

Improved Loading of Sulfate-Limited Waste in Glass

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ABSTRACT

The allowable sulfate concentration limits waste loading in borosilicate glasses (e.g., Hanford low-activity waste [LAW] and Idaho National Laboratory sodium-bearing waste. By the Hanford baseline formulation method, the tolerated amount of sulfate in LAW is 0.77 wt% (as SO₃) at the lowest soda contents, decreasing to 0.35 wt% at the highest soda contents. Roughly half of the Hanford LAW (on a glass mass basis) will be limited by sulfate tolerance of the glass melt. If the allowable concentrations of sulfate were to be increased only moderately, the cost and time required to vitrify the Hanford LAW would be significantly reduced

A series of high-sulfate glass formulations were developed by Khlopin Radium Institute (Russian Federation) and Pacific Northwest National Laboratory. These glasses were tested at crucible, small melter, and larger test melter scales for not only sulfate retention but key product quality criteria as well. The key properties of the glasses to be disposed of at Hanford were measured (product consistency test and vapor hydration test), and processing-related properties (viscosity and electrical conductivity) were predicted using property composition models. The results for 28 glass compositions tested at crucible-scale, 6 glass compositions tested at small-melter-scale, and 4 glass compositions tested at larger melter-scale are presented in this paper. The melter tests were all performed with waste composition and processing parameters (e.g., bubbling rate, melting rate, temperature) prototypic for the Hanford LAW melter design.

The results show that sulfate loadings as high as 1.5 wt% with soda concentrations as high as 20 wt% are viable with improved formulation methods. These results suggest that the loading of sulfate-limited Hanford LAW may be increased by over 300%, relative to the current formulation. However, additional work is recommended before implementing the new formulations.

INTRODUCTION

The U.S. Department of Energy (DOE) is responsible to treat and dispose of a number of nuclear waste streams, including high-sodium, high-sulfur wastes such as Idaho National Laboratory (INL) sodium-bearing waste (SBW) and Hanford low-activity waste (LAW). The loadings of these wastes in borosilicate glasses are largely determined by either salt accumulation or chemical durability constraints. The chemical durability constraints can be reliably met with glasses containing between 20 wt% and 23 wt% combined $\text{Na}_2\text{O}+\text{K}_2\text{O}$ [1,2]. However, there has been an ongoing dispute about the amount of SO_3 that can be tolerated or incorporated into these glasses before a molten salt accumulates under normal melter operating conditions. The formulation approach used by The Catholic University of America (CUA) in support of the Hanford Waste Treatment and Immobilization Plant (WTP) is to limit sulfur in glass by soda concentration according to the *rule-of-five*:

$$g_{\text{Na}_2\text{O}} \times g_{\text{SO}_3} \leq 5 \quad (\text{Eq. 1})$$

where g_i is the wt% of the i^{th} component in glass [2,3]. In later work, the allowable concentrations have increased; however, the relationship between Na_2O and allowable SO_3 concentrations remain negative with a maximum g_{SO_3} of 0.77 wt% at $g_{\text{Na}_2\text{O}} \leq 3.2$ wt% and $g_{\text{SO}_3} \leq 0.35$ wt% for $g_{\text{Na}_2\text{O}} = 21$ wt% [4].

Vienna and colleagues have developed a different (PNNL) approach to the limit of sulfate in sodium-rich borosilicate waste glasses [5-8]. In their approach, the tolerable sulfate concentration increases with increasing concentrations of alkali (Li_2O , Na_2O , and K_2O) and alkali-earth (MgO , CaO , SrO) oxides. Therefore, a 20 wt% Na_2O glass would have SO_3 concentrations of 1 wt% or higher, the basic concept being that alkali and alkali-earth components increase the solubility of sulfate in silicate-based glasses [9,10] and that the rate of incorporation would be increased by increased solubility. Sulfate incorporation is generally lower than the solubility limit because sulfate can be carried to the melt surface in bubbles as described by Hrma et al. [11,12]. Fig. 1. visually displays the difference in the two approaches.

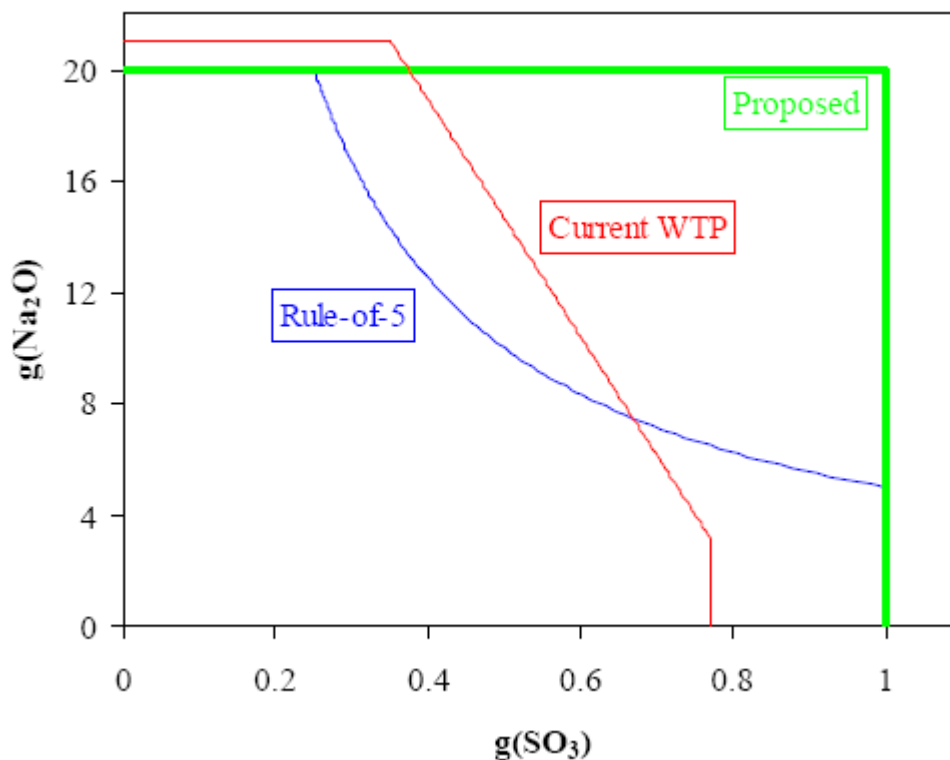
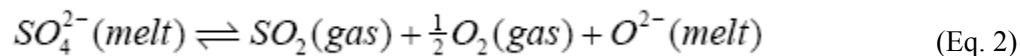


Fig. 1. Schematic of soda-sulfate waste-loading limits by different approaches (wt%).

In this work, it is proposed that sulfate tolerance can be increased by increasing alkali and alkali-earth oxide concentrations (i.e., the Pacific Northwest National Laboratory [PNNL] approach), but also, the sulfate retention will be enhanced by adding oxidizing agents (V_2O_5 , SnO_2 , and/or MnO_2). The aim of these oxidizing agents is to reduce the temperature range of sulfur reduction to SO_2 , thereby driving the sulfur reduction reaction to the left:



This paper describes the results of preliminary formulations for a typical sulfate-limited Hanford LAW, followed by scale-up testing of selected compositions through medium-scaled test melters at Khlopin Radium Institute (KRI).

FORMULATION AND SELECTION OF TEST GLASSES

The simulated waste composition selected for use in this study was that corresponding to Hanford LAW from Tank 241-AN-107 (composition listed in Table I). This waste is representative of high-soda, high-sulfate wastes that have soda:sulfate ratios in the range appropriate to show a difference between the different formulation approaches described above. If this LAW were loaded in glass using the three formulation constraints above, the gNa_2O and gSO_3 would be (20, 0.52), (17.2, 0.44), and (14, 0.36) for the proposed approach, the current WTP approach, and the *rule-of-5*, respectively.

Table I. Composition of Hanford Tank 241-AN-107 LAW simulant and glass

Simulant Component	mass (g)	Simulant Component	mass (g)	Glass	Fraction (wt%)
Water	1670	La ₂ O ₃	0.0642	Al ₂ O ₃	3.52
Sodium Acetate	26.9	NaCl	5.49	CaO	0.22
Sodium Oxalate	14.7	NaF	13.3	Cl	0.50
Glycolic Acid	38.7	Na ₃ PO ₄ ·12H ₂ O	26.1	Cr ₂ O ₃	0.12
Citric Acid	48.4	Na ₂ SO ₄	22.4	F	0.91
Nitrilotriacetic Acid	16.5	NaNO ₃	378	Fe ₂ O ₃	1.08
Iminodiacetic Acid	15.5	NaOH, 50% soln.	457	Na ₂ O	90.19
Na ₂ EDTA·2H ₂ O	24.8	KOH	5.92	NiO	0.17
Na ₃ HEDTA·2H ₂ O	26.8	Na ₂ CrO ₄	2.42	P ₂ O ₅	0.74
Sodium Gluconate	16.2	HCOONa	29.3	PbO	0.11
Al(NO ₃) ₃ ·9H ₂ O, 60% soln.	286	NaNO ₂	161	SO ₃	2.35
Ca(NO ₃) ₂ ·4H ₂ O	6.00	NH ₄ NO ₃	6.18		
Fe(NO ₃) ₃ ·9H ₂ O	36.1	Na ₂ CO ₃	238		
NiO	1.11	Sucrose ^a	135		
PbO	0.706				

^a Sucrose, not in the waste, was added to match the amount of reductant used in the WTP operation.

Twenty-seven glass compositions were formulated to demonstrate the proposed theory that sulfur loading could be increased substantially by changing the formulation method using the AN-107 LAW composition. The formulation approach was to increase the concentrations of alkali and alkali-earths while maintaining the viscosity and conductivity in the appropriate range for processing in the WTP. Existing property models were used to predict the viscosity at 1150°C, the electrical conductivity at 1150°C, the product consistency test (PCT) responses, and the propensity for secondary phase formation of the glasses [13]. Oxidizing agents (MnO₂, SnO₂, and V₂O₅ were also added to selected glasses). ZrO₂ and SnO₂ were also added to improve the chemical durability of the glasses. Table II lists these glasses.

Each of the 28 glasses listed in Table II (27 new glasses plus one previously tested glass) were fabricated from liquid simulant and additives in roughly 30-g batches in an uncovered alumina crucible for 2 hours at 1150°C. The glasses were analyzed for separated salt phases and were sampled for further testing. Compositions of the glasses were analyzed by scanning electron microscopy (SEM) with electron beam microprobe analyses (EMPA) for composition. The 200°C vapor hydration test (VHT) responses were measured on samples using procedures previously published [1]. Other key properties were predicted using previously published glass property models [13]. Table III lists the measured and/or calculated properties of these glasses.

Based on the results listed in Table III, five glass compositions were selected for small crucible testing. Of the 27 newly formulated glasses, 13 glasses passed the constraints for disposal of Hanford LAW (50 g/m²/d VHT and 2 g/m² PCT) and the processing constraints for the test melters (2 Pa·s ≤ viscosity at 1150°C ≤ 10 Pa·s and 20 S/m ≤ electrical conductivity at 1150°C ≤ 90 S/m). Of the glasses passing all constraints, L22, L24, and L17 had the highest SO₃ retention and were selected for testing. L19 had the lowest VHT response for a 20 wt% Na₂O glass. Finally, C22, the glass formulated and tested for the WTP, was selected throughout the testing program to supply a method of comparison to the results of other testing. These five glasses (L22, L24, L17, L19, and C22) were selected for the small-scale melter test described in the following section.

Table II. Target Compositions of Glasses Tested in this Study (wt% of oxides and LAW loading)

Glass	LAW ^a	Al ₂ O ₃	B ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Li ₂ O	MgO	P ₂ O ₅	MnO ₂	SiO ₂	SnO ₂	TiO ₂	V ₂ O ₅	ZnO	ZrO ₂
C22 ^b	16.15	5.52	10.05	5.06	5.39	-	2.50	1.51	-	-	46.60	-	1.14	-	3.06	3.01
L01	22.15	2.22	6.00	3.95	1.26	0.75	2.50	2.00	1.14	-	52.53	-	-	3.50	-	2.00
L02	21.05	2.26	8.00	3.70	2.27	-	1.90	1.50	0.84	-	52.22	-	-	3.00	-	3.25
L03	22.15	2.22	8.00	2.95	1.26	-	2.00	1.00	0.83	-	53.59	-	-	2.50	-	3.50
L04	22.15	2.22	9.00	2.45	2.26	-	2.00	1.00	1.34	-	51.58	-	-	2.00	-	4.00
L05	22.15	3.22	8.00	0.95	-	-	2.00	2.50	-	-	53.68	-	-	3.00	-	4.50
L06	22.15	2.22	10.00	-	1.26	-	3.50	-	-	-	52.87	-	-	4.00	-	4.00
L07	22.15	2.00	11.25	7.00	-	0.75	1.50	2.00	-	-	46.85	5.00	-	-	-	1.50
L08	25.00	2.00	10.50	6.00	-	0.50	1.75	1.93	1.29	-	45.03	4.00	-	-	-	2.00
L09	22.15	2.00	10.25	7.50	-	-	1.25	-	-	5.50	49.59	-	-	-	-	1.75
L10	25.00	2.00	9.50	6.50	-	-	1.50	-	-	5.00	48.56	-	-	-	-	1.93
L11	22.15	2.72	6.00	3.95	1.76	2.00	1.00	2.00	-	-	51.92	1.00	2.00	-	-	3.50
L12	22.15	2.22	8.00	2.95	1.26	-	2.00	2.00	-	-	52.92	2.00	-	-	-	4.50
L13	22.15	2.22	7.00	3.45	-	2.50	1.00	2.00	-	-	54.19	-	1.00	-	-	4.50
L14	22.15	2.22	7.00	2.95	1.76	1.50	1.00	2.00	1.34	-	46.58	4.00	2.00	2.50	-	3.00
L15	22.15	3.50	8.25	6.35	0.24	0.75	1.25	-	-	-	48.51	4.50	-	-	3.00	1.50
L16	22.15	3.50	8.50	6.35	0.24	1.00	-	-	-	-	48.75	5.00	-	-	3.00	1.50
L17	22.15	3.80	8.00	6.46	0.24	-	1.25	-	-	4.50	48.60	-	-	-	3.00	2.00
L18	22.15	3.80	8.25	6.46	0.24	-	-	-	-	5.00	49.10	-	-	-	3.00	2.00
L19	22.15	2.72	10.00	6.45	-	-	1.00	1.50	-	-	47.68	5.00	-	-	-	3.50
L20	22.15	2.79	8.50	6.35	-	-	1.00	-	-	2.50	47.20	5.00	-	-	3.00	1.50
L21	22.15	2.79	9.00	6.85	-	-	1.00	-	-	2.50	48.70	5.00	-	-	-	2.00
L22	22.15	2.79	9.50	6.00	-	-	1.00	1.00	-	2.50	47.55	5.00	-	-	-	2.50
L23	20.00	2.87	10.00	6.96	-	-	1.25	-	-	2.50	47.42	5.50	-	-	-	3.50
L24	22.15	3.22	8.50	5.96	-	-	2.00	-	-	2.00	50.18	2.00	-	-	-	4.00
L25	22.15	2.72	9.00	6.45	-	-	2.00	-	-	3.00	50.18	1.00	-	-	-	3.50
L26	22.15	3.72	9.00	6.95	-	-	2.00	-	-	-	49.68	3.00	-	-	-	3.50
L27	22.15	2.72	10.00	4.45	-	-	1.00	-	-	1.00	53.18	1.50	-	-	-	4.00

^a The LAW is that composition listed in Table I for 241-AN-107 LAW as glass components. The values in this column are the waste loading.

^b The glass composition LAW-C22 was formulated and tested by CUA for WTP [2] and carried through all testing performed in this study as a check of test validity and scale effects.

Table III. Data from the Crucible Scale Glasses and Compositions Selected for Melter Tests

ID	Measured g_{SO_3} (wt%)	% SO_3 Retained	Measured VHT ($g/m^2/d$)	Predicted PCT (g/m^2)	Predicted Viscosity (Pa·s)	Predicted Conductivity (S/m)	Passes	Selected for Small Melter
C22	0.21	55	7.7	0.5	5.1	44	yes	yes
L01	na	-	>276	2.0	4.6	83	-	-
L02	na	-	216	1.4	6.1	67	-	-
L03	na	-	262	1.5	6.6	80	-	-
L04	na	-	206	1.6	5.6	81	-	-
L05	na	-	>264	1.8	8.2	68	-	-
L06	0.27	52	24	2.7	3.6	132	-	-
L07	0.28	54	>298	1.0	7.8	52	-	-
L08	na	-	165	1.6	6.6	69	-	-
L09	0.36	69	>298	1.2	9.3	49	-	-
L10	na	-	>281	1.6	4.6	63	-	-
L11	0.32	61	0.73	3.3	2.1	83	yes	-
L12	0.25	48	255	4.5	1.6	119	-	-
L13	0.27	52	248	1.2	2.5	89	-	-
L14	0.30	58	>292	1.8	1.9	127	-	-
L15	0.29	56	2.2	1.1	4.6	82	yes	-
L16	0.14	27	1.3	0.9	7.3	63	yes	-
L17	0.35	67	5.6	0.6	4.0	80	yes	yes
L18	0.34	65	7.3	0.5	6.3	62	yes	-
L19	0.24	46	0.97	1.7	4.1	67	yes	yes
L20	na	-	1.0	1.0	3.7	83	yes	-
L21	na	-	1.5	1.1	4.0	82	yes	-
L22	0.42	81	2.4	1.4	3.6	76	yes	yes
L23	0.30	64	0.79	0.9	4.1	65	yes	-
L24	0.38	73	7.9	1.0	4.3	85	yes	yes
L25	na	-	118	1.1	3.4	89	-	-
L26	0.24	46	1.3	1.2	4.2	87	yes	-
L27	na	-	3.7	1.0	7.7	72	yes	-

SMALL-SCALE MELTER TESTING

The small-scale melter testing was conducted using the steklo metallicheskie kompozitsions (SMK) melter at KRI. The melter consists of an insulated enclosure with eight silicon carbide heaters as shown in Fig. 2. The BeO crucible with the volume of 1000 cm³ (with an operational volume of 500 cm³) is placed into the melter. A water-cooled lid designed to be connected with the feed pump, off-gas system, air bubbler, and the drain system is attached to the crucible. The lid also has openings for visual monitoring and glass sampling. The melter feeds consisted of the simulants fabricated according to the recipe in Table I and minerals (where possible, the glass-forming chemicals selected by the WTP were used). The slurry feed was continuously fed to the SMK through a water-cooled steel feeding tube at 600 mL/h. After the initial glass melt was formed, air was bubbled into the melter from a 1/4-inch tube (Inconel 625) at 2 L/min. The melter temperature was maintained at 1150°C during the entire melting period. The off gas flowed through a water-cooled gas line, a bubbler, a condenser, a fine filter, an alkaline trap, a flow meter, and a pump.

Each test operated for roughly 11 h, feeding ~2400 mL of feed and producing ~1000 mL of glass. After the last feeding, the coldcap was allowed to burn off, and the top of the melt was analyzed for signs of molten salt accumulation using a ceramic rod to probe the surface in several spots. Samples of the glass

were analyzed using SEM/EMPA for composition (including SO_3 concentration). Samples were slow cooled according to a simulated WTP container centerline cooling schedule and analyzed for the formation of any separated phases.

After completing a test, the target concentration of SO_3 was increased (if no evidence of salt accumulation was found) or decreased (otherwise) using Na_2SO_4 as an additional additive. The revised SO_3 content feeds were then tested until the highest SO_3 concentration without the accumulation of molten salt was reasonably narrowed. Table IV lists the results from testing. Based on these results, four of the five compositions were selected for larger scale melter testing. The C22 composition was carried because of its reference to other melter systems. The L24 showed no salt, even at target loadings of 1.52 (wt% SO_3), and retained the highest fraction of SO_3 in the glass at all three sulfate levels (94%, 86%, and 76% for $g\text{SO}_3$ of 0.52, 1.02, and 1.52, respectively). The glasses L17 and L22 both showed no salt accumulation at 1.02 wt% SO_3 and some salt accumulation at 1.52 wt% SO_3 , and their fraction of SO_3 retained in the glass were similar. Therefore, they were both carried to larger scaled testing.

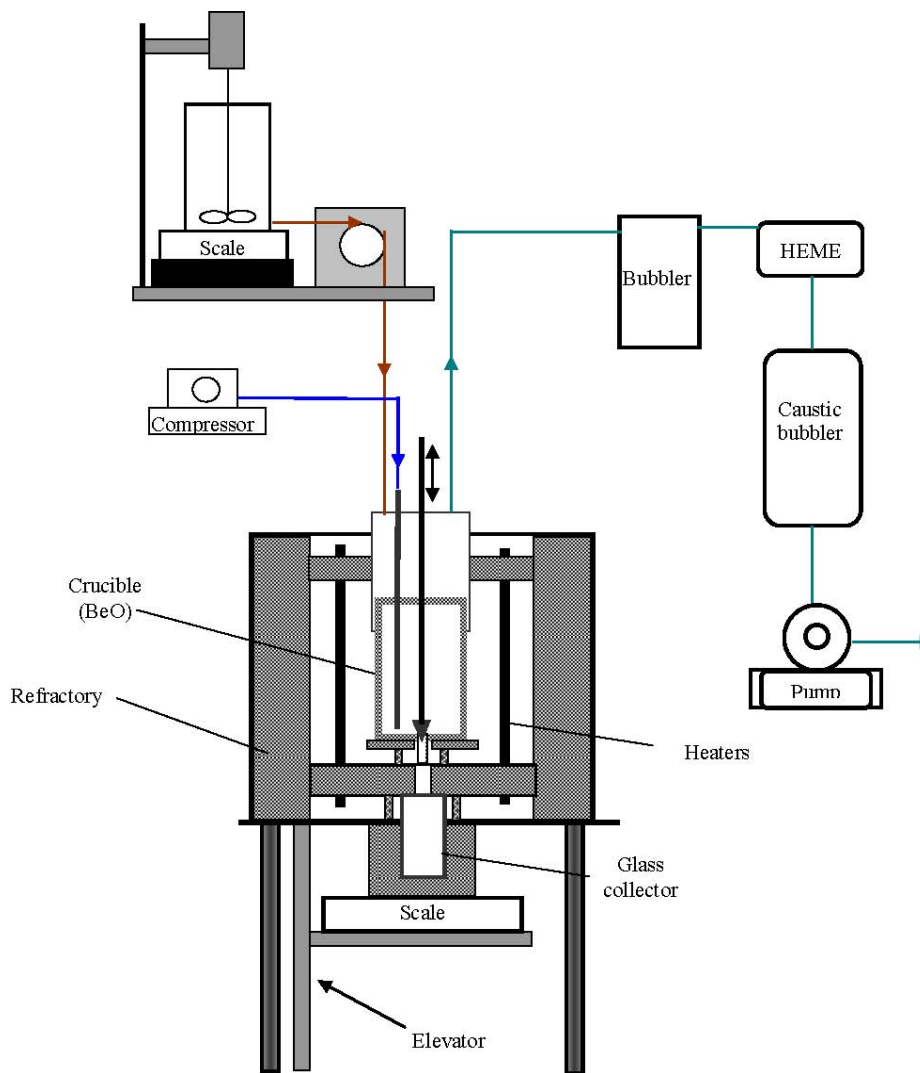


Fig. 2. Small-scale (SMK) melter system schematic

Table IV. Summary of SMK Small-scale Melter Test Results (wt% SO₃)

Glass	C22		L17		L19		L22		L24	
Target g _{SO₃}	g _{SO₃}	Salt	g _{SO₃}	Salt	g _{SO₃}	Salt	g _{SO₃}	Salt	g _{SO₃}	Salt
0.38	0.23	no	-	-	-	-	-	-	-	-
0.52	-	-	0.41	no	0.40	no	0.43	no	0.49	no
0.70	0.40	no	-	-	-	-	-	-	-	-
0.88	0.42	yes	-	-	-	-	-	-	-	-
1.02	-	-	0.84	no	0.61	no	0.79	no	0.88	no
1.52	-	-	0.97	yes	0.83	yes	0.95	yes	1.15	no
Selected	yes		yes		no		yes		yes	

LARGER SCALE MELTER TESTING

The larger scale melter testing was conducted in the EP-5 melter at KRI. The EP-5 melter is a rectangular Joule-heated melter. Its main electrodes are made of heat-resistant steel EI-652 (70% Cr, 30% Ni, and 1% Fe). The electrodes are placed immediately adjacent to each other, along the longitudinal walls of the chamber. The melter is also equipped with silicon carbide startup electrodes to generate the initial melt bath. A lid designed to be connected with the feed pump, off-gas system, air bubbler, and the drain system is attached to the melter. The lid also has openings for visual monitoring and glass sampling. Fig. 3 shows the melter schematically and lists the melter's key parameters.

The melter feed was prepared in the same manner as that used in the small-scale melter testing. To initiate testing, the EP-5 melter was warmed up using the SiC startup heaters. Once the melt temperature reached 700 to 800°C, Joule-heating was initiated, and the startup batch was added. The melt temperature was brought to 1150°C, and a bubbler tube was inserted into the center of the melt. Slurry feeding began at 1 L/h and increased to between 2 and 2.5 L/h with a bubbling rate of 3.5 L/h. The off-gas temperature was monitored and stayed between 750 and 800°C. Each experiment lasted for roughly 24 h of continuous feeding, which generated between 18 and 20 kg of glass.

Periodically, the coldcap was allowed to burn off, and the surface of the melt was probed using a ceramic rod for visual signs of a salt layer. If the salt was found to accumulate, the test was stopped short (after roughly 16 h of testing and 11 kg of glass poured). The melt surface was examined, and samples were collected for analyses after completion of the test. Samples were analyzed in much the same manner as for the small-scale melter samples described above. Table V summarizes the results from the tests.

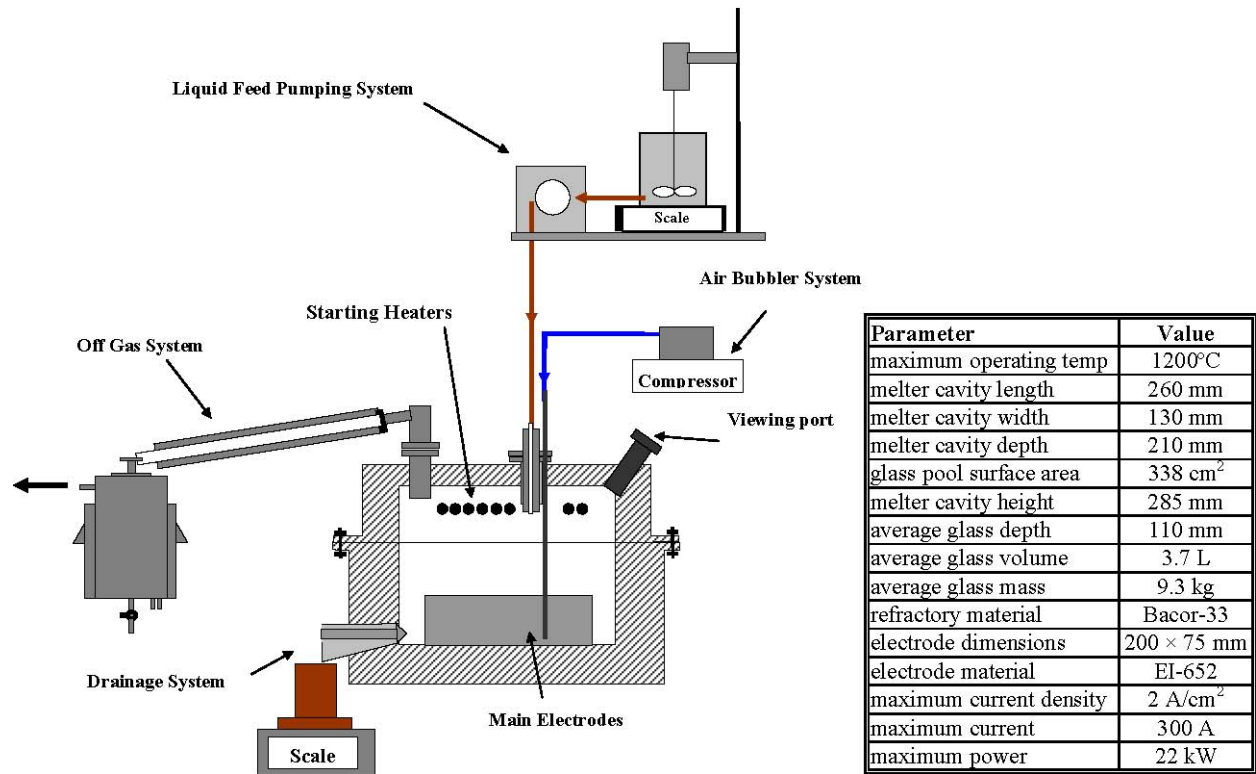


Fig. 3. Larger scale melter (EP-5) schematic

Table V. Result Summary for Larger Scale Melter (EP-5) Testing

Glass	Volume ^a	Measured g_{SO_3}	% SO_3 retention	Salt
C22 - $g_{SO_3} = 0.60$	1	0.31	52	no
	1	0.45	64	
C22 - $g_{SO_3} = 0.70$	2	0.37	53	no
	3	0.35	50	
	1	0.41	47	
C22 - $g_{SO_3} = 0.88$	2	0.46	52	no
	3	0.51	58	
	1	0.49	49	yes
C22 - $g_{SO_3} = 1.0$	1	1.06	88	
	1	1.06	88	
L17 - $g_{SO_3} = 1.2$	2	1.04	87	no
	3	1.00	83	
	1	1.18	79	yes
L22 - $g_{SO_3} = 1.3$	1-3	1.15	88	no
L22 - $g_{SO_3} = 1.5$	1	1.06	71	yes
L24 - $g_{SO_3} = 1.2$	1	0.70	58	no
	2	0.64	53	
	3	electrode failure		
L24 - $g_{SO_3} = 1.5$	1	1.00	67	
	2	1.07	71	no
	3	1.03	69	
L24 - $g_{SO_3} = 1.7$	1	1.10	65	yes

^a Melter volumes worth of glass produced.

DISCUSSION

Of the 27 newly formulated glasses for higher sulfate tolerance, 13 met all of the processing and product quality constraints. Four of these glasses were tested in the KRI small scale melter and were found to tolerate significantly higher sulfate loading than the corresponding CUA formulation (C22). Three of these glasses were tested at larger scale, again, showing that higher sulfate concentrations should be obtainable. Fig. 4. compares the soda and sulfate content of the three large-scale melter test data along with the large-scale tested C22 composition and the limiting lines currently being considered.

Compared to the small scale melter, slightly higher sulfate concentrations were processed before salt separation and higher sulfur retentions were observed. This suggests that smaller scale testing may give conservative responses and thus may be used instead of larger scale testing.

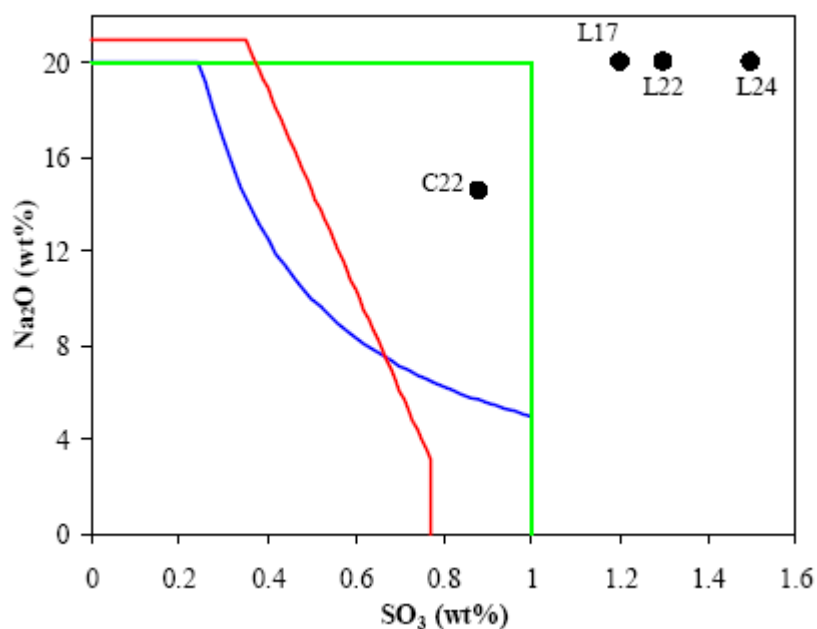


Fig. 4. Comparison of Larger Scale Melter Data with Formulation Rules

CONCLUSIONS

A series of glass compositions were developed to determine if the tolerable sulfate loading in borosilicate glasses would increase or decrease with added alkali (e.g., Na_2O) and if adding oxidizing agents would improve sulfate retention in the melt. Scaled melter tests were performed using a typical Hanford LAW simulant as the basis, and the associated WTP “baseline” glass for that waste was tested alongside the new glass formulations to serve as a reference. The results clearly demonstrate that significantly higher sulfate loadings are possible with the formulation method proposed by PNNL [5-8] with feed sulfate concentrations as high as 1.5 wt% SO_3 (~1.03 wt% measured in glass) being fabricated without salt accumulation while meeting all the processing and product quality requirements (an increase of over 300%, relative).

It was proposed that oxidizing agents (MnO_2 , SnO_2 , and V_2O_5) may improve the sulfate retention during melting of high-soda, high-sulfate waste glasses. Although the data are

Additionally, it was shown that the smaller scale melter results on salt accumulation match the larger scale results quite closely. This conclusion allows for testing salt behavior in smaller melter platforms, with a potential for significant cost savings.

These tests prove the concept on a prototypic composition and at small scale. However, we still need to address the wide variations in compositions of Hanford LAW.

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