0	12.9	12.8	13.2
NiO	0.448	0.420	0.404	0.377	0.383	0.418
P_2O_5	0.078	0.074	0.071	0.073	0.071	0.070
PbO	0.023	LTD	0.038	0.039	0.039	0.037
SO_4	0.342	0.477	0.477	0.479	0.453	0.524
SiO_2	50.1	50.0	51.6	51. 3	51.9	52.8
TiO_2	0.00	0.017	0.017	0.038	0.018	0.017
ZnO	0.132	0.151	0.144	0.144	0.143	0.142
ZrO_2	0.145	0.240	0.247	0.252	0.258	0.237
Totals$^{\#}$	100	100	102	101	102	104

* Baseline composition for SB3
LTD = Less than detection limit
\# Totals were not renormalized, Sample results for oxides are calculated from elemental results based on assumed oxide forms, therefore, presence of different forms of multivalent cations can cause total to exceed 100%

Several items should be noted in the composition data. Although mercury is present in the waste sludge, it was not added during the testing to avoid mercury emissions during melt rate testing. Also, sodium is not the only alkali in the frits or sludges, but was the only alkali varied during the testing. The 12% Na test is comparable to the composition during Sludge Batch 2 processing at DWPF while the 0% and 16% Na represent extreme cases that are likely not practical for DWPF processing. Finally, the carbonate, nitrite, and hydroxide are present in the sludge as soluble sodium salts and are removed by washing. The amount of acid required during processing is impacted by these species and varied considerably during the testing.

Chemical Process Cell Impacts

DWPF prepares the incoming sludge for vitrification in the Chemical Process Cell (CPC) with two batch processes. The Sludge Receipt and Adjustment Tank (SRAT) process involves acidification of the sludge to a pH of ~5 using nitric and formic acids, steam stripping of mercury, and concentration by evaporation while the Slurry Mix Evaporator (SME) process consists of adding the frit and concentration by evaporation to the targeted solids content.

The amount of acid required for each SRAT batch is determined from the concentration of five components in the incoming sludge: manganese, carbonate, mercury, nitrite, and hydroxide (as measured by titration). During acid addition, carbonate reacts to form carbon dioxide, nitrite reacts to form nitrate and NOx, manganese and mercury are reduced, and hydroxide is neutralized. Other reactions are also taking place, such as hydrogen generation from reactions of the formic acid with the small amounts of noble metals present in the sludge. These side reactions are significant and cause a stoichiometry factor to be added to the acid requirement calculation based on operating experience.

This factor has been as low as 125% during SB1, as high as 185% during processing of SB2, and is set at 155% for SB3 operation. The lower limit for this factor is typically based on the amount of acid required to ensure nitrite destruction during the SRAT cycle while the upper limit is typically based on the limit on hydrogen generation. The acidification of the sludge significantly alters the rheological properties of the feed. Operationally, the factor is set as low as possible while generating product slurries than can be pumped. This factor was set at 155% during all SOA tests. Acid calculation inputs and results are shown in Table 4.

Table 4. Acid Addition Calculation Inputs and Results for a 2.5 liter Batch

	0% Na	4% Na	8% Na	12% Na	16% Na	Units
Nitrite (NO_2^-)	1.452	1.132	0.803	0.466	0.032	moles
Mn	0.384	0.403	0.398	0.410	0.357	moles
Carbonate	0.770	0.690	0.553	0.501	0.383	moles
OH^-	1.899	1.635	1.456	0.857	0.372	moles
Nitric Acid Added	271.5	229.8	187.8	128.6	60.9	ml
Formic Acid Added	51.7	50.9	49.6	39.3	31.2	ml

A SRAT cycle was performed on each of the simulants utilizing a 2.5 liter batch size and the acid additions shown in Table 4. Offgas emissions were monitored utilizing a high-speed micro-gas chromatograph and samples were taken of the condensate and SRAT product. The SME cycle was not performed during these runs.

The generation of hydrogen, nitric oxide, nitrous oxide, and carbon dioxide were generally maximum for the 0% Na_2O runs (least washed sludge) and minimum for the 16% Na_2O runs (most washed sludge). The generation of gas corresponds with the amounts of anions present in the initial sludge and the amount of acids added. Figure 1 shows a typical offgas profile from one of the runs and Figure 2 highlights the minor species emitted. Helium is added as a tracer.

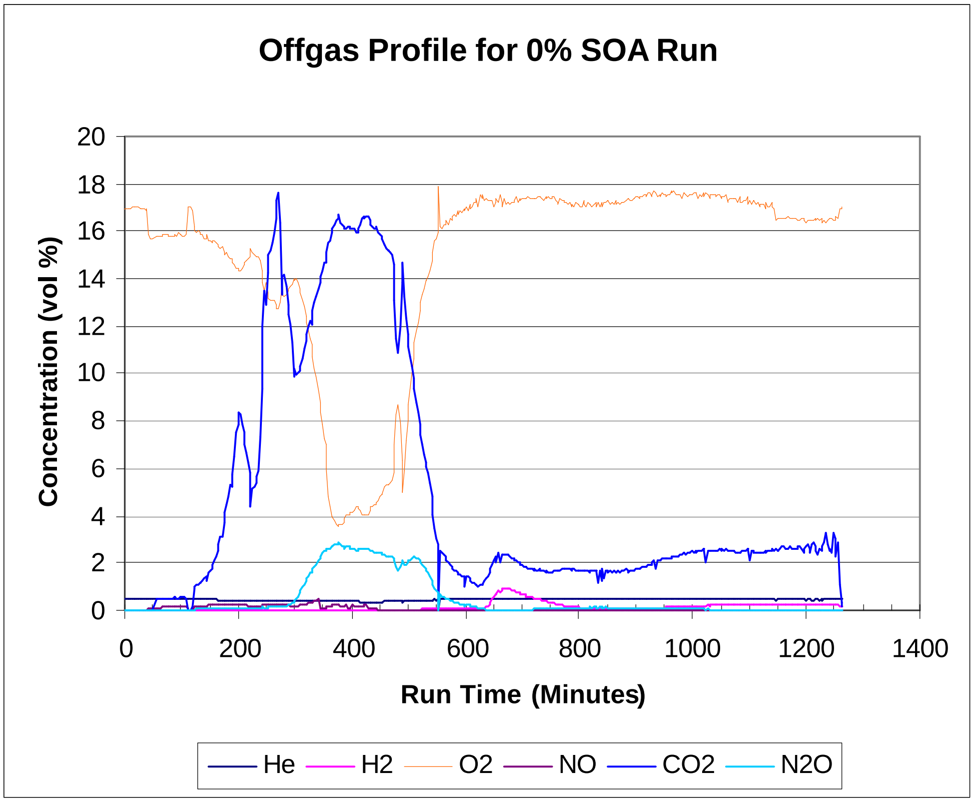

Figure 1. Offgas Profile for 0% SOA Run – All Analytes except N_2

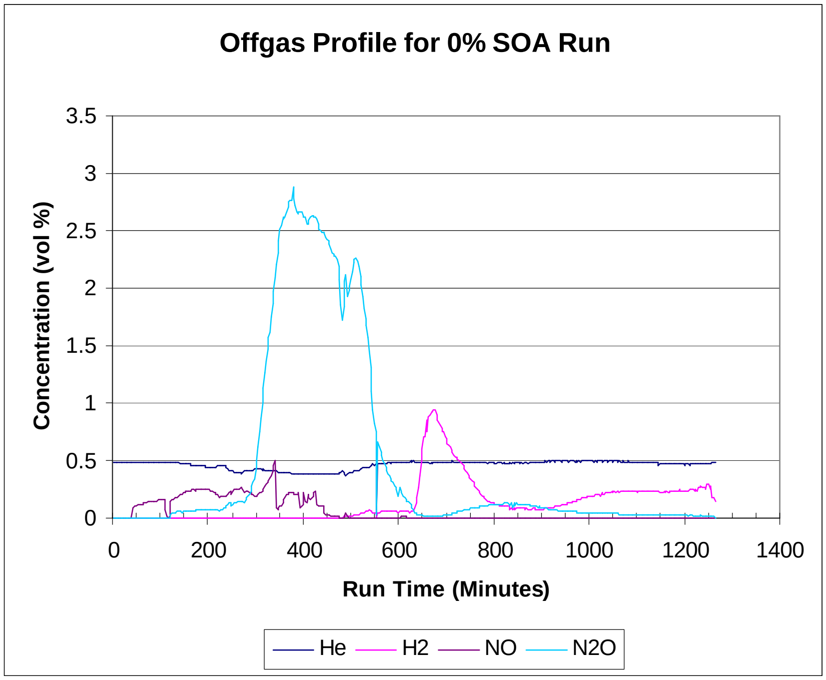

Figure 2. Offgas Profile for 0% SOA Run – Analytes < 4%

As shown from the Figures, carbon dioxide and nitrous oxide are the primary gases emitted during a SRAT cycle, primarily from the destruction of carbonate and nitrite. NO_2 is not detectable by the gas chromatograph but the coloration of the offgas indicates the presence of significant amounts of this gas.

The maximum hydrogen generation rate during the 0% SOA run was near the process limit of one volume percent, while hydrogen generation was <0.1 volume percent during the 16% Na run, as shown in Figure 3. The GC used during the baseline run (8% Na) had difficulties during that run and the results may not be representative.

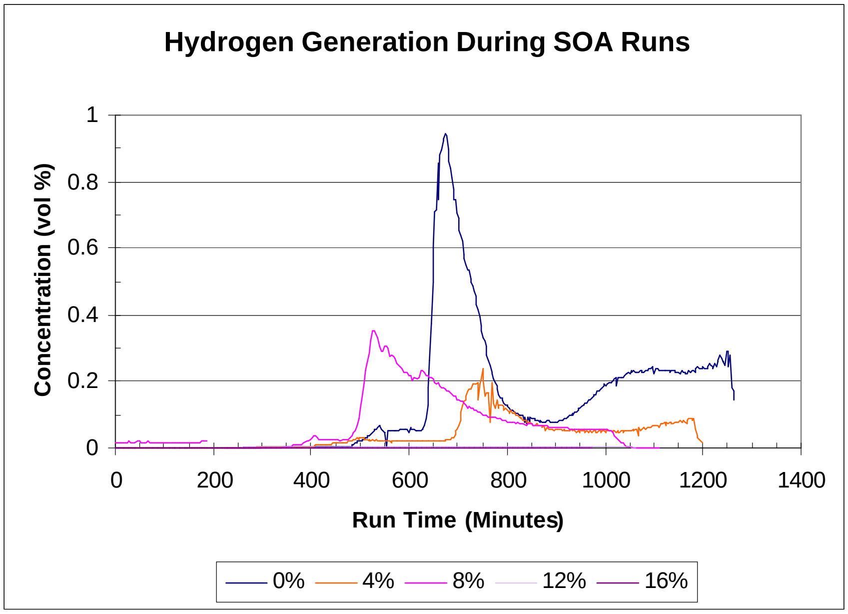

Figure 3. Hydrogen Generation during SOA Runs

The sample results for the SRAT products are shown in Table 6.

Table 6. SRAT Product Results

wt% (solids basis)	0% Na	4% Na	8% Na	12% Na	16% Na
Al	8.37	8.73	9.82	10.35	11.75
Ba	0.111	0.121	0.1335	0.1475	0.162
Ca	1.85	2.02	2.16	2.23	2.58
Cr	0.13	0.14	0.16	0.15	0.18
Cu	0.13	0.11	0.14	0.18	0.19
Fe	24.7	27.0	28.5	32.0	34.2
K	0.08	<0.010	0.112	0.127	0.163
Mg	2.395	2.52	2.87	2.775	3.68
Mn	3.45	3.74	4.00	4.40	4.80
Gd	0.061	nm	0.0735	nm	0.0975
Na	22.35	18.15	15.8	9.955	3.895
Ni	0.926	0.979	1.070	1.195	1.220
P	0.040	0.038	0.039	0.038	0.037
Pb	0.0195	<0.010	0.013	0.031	0.038
Pd	<0.010	0.019	<0.010	0.015	<0.010
Ru	0.0295	0.0195	0.0235	0.0150	0.0235
S	0.412	0.416	0.494	0.465	0.637
Si	1.00	1.13	1.17	1.42	1.31
Ti	0.019	0.022	0.0225	0.024	0.027
Zn	0.292	0.306	0.332	0.377	0.399
Zr	0.335	0.354	0.378	0.405	0.384
mg/kg	0% Na	4% Na	8% Na	12% Na	16% Na
HCO_2	82850	81200	66400	51300	24900
NO_2	<100	<100	<100	477.5	349
NO_3	45800	37400	33900	21000	10850
Cl	107	113	107	113.5	<100
SO_4	1115	nm	1420	nm	1505
Total Solids, wt %	32.1	30.0	27.5	23.8	18.0
Soluble Solids, wt %	14.31	13.96	13.94	14.48	13.46
Insoluble Solids, wt %	19.35	18.48	17.34	16.12	12.96
Density, g/mL	1.31	1.29	1.22	1.19	1.09
pH	8.12	7.66	6.64	7.16	7.49
g Calcine Solids / g Dry Solids	0.602	0.617	0.631	0.678	0.721

nm = not measured

The destruction of nitrite was not fully completed during the 12% Na and the 16% Na runs, although the final SRAT pH was below the pH obtained during the 0% Na and the 4% Na runs.

The nitrite destruction and offgas generation indicate that the side reactions not incorporated into the acid calculation become less important as the soluble salts are increased and vice versa. The fact that nitrite destruction was not 100% and the absence of hydrogen in the low alkali sludges indicates that the acid addition factor needs to be higher than 155% while the high levels of hydrogen in 0% Na run indicate that the factor should be less than 155%.

The rheological properties of the SRAT products were all nearly equal and well below the processing limits for DWPF. Two larger scale runs were conducted using the 4% Na and 12% Na compositions. These larger runs were utilized to provide feed for slurry-fed melt rate tests and included the SME cycle after the SRAT cycle was completed. The SRAT cycles were performed in the same manner as the 2.5 liter runs, then the SME cycle was performed targeting a final solids content of 50 wt% total solids for both runs.

The 4% Na SME product was free flowing while the 12% Na SME product was more viscous. The solids content of these products indicates that insoluble solids content of the 12% Na SME product was much higher than the 4% Na SME product. The 12% Na SME product was diluted to 45% total solids to match the insoluble solids content of the 4% Na run, and the yield stress was close to the 4% Na run, as shown in Table 7 and Figure 4. Properties were determined using the Bingham Plastic model.

Table 7. Rheological Properties of SME Products

	Total Solids	Insoluble Solids	Soluble Solids	Consistency (cP)	Yield Stress (Pa)
	(wt %)	(wt %)	(wt %)		
4% Na	49.1	36	13	75	30
12% Na	49.7	41	8.6	143	68
12% Na	45	37	7.8	54	34

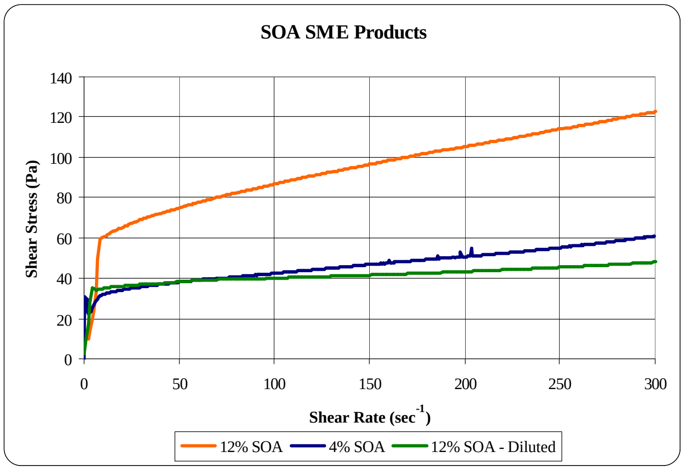

Figure 4. Flow Curves for SOA SME Products

Melt Rate Discussion

Melt rate is defined as the amount of glass produced per hour produced during the vitrification process. Various means of increasing the melt rate at DWPF has been extensively studied to allow stabilization of the radioactive waste to be accelerated. Trends noted during this testing include: increased alkali in the frit increases melt rate for a given sludge composition, increased alkali in the sludge increases melt rate for a given frit, increased acid additions decrease melt rate for a given sludge composition, and more reduced feed increases melt rate.

Melt rate testing at SRNL is conducted using dry-fed tests in a 4” diameter dry-fed melt rate furnace (MRF) as well as an 8” diameter slurry-fed melt rate furnace (SMRF). A portion of each of the SRAT products from the 2.5 liters runs was combined with frit at the targeted waste loading and dried to prepare feed for the MRF tests. The feed from two 12.5 liter SRAT/SME runs were blended to provide material for each of the SMRF tests.

The dry-fed MRF has a cylindrical inner chamber that is approximately 0.5 cubic feet in size, with heating coils winding around the chamber walls. The diameter of the chamber is ~7”, and an insulating sleeve and a 1200 mL stainless steel beaker (6” deep) were inserted from the top. The tests were conducted with the stainless steel beakers inserted with the sleeve so that the beaker bottom was approximately flush with the top of the uppermost chamber coil. An insulating block was used to cover the beaker. The furnace was heated to 1150°C with the top opening covered. Once the furnace reached the setpoint, the cover was removed and the beaker containing sufficient dried, sieved material to produce 500 grams of glass was inserted. After 50 minutes, the beaker was removed from the furnace and allowed to cool to room temperature. This residence time in the furnace was determined during testing in 2002 to establish a standard test time for melt rate comparison for this dry-fed furnace (Lorier et al. 2002). After cooling down, the beakers are then sectioned.

The relative melt rate is determined by measuring the height of the glass layer in the bottom of each sectioned beaker at 0.25” intervals. The average height and duration in the furnace is used to yield a relative linear melt rate number (LMR) (inches/hour). General observations of the sectioned beaker are also used to describe differences between runs. A waste throughput factor (LMR times the waste loading) is then calculated from the results. Results from the SOA tests are shown in Table 8 and Figure 5.

Table 8. MRF Results

SOA MRF Feed	LMR (in/hr)	WTF (Target WL)
0% SOA	0.39	15.7 (40.2)
4% SOA	0.55	20.7 (37.7)
SB3/Frit 418 (8%SOA)	0.59	20.7 (35.0)
12% SOA	0.55	17.7 (32.1)
16% SOA	0.38	11.0 (29.0)

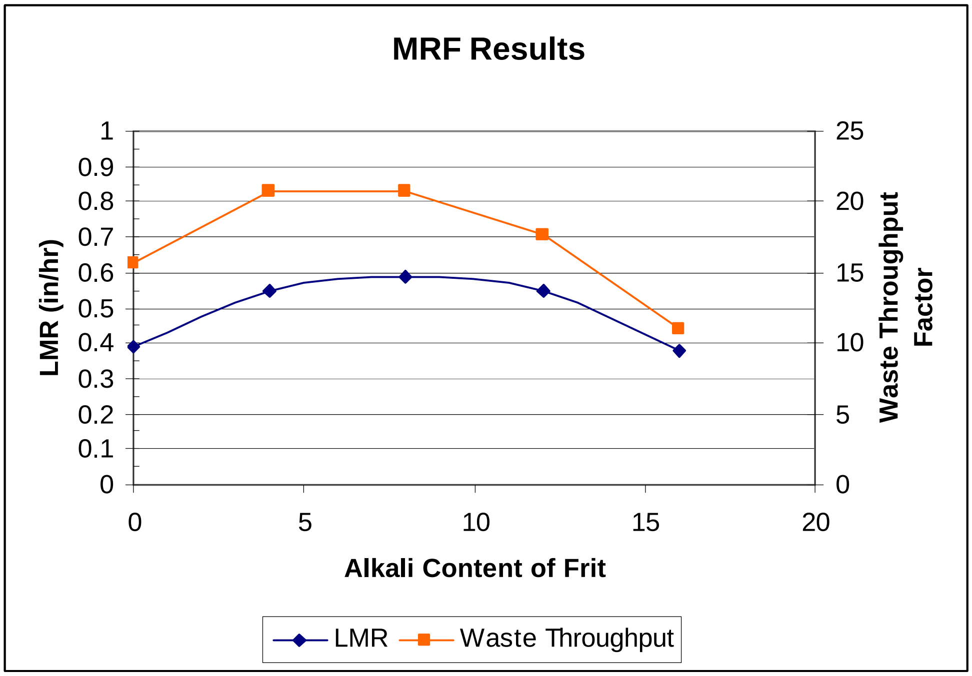

Figure 5. MRF Results

The SMRF utilizes a vessel with integrated overflow and drain tubes with heating tubes underneath the vessel to maintain the 3.5” glass pool in the vessel at 1150° C. Additional heating tubes are located along the sides of the vessel to maintain a vapor space temperature of 750° C during feeding. The power to the upper heaters is fixed during operation. The overflow and drain tubes are inductively heated as required to pour molten glass from the melter onto a pan. The feed system consists of a feed tank with agitator, peristaltic feed pump, and a water-cooled feed tube. The weight of the feed tank and glass poured from the melter is monitored during the run along with heater power, vapor space and melt pool temperature, and agitator speed.

The furnace is operated by adding a set amount (~100 grams in 20 seconds) of SME product slurry to the top of the glass pool. The vaporization of water in the feed cools the vapor space below the setpoint of 750° C. As the feed melts, the vapor space temperature recovers to the temperature setpoint, and an additional charge of SME product is added to the melter. Thus, the feed rate is dictated by the recovery time of the vapor space temperature. This recovery time is dependent on the type of cold cap (the layer of melting feed on top of the molten glass pool) that is formed. The cold cap insulates the vapor space from the molten glass pool, therefore feed that forms a small cold cap will allow heat from the glass pool to reach the vapor space and will have a higher feed rate than a feed that develops a larger or thicker cold cap.

Two SMRF runs were conducted during the SOA tests: a 4% Na run and a 12% Na run. The results matched the dry-fed MRF tests in that the difference in melt rate between the two tests was small, as shown in Table 9. Comparisons to previous runs using the baseline feed (8% Na) were complicated by the necessity of diluting the feed from 50 wt% solids typically processed in the SMRF to 45 wt% solids to allow the 12% Na feed to be pumped by the SMRF feed pump.

Table 9. SMRF Results

	4% SOA Feed	12% SOA Feed
45 weight % solids	14.4	13.6

Conclusions

The results indicated that a broad optimum region exists in sludge washing for maximum melt rate of SB3 with a maximum at approximately 21% sodium in the sludge (oxide basis) and 16% total alkali content (8% Na, 8% Li; oxide basis) in the frit. Since the alkali metals act as a flux during melting, it is speculated that melt rate is reduced as either the frit or waste becomes more refractory on either side of the optimal region.

As sodium salts in the waste were increased, more acid was required during sludge processing. The additional acid led to increased processing time and higher hydrogen evolution during the pretreatment process.

The higher percentage of insoluble solids in the more washed sludges led to difficulties with pumping and required dilution to 45% solids prior to SMRF testing. The melter feed is typically concentrated to 50% solids (soluble and insoluble) during pretreatment. The optimal point for melt rate (21% sodium in sludge on an oxide basis) and higher concentrations of sodium in the sludge did not lead to processing difficulties.

References

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