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SILO PROJECT INDEPENDENT REVIEW TEAM DOCUMENTATION - VITRIFICATION OF THE SILO WASTES

04/24/96

ROD F. GIMPLE
16
PAPER

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R2 4/24/96

Vitrification Of The Silo Wastes

If the RI data were the only source of information, neither the K-65 Silos nor the Silo 3 would be good candidates for vitrification. For example, a K-65 glass could only have 20% waste loading. The PNL data is much more encouraging, but mixed. The K-65 Silos are high in Silica, which is good for vitrification, but is also high in lead which can hinder the vitrification process. Silo 3 is lower in silica, but high in magnesium, calcium, and iron which are good fluxes and glass formers. It is also high in sulfate and phosphates which can hinder the vitrification process. The chemical makeup of both K-65 and Silo 3 will need to be adjusted, by the use of additives, to make glass. Minimelters were used at the Vitreous State Laboratory at the Catholic University of America in Washington D.C. to develop simulated Fernald glass formulas with the correct viscosities and electrical conductances for operation and testing in the Fernald Vitrification Pilot Plant. Given below are the amounts of Silo wastes and additives used in these recipes to make 100 pounds of glass. The extra pounds over a hundred are lost to the off-gas system as standard process gases (e.g., CO_2, H_2O, SO_x, etc.)

	Silos 1 & 2 Alone	Silo 3 Alone	Silos 1,2,&3 Combined
Silo Residues (dry)	71.60	81.60	71.84
Additives (as oxides)	33.00	40.00	37.00
Totals	104.60	121.00	108.84

The glasses developed can disolve between ½ and 1½% sulfate depending on glass composition and temperature. Above this concentration, the sulfate will normally off-gas as SO_3 and SO_2 (if decomposed) or float to the surface as a sulfate salt (if not decomposed). Both the K-65 and Silo 3 residues contain more than 2% sulfate and both have resulted in foaming, caused by release of SO_x, during temperature excursions in the minimelter runs. Fortunately, measures were later devised to help control the foaming. VSL studies show that blending the Silo 3 with the K-65 residues does not hamper production if processed correctly, but may actually increase the production rate. Glasses made with sulfate tend to be more durable or be "less likable to devitrify" as stated by Henry Chance, in 1883 when sheet glass was made with sulfates[1]. The high phosphates were not noticed to be a problem during any of the VSL crucible melts or minimeltr runs because alumina, which was used as an additive, helps dissolve phosphates in the glass.

The Silo 3 glasses and glass blends are thin (less viscous) glasses and the alumina helps thicken the glasses and make them more durable. Where as, bentonite can hinder the K-65 glasses because K-65 glasses are thick glasses to begin with. Blending the Silo wastes appears to make glasses with good viscosity (and conductivity) values for use in the pilot melter.

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[1] The Principles of Glass-Making, by Harry J. Powell, B.A., Henry Chance, M.A., and H.G. Harris, George Bell and Sons Publisher, York Street, London, 1883. Technical study book for examination to qualify glass makers.

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Rank	SILO 1			SILO 2			SILO 3		
	Component	Measured	Normalized	Component	Measured	Normalized	Component	Measured	Normalized
1	SiO_2	50.00	58.06	SiO_2	51.00	60.23	SO_3	15.00	17.26
2	PbO	12.00	13.93	PbO	6.20	7.32	SiO_2	14.00	16.11
3	BaO	6.30	7.32	Fe_2O_3	6.10	7.20	MgO	10.00	11.51
4	CO_2	3.20	3.72	Al_2O_3	3.40	4.02	P_2O_5	9.30	10.70
5	Al_2O_3	2.60	3.02	CO_2	3.40	4.02	Fe_2O_3	8.00	9.21
6	Fe_2O_3	2.50	2.90	BaO	3.00	3.54	N_2O_5	6.10	7.02
7	Na_2O	1.80	2.09	CaO	2.50	2.95	Na_2O	5.90	6.79
8	SO_3	1.80	2.09	MgO	1.70	2.01	Al_2O_3	5.30	6.10
9	MgO	1.20	1.39	SO_3	1.70	2.01	CaO	4.70	5.41
10	K_2O	0.68	0.79	Na_2O	0.88	1.04	CO_2	1.90	2.19
11	P_2O_5	0.62	0.72	K_2O	0.68	0.80	K_2O	1.80	2.07
12	MnO_2	0.43	0.50	P_2O_5	0.68	0.80	MnO_2	0.67	0.77
13	La_2O_3	0.42	0.49	N_2O_5	0.62	0.73	NiO	0.52	0.60
14	NiO	0.42	0.49	UO_2	0.47	0.56	V_2O_3	0.50	0.58
15	Ce_2O_3	0.41	0.48	NiO	0.36	0.43	Li_2O	0.47	0.54
16	CaO	0.37	0.43	Ce_2O_3	0.33	0.39	CuO	0.41	0.47
17	N_2O_5	0.29	0.34	TiO_2	0.33	0.39	CoO	0.36	0.41
18	TiO_2	0.28	0.33	La_2O_3	0.29	0.34	UO_2	0.34	0.39
19	CoO	0.19	0.22	CoO	0.21	0.25	ThO_2	0.31	0.36
20	Nd_2O_3	0.19	0.22	Nd_2O_3	0.16	0.19	As_2O_3	0.29	0.33
21	SrO	0.08	0.10	ZrO_2	0.14	0.17	TiO_2	0.22	0.25
22	Cl	0.08	0.09	CuO	0.08	0.10	PbO	0.19	0.22
23	V_2O_3	0.06	0.07	Cr_2O_3	0.08	0.10	MoO_2	0.18	0.21
24	CuO	0.06	0.07	V_2O_3	0.08	0.10	Cr_2O_3	0.08	0.10
25	ZrO_2	0.05	0.06	MoO_2	0.08	0.09	F	0.07	0.08
26	SeO_2	0.05	0.05	SrO	0.06	0.07	ZnO	0.07	0.08
27	Cr_2O_3	0.02	0.02	As_2O_3	0.05	0.06	Y_2O_3	0.04	0.04
28	MnO_2	0.01	0.02	SeO_2	0.04	0.05	BaO	0.03	0.04
29	BeO	0.01	0.01	MnO_2	0.03	0.04	SeO_2	0.03	0.03
30	F	0.00	0.01	ZnO	0.01	0.01	SrO	0.03	0.03
31	As_2O_3			Cl	0.00	0.01	Ce_2O_3	0.02	0.02
32	CdO			F	0.00	0.01	ZrO_2	0.02	0.02
33	Li_2O			BeO			Cl	0.02	0.02
34	ThO_2			CdO			Nd_2O_3	0.01	0.01
35	UO_2			Li_2O			La_2O_3	0.01	0.01
36	Y_2O_3			ThO_2			BeO	0.01	0.01
37	ZnO			Y_2O_3			CdO	0.00	0.01
	Totals	86.12	100.00		84.68	100.00		86.89	100.00

Silo Compositions According To PNL Analysis

Oxide Ranges In Silos -- Normalized

Rod F. Gimpel 12/04/96

Component	Silo 1 Average	Silo 1 Delta +/-		Silo 1 Delta % Comp.		Silo 2 Average	Silo 2 Delta +/-		Silo 2 Delta % Comp.		Silo 3 Average	Silo 3 Delta +/-		Silo 3 Delta % Comp.	
Al2O3	3.02	0.12	0.00	3.85	0.00	4.02	0.35	-0.24	8.82	-5.88	6.10	1.27	-1.04	20.75	-16.98
As2O3						0.06	0.04	-0.02	60.00	-40.00	0.33	0.13	-0.13	37.93	-37.93
B2O3															
BaO	7.32	0.58	-0.35	7.94	-4.76	3.54	0.94	-1.77	26.67	-50.00	0.03	0.01	-0.00	23.33	-6.67
BeO											Trace				
CO2	3.72	1.63	-2.09	43.75	-56.25	4.02	0.12	-0.12	2.94	-2.94	2.19	0.00	0.00	0.00	0.00
CaO	0.43	0.29	-0.17	67.57	-40.54	2.95	0.71	-0.35	24.00	-12.00	5.41	0.58	-0.69	10.64	-12.77
CdO											Trace				
Ce2O3	0.48	0.27	-0.16	56.10	-34.15	0.39	0.08	-0.05	21.21	-12.12	0.02	0.02	-0.02	75.00	-100.00
CoO	0.22	0.03	-0.02	15.79	-10.53	0.25	0.05	-0.04	19.05	-14.29	0.41	0.03	-0.05	8.33	-11.11
Cr2O3	0.02	0.01	-0.01	45.00	-25.00	0.09	0.05	-0.05	50.00	-50.00	0.09	0.01	-0.01	11.25	-6.25
CuO	0.07	0.00	-0.01	5.00	-13.33	0.09	0.02	-0.01	25.00	-12.50	0.47	0.06	-0.08	12.20	-17.07
Fe2O3	2.90	0.23	-0.23	8.00	-8.00	7.20	2.72	-3.19	37.70	-44.26	9.21	0.69	-0.58	7.50	-6.25
K2O	0.79	0.05	-0.09	5.88	-11.76	0.80	0.05	-0.09	5.88	-11.76	2.07	0.58	-0.69	27.78	-33.33
La2O3	0.49	0.27	-0.15	54.76	-30.95	0.34	0.08	-0.07	24.14	-20.69	0.01	0.00	-0.00	10.00	-18.00
Li2O											0.54	0.05	-0.02	8.51	-4.26
MgO	1.39	0.00	-0.12	0.00	-8.33	2.01	0.71	-0.71	35.29	-35.29	11.51	1.15	-0.46	10.00	-4.00
MnO2	0.01	0.01	0.00	60.00	0.00	0.04	0.00	-0.00	12.50	-6.25	0.77	0.06	-0.06	7.46	-7.46
MoO2	0.50	0.30	-0.19	60.47	-37.21	0.09	0.05	-0.05	50.00	-50.00	0.21	0.06	-0.07	27.78	-33.33
N2O5	0.34	0.15	-0.09	44.83	-27.59	0.73	0.05	-0.06	6.45	-8.06	7.02	0.23	-0.12	3.28	-1.64
Na2O	2.09	0.46	-0.93	22.22	-44.44	1.04	0.14	-0.32	13.64	-30.68	6.79	0.35	-0.23	5.08	-3.39
Nd2O3	0.22	0.13	-0.07	57.89	-31.58	0.19	0.04	-0.04	18.75	-18.75	0.01	0.01	-0.01	70.00	-100.00
NiO	0.49	0.10	-0.15	21.43	-30.95	0.43	0.12	-0.06	27.78	-13.89	0.60	0.08	-0.10	13.46	-17.31
P2O5	0.72	0.36	-0.19	50.00	-25.81	0.80	0.06	-0.08	7.35	-10.29	10.70	0.81	-1.04	7.53	-9.68
PbO	13.94	1.16	-2.32	8.33	-16.67	7.32	1.18	-1.54	16.13	-20.97	0.22	0.03	-0.03	15.79	-15.79
SO3	2.09	0.12	-0.12	5.56	-5.56	2.01	1.30	-0.98	64.71	-48.82	17.26	0.00	0.00	0.00	0.00
SeO2	0.05	0.01	-0.01	19.15	-25.53	0.05	0.00	0.00	0.00	0.00	0.03	0.00	-0.00	0.00	-6.67
SiO2	58.07	2.32	-2.32	4.00	-4.00	60.24	7.09	-5.91	11.76	-9.80	16.11	2.30	-1.15	14.29	-7.14
SrO	0.10	0.01	-0.01	8.54	-8.54	0.07	0.02	-0.04	33.33	-50.00	0.03	0.00	-0.01	0.00	-20.00
ThO2											0.36	0.03	-0.09	9.68	-25.81
TiO2	0.33	0.08	-0.05	25.00	-14.29	0.39	0.04	-0.04	9.09	-9.09	0.25	0.03	-0.01	13.64	-4.55
UO2						0.56	0.05	-0.02	8.51	-4.26	0.39	0.13	-0.13	32.35	-32.35
V2O3	0.07	0.00	-0.00	4.92	-6.56	0.09	0.01	-0.00	10.00	-3.75	0.58	0.17	-0.17	30.00	-30.00
Y2O3	0.00										0.05	0.00	-0.00	10.00	-10.00
ZnO						0.01	0.01	0.00	70.00	0.00	0.08	0.01	-0.02	17.14	-21.43
ZrO2	0.06	0.01	-0.02	15.69	-29.41	0.17	0.05	-0.02	28.57	-14.29	0.02	0.00	-0.01	0.00	-30.00
	0.00	0.00	0.00												
Cl	0.09	0.02	-0.02	26.58	-24.05	0.01	-0.01	-0.01	-100.00	-100.00	0.02	0.00	-0.01	5.00	-35.00
F											0.09	0.02	-0.03	25.00	-37.50
Total	100.00	8.73	-9.89			100.00	16.10	-15.86			100.00	8.89	-7.05		
Gases	6.14	1.89	-2.30			6.76	1.46	-1.16			26.47	0.23	-0.12		

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Rank	BENTONITE		
	Component	Measured	Normalized
1	SiO_2	65.40	67.35
2	Al_2O_3	15.80	16.27
3	MgO	6.30	6.49
4	Fe_2O_3	3.60	3.71
5	Na_2O	3.40	3.50
6	CaO	1.80	1.85
7	K_2O	0.80	0.82
	Total	97.10	100.00

AVERAGE BENTONITE COMPOSITION (wt%)

Formula Description: **Series A Glass With PNL Data For Silo 1** Rod F Gimpel V2 5 03/07/98

Component	mol wt.	Silo 1	Silo 1n	Silo 2	Silo 2n	Silo 3	Silo 3n	Bento-grout	Bento-grout n	Portions norm.	Portions in glass	Additives as oxides	Glass Result	Target Glass	Delta	Additives mol%	Glass mol%
Al2O3	101.96	2.60	3.02	3.40	4.02	5.30	6.10	13.60	13.74	3.02	2.17	3.75	5.92	5.92	0.00	2.61	4.13
As2O3	197.84			0.05	0.06	0.29	0.33										
B2O3	69.62											13.00	13.00	12.94	0.06	13.27	13.27
BaO	153.34	6.30	7.32	3.00	3.54	0.03	0.04			7.32	5.26		5.26	4.51	0.75		2.44
BeO	25.01	0.01	0.01			0.01	0.01			0.01	0.01		0.01		0.01		0.01
CO2	44.01	3.20	3.72	3.40	4.02	1.90	2.19			3.72	2.67		2.67	released	-		4.32
CaO	56.08	0.37	0.43	2.50	2.95	4.70	5.41	1.53	1.55	0.43	0.31	4.75	5.06	5.12	-0.06	6.02	6.41
CdO	128.40					0.00	0.01										
Ce2O3	328.24	0.41	0.48	0.33	0.39	0.02	0.02			0.48	0.34		0.34		0.34		0.07
CoO	74.93	0.19	0.22	0.21	0.25	0.36	0.41			0.22	0.16		0.16		0.16		0.15
Cr2O3	151.99	0.02	0.02	0.08	0.10	0.08	0.10			0.02	0.02		0.02		0.02		0.01
CuO	79.54	0.06	0.07	0.08	0.10	0.41	0.47			0.07	0.05		0.05		0.05		0.04
Fe2O3	159.69	2.50	2.90	6.10	7.20	8.00	9.21	3.07	3.10	2.90	2.09		2.09	4.01	-1.92		0.93
K2O	94.20	0.68	0.79	0.68	0.80	1.80	2.07	0.66	0.67	0.79	0.57		0.57	0.61	-0.04		0.43
La2O3	325.82	0.42	0.49	0.29	0.34	0.01	0.01			0.49	0.35		0.35		0.35		0.08
Li2O	29.88					0.47	0.54					1.50	1.50	1.52	-0.02	3.57	3.57
MgO	40.31	1.20	1.39	1.70	2.01	10.00	11.51	5.40	5.46	1.39	1.00		1.00	1.32	-0.32		1.77
MnO2	86.94	0.01	0.02	0.03	0.04	0.67	0.77	0.05	0.05	0.02	0.01		0.01		0.01		0.01
MoO2	127.94	0.43	0.50	0.08	0.09	0.18	0.21			0.50	0.36		0.36		0.36		0.20
N2O5	108.01	0.29	0.34	0.62	0.73	6.10	7.02			0.34	0.24		0.24	released	-		0.16
Na2O	61.98	1.80	2.09	0.86	1.04	5.90	6.79	2.82	2.85	2.09	1.50	4.25	5.75	5.70	0.05	4.87	6.60
Nd2O3	336.48	0.19	0.22	0.16	0.19	0.01	0.01			0.22	0.16		0.16		0.16		0.03
NiO	74.71	0.42	0.49	0.36	0.43	0.52	0.60			0.49	0.35		0.35	0.38	-0.03		0.33
P2O5	141.94	0.62	0.72	0.68	0.80	9.30	10.70	1.22	1.23	0.72	0.52		0.52	0.63	-0.11		0.26
PbO	223.19	12.00	13.93	6.20	7.32	0.19	0.22			13.93	10.02		10.02	8.66	1.36		3.19
SO3	80.06	1.80	2.09	1.70	2.01	15.00	17.26			2.09	1.50		1.50	released	-		1.33
SeO2	110.96	0.05	0.05	0.04	0.05	0.03	0.03			0.05	0.04		0.04		0.04		0.03
SiO2	60.08	50.00	58.06	51.00	60.23	14.00	16.11	56.20	56.80	58.06	41.75	5.25	47.00	47.05	-0.05	6.21	55.60
SrO	103.62	0.08	0.10	0.08	0.07	0.03	0.03			0.10	0.07		0.07		0.07		0.05
ThO2	264.04					0.31	0.36										
TiO2	79.90	0.28	0.33	0.33	0.39	0.22	0.25	0.22	0.22	0.33	0.23		0.23		0.23		0.21
UO2	270.03			0.47	0.56	0.34	0.39										
V2O3	149.88	0.06	0.07	0.08	0.10	0.50	0.58			0.07	0.05		0.05		0.05		0.02
Y2O3	225.81					0.04	0.04										
ZnO	81.37			0.01	0.01	0.07	0.08										
ZrO2	123.22	0.05	0.06	0.14	0.17	0.02	0.02			0.06	0.04		0.04		0.04		0.02
Cl	35.45	0.08	0.09	0.00	0.01	0.02	0.02			0.09	0.07		0.07		0.07		0.13
F	19.00	0.00	0.01	0.00	0.01	0.06	0.09			0.01	0.00		0.00		0.00		0.01
Ignition loss								14.06	14.23					released	-		
SO3 in glass	80.06												0.00	0.00			0.00
Other A	1.00																
Other B	1.00																
Total	n/a	86.12	100.00	84.66	100.00	86.90	100.00	96.95	100.00	93.86	67.50	32.50	100.00	98.37	1.63	36.56	100.00
Gases		5.29	6.14	5.72	6.75	23.00	26.47	14.06	14.23	6.14	4.42		4.42				5.61

Ratios (dry wt.)	Silo 1	Silo 2	Silo 3	Bentonite	All Wastes	Additives	Total In	Glass	Gases	Total Out
Mass balance	71.92				71.92	32.50	104.42	100.00	4.42	104.42
Silo mix Ratio	100.00				100.00	–	–	–	–	–

Waste loading = 100% - % Additives = 67.5%

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Formula Description: **Series A Glass With RI/FS Data For Silo 1**

Rod F Gimpel V2 5 03/07/96

Component	mol wt.	Silo 1	Silo 1n	Silo 2	Silo 2n	Silo 3	Silo 3n	Bento-grout	Bento-grout n	Portions norm.	Portions in glass	Additives as oxides	Glass Result	Target Glass	Delta	Additives mol%	Glass mol%
Al2O3	101.96	0.20	0.85	3.40	4.02	5.30	6.10	13.60	13.74	0.85	0.31	5.50	5.81	5.92	-0.11	3.87	4.09
As2O3	197.84			0.05	0.06	0.29	0.33										
B2O3	69.62	0.01	0.04							0.04	0.02	13.00	13.02	12.94	0.08	13.41	13.43
BaO	153.34	1.30	5.54	3.00	3.54	0.03	0.04			5.54	2.02		2.02	4.51	-2.49		0.85
BeO	25.01					0.01	0.01										
CO2	44.01	7.04	30.00	3.40	4.02	1.90	2.19			30.00	10.98		10.96	released	-		17.89
CaO	56.08	0.41	1.75	2.50	2.95	4.70	5.41	1.53	1.55	1.75	0.64	4.25	4.89	5.12	-0.23	5.44	6.26
CdO	128.40					0.00	0.01										
Ce2O3	328.24			0.33	0.39	0.02	0.02										
CoO	74.93	0.12	0.51	0.21	0.25	0.36	0.41			0.51	0.19		0.19		0.19		0.18
Cr2O3	151.99	0.01	0.04	0.08	0.10	0.08	0.10			0.04	0.02		0.02		0.02		0.01
CuO	79.54	0.04	0.17	0.08	0.10	0.41	0.47			0.17	0.06		0.06		0.06		0.06
Fe2O3	159.69	2.10	8.95	6.10	7.20	8.00	9.21	3.07	3.10	8.95	3.27		3.27	4.01	-0.74		1.47
K2O	94.20	0.05	0.21	0.68	0.80	1.80	2.07	0.66	0.67	0.21	0.08		0.08	0.61	-0.53		0.08
La2O3	325.82			0.29	0.34	0.01	0.01										
Li2O	29.88					0.47	0.54					1.50	1.50	1.52	-0.02	3.61	3.61
MgO	40.31	0.48	2.05	1.70	2.01	10.00	11.51	5.40	5.46	2.05	0.75		0.75	1.32	-0.57		1.33
MnO2	86.94	0.01	0.04	0.03	0.04	0.67	0.77	0.05	0.05	0.04	0.02		0.02		0.02		0.01
MoO2	127.94	0.65	2.77	0.08	0.09	0.18	0.21			2.77	1.01		1.01		1.01		0.57
N2O5	108.01	0.26	1.11	0.62	0.73	6.10	7.02			1.11	0.40		0.40	released	-		0.27
Na2O	61.98	1.17	4.99	0.88	1.04	5.90	6.79	2.92	2.95	4.99	1.82	3.75	5.57	5.70	-0.13	4.35	6.48
Nd2O3	336.48			0.16	0.19	0.01	0.01										
NiO	74.71	0.23	0.98	0.36	0.43	0.52	0.60			0.98	0.36		0.36	0.38	-0.02		0.34
P2O5	141.94	0.26	1.11	0.68	0.80	9.30	10.70	1.22	1.23	1.11	0.40		0.40	0.63	-0.23		0.20
PbO	223.19	8.80	37.49	6.20	7.32	0.19	0.22			37.49	13.70		13.70	8.66	5.04		4.41
SO3	80.06	0.11	0.47	1.70	2.01	15.00	17.26			0.47	0.17	-	0.17	released	-		0.15
SeO2	110.96	0.04	0.17	0.04	0.05	0.03	0.03			0.17	0.06		0.06		0.06		0.04
SiO2	60.08	0.15	0.64	51.00	60.23	14.00	16.11	56.20	56.80	0.64	0.23	47.00	47.23	47.05	0.18	56.19	56.47
SrO	103.62			0.06	0.07	0.03	0.03										
ThO2	264.04					0.31	0.36										
TiO2	79.90			0.33	0.39	0.22	0.25	0.22	0.22								
UO2	270.03			0.47	0.56	0.34	0.39										
V2O3	149.88	0.02	0.09	0.08	0.10	0.50	0.58			0.09	0.03		0.03		0.03		0.01
Y2O3	225.81					0.04	0.04										
ZnO	81.37			0.01	0.01	0.07	0.08										
ZrO2	123.22			0.14	0.17	0.02	0.02										
Cl	35.45	0.01	0.04	0.00	0.01	0.02	0.02			0.04	0.02		0.02		0.02		0.03
F	19.00			0.00	0.01	0.08	0.09										
Ignition loss								14.08	14.23					released	-		
SO3 in glass	80.06												0.00	0.00			0.00
Other A	1.00																
Other B	1.00																
Total	n/a	23.47	100.00	64.68	100.00	86.90	100.00	98.95	100.00	68.43	25.00	75.00	100.00	98.37	1.63	86.88	100.00
Gases		7.41	31.57	5.72	6.75	23.00	26.47	14.08	14.23	31.57	11.53		11.53				18.31

Ratios (dry wt.)	Silo 1	Silo 2	Silo 3	Bentonite	All Wastes	Additives	Total In	Glass	Gases	Total Out
Mass balance:	36.53				36.53	75.00	111.53	100.00	11.53	111.53
Silo mix Ratio	100.00				100.00	--	--	--	--	--

Waste loading = 100% - % Additives = 25%

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Final PNL Crucible Melts

1. Sequence A Melt, AFR-1. Produced a good glass but melted at a temperature of 1450°C. The alumina was 3.6 times (3.2% to 11.5%) the surrogate concentration which were based on the PNL characterization data.

2. Sequence A Melt, AFR-2. The melt separated with the formation of large crystals. The TCLP for lead was 4.4, which is close to the EPA limit of 5. Melting point above 1450°C. The alumina was 5 times (3.2% to 16.2%) the surrogate concentration. Silica and sodium were somewhat lower (54.7% to 47.4% and 6.3% to 4.0% respectively).

3. Sequence B Melt. Produced good glass. Melt temperature not reported but probably around 1450°C (or higher). The alumina was 2.3 times (8.0% to 18.5%) the surrogate concentration. Sodium oxide (a flux) was significantly lower from 8.2% to 4.8%.

4. Sequence C Melt. Produced a good glass, except it had a brownish opacity (compared to the homogeneous black glass of the surrogate). The temperature of the melt was not reported, but assumed to be 1350°C. Constituents in the glass matched closely to the surrogate, however, the silica and sodium oxide content were a little lower (33.9% to 30.7% and 5.2% to 4.0%).

5. Sequence D Melt. Produced a good glass, except it had a brownish opacity (compared to the homogeneous black glass of the surrogate). The temperature of the melt was not reported, but assumed to be 1400°C. Constituents in the glass closely matched the surrogate.

6. Sequence E Melt. Scum layer formed on the melt surface. The melt was heated for four hours at 1450°C, then 2 hours at 1500°C. The concentrations closely matched the surrogate, with the exception of alumina and calcium oxide. Alumina concentration was 1.5 times the surrogate and the was 0.72 times the surrogate (6.3% to 9.4% and 15.3% to 11.1% respectively). (Because of this melt and other data the use of soils as an additive were dropped from the development program.)

7. Sequence F Melt. Scum layer formed on the melt surface. The melt was heated for four hours at 1450°C, then 2 hours at 1500°C. The concentrations closely matched the surrogate, with the exception of alumina and calcium oxide. Alumina concentration was 1.4 times the surrogate and the was 0.69 times the surrogate (8.5% to 11.45% and 15.1% to 10.5% respectively).

Series - Run	A		C_1		C_2	
Melt Number	C4A-03		C4C-03		C4C-08	
Comp. (Wt%)	Calc.	Analy.	Calc.	Analy.	Calc.	Analy.
Al_2O_3	5.89	6.08	12.35	11.98	14.43	13.75
B_2O_3	12.89	11.84	12.23	11.77	6.00	5.79
BaO	4.47	4.11	0.03	0.04	0.03	0.04
CaO	5.08	5.49	9.43	9.08	8.61	8.09
Fe_2O_3	3.98	3.60	5.72	5.47	7.70	7.02
K_2O	0.61	0.55	1.35	1.38	1.74	1.63
La_2O_3	0.34	0.02	-	-	-	-
Li_2O	1.52	1.44	2.13	1.97	1.88	1.82
MgO	1.32	1.20	7.18	6.74	9.63	9.07
MnO_2	-	-	0.48	0.53	0.64	0.64
Na_2O	5.68	4.66	7.86	6.91	5.27	4.88
NiO	0.38	0.33	0.37	0.35	0.50	0.43
P_2O_5	0.63	0.65	6.73	6.67	8.95	6.41
PbO	8.63	7.87	0.20	0.24	0.20	0.25
SO_3	1.62	1.44	0.00	na	0.00	na
SiO_2	46.90	40.70	33.56	33.68	33.93	33.33
V2O5	-	-	0.36	na	0.48	na
ZrO_2	0.09	0.11	-	na	na	na
Total	100.00	90.81	100.00	96.81	100.00	93.36
Appearance upon cooling	Dark brown glass		Opaque on top black on bottom		Dark brown	
Liquidus	<1100°C		<1000°C		about 1050°C	
Density, g/cm³	2.76		2.49		2.7	
Temp., °C						
1100						
1150	234.0	0.06-0.08	40.07	0.11	53.47	0.055
1200	123.1		25.21	0.15	34.96	0.084
1250	76.2	0.07-0.09	16.96	0.21	23.51	0.125
1300	52.6		12.03	0.28	16.21	0.180
1350	39.1		8.91	0.38	11.44	0.255
1400						
TCLP, ppm						
Pb	2.6		0.05		0.07	
Ba	2.06		0.24		0.88	
Ni	0.10		0.47		0.71	
Waste Loading:						
g dry waste/g glass	79.08 %		68.00 %		81.60 %	
as oxides in glass (100% - additives)	74.00% (74.50% w/SO_3)		50.00% (~52% w/SO_3)		60.00% (~62.00% w/SO_3)	

Series, Run	D_1		D_2		D_3	
Glass Number	C4D-04		C4D-15		C4D-01	
Comp. (Wt%)	Calc.	Anal.	Calc.	Anal.	Calc.	Anal.
Al_2O_3	9.63	9.34	15.13	12.69	13.98	13.37
B_2O_3	14.96	13.98	10.06	7.87	10.04	9.60
BaO	2.46	2.11	2.45	2.30	2.66	2.32
CaO	6.97	6.78	7.70	6.91	13.88	13.18
Fe_2O_3	5.33	5.01	5.58	5.01	4.33	4.15
K_2O	1.13	1.04	1.10	1.06	0.79	0.67
La_2O_3	-	-	-	-	-	-
Li_2O	0.2	0.25	0.18	0.24	1.08	1.22
MgO	4.51	3.64	5.03	4.28	2.76	2.41
MnO	-	-	-	-	-	-
Na_2O	6.66	5.93	7.01	5.92	7.09	6.12
NiO	0.41	0.40	0.40	0.36	0.10	0.10
P_2O_5	3.48	3.20	3.87	3.42	2.46	2.33
PbO	5.53	5.02	4.85	4.61	5.22	5.41
SO_3	2.05	na	-	-	1.97	1.56
SiO_2	36.58	34.38	36.56	33.59	33.66	34.27
V2O5	-	-	-	-	-	-
ZrO_2	0.10	0.11	0.06	0.07	0.00	0.00
Total	100.00	91.33	100.00	88.33	100.00	96.71
Appearance upon cooling	bottom black; top opaque blue/green		black glass		dark brown homogeneous	
Liquidus	<1100°C		<1050°C		<1050°C	
Density, g/cm³	2.71		na		2.79	
Temp., °C						
1100	205.15	0.017	314.1*	0.02	87.45	0.046
1150	114.92	0.026	161.3	0.032	53.16	0.067
1200	69.73	0.038	92.6	0.051	34.52	0.095
1250	45.13	0.055	57.9	0.078	23.64	0.133
1300	30.79	0.077	38.8	0.116	16.92	0.181
1350	21.94	0.106	27.4	0.169	12.57*	0.243
1400			*extrapolated		*extrapolated	
TCLP, ppm						
Pb	2.43		1.4		3.15	
Ba	1.56		1.2		1.88	
Ni	0.32		0.12		0.10	
Waste Loading:						
g dry waste/g glass	79.82%		78.68%		71.84%	
as oxides in glass (100% - additives)	70.00% (70.50% w/SO_3)		69.00% (69.5% w/SO_3)		63.00% (63.5% w/SO_3)	

Series - Run	Ax	
Melt Number	S12-04 (C4A-03 mod.)	
Comp. (Wt%)	Calc.	Analy.
Al_2O_3	6.15	na
B_2O_3	10.51	na
BaO	4.09	na
CaO	13.31	na
Fe_2O_3	3.60	na
K_2O	0.58	na
La_2O_3	-	na
Li_2O	1.28	na
MgO	1.23	na
MnO_2	-	-
Na_2O	7.33	na
NiO	0.56	na
P_2O_5	0.56	na
PbO	7.98	na
SO_3	-	na
SiO_2	43.38	na
V2O5	-	-
ZrO_2	-	na
Total	100.00	na
Appearance upon cooling	brown clear transparent glass	
Liquidus	<na°C	
Density, g/cm³	na	
Temp., °C		
1100	258	na
1150	140	na
1200	84	na
1250	53	na
1300	35	na
1350	23	na
1400	17	na
TCLP, ppm		
Pb		na
Ba		na
Ni		na
Waste Loading:		
g dry waste/g glass		71.60 %
as oxides in glass (100% - additives)		67.00 %

Robustness of Series D Glass AG-10/C4D-01

Rick Frost & Rod Gimpel R2 4/24/96

Changed Component	Original AG-10/C4D-01 g/100g glass	Silo 3 Portions g/100g glass	Changed Amount g/100g glass	Change in Silo 3 wt%	Density g/cc	Visual Viscosity 1 thru 10 *a	Viscosity at 1250^C	Good Glass at 1250^C	Melt No.	Appearance
Control - no change					2.87	3	57	yes	AG-10a-25	Transparent, dark-amber glass, no bubbles
Al2O3	14.21	1.18	-5.00	425	2.54	3	66	yes	AG-11-26	Same as control w/slight glaze -- disappears w/> time or temp.
	"	"	-10.00	849	2.78	3		yes	AG-19a-31	looks better than control -- melts good at 1150^C (AG-19b-57)
B2O3	10.24	0.00	-5.00	na	2.87	3	70	yes	AG-12-26	Same as control but a little less fluid.
	"	"	-10.24	na	2.82	7		yes	AG-20-31	Transluscent, dark-amber glass w/small air bubbles
BaO	2.69	0.01	nd	nd						
CaO	14.06	1.04	-5.00	479	2.79	3	34	yes	AG-13-26	Same as control w/small bubbles -- disappear w/> time or temp.
	"	"	-10.00	958	2.71	4			AG-21-32	Same as control w/small bubbles -- disappear w/> time or temp.
Fe2O3	4.28	1.78	nd	nd						
K2O	0.81	0.40	nd	nd						
Li2O	1.13	0.10	-1.13	1084	2.78	4		yes	AG-26-34	Same as control w/small bubbles -- disappear w/> time or temp.
MgO	3.27	2.22	nd	nd						
MnO2	0.15	0.14	nd	nd						
Na2O	7.08	1.31	-2.50	191	2.87	3	63	yes	AG-14-27	Same as control w/small bubbles -- disappear w/> time or temp.
	"	"	-5.00	382	2.83	5		yes	AG-22-32	Transparent, very dark-amber glass, w/small air bubbles
NiO	0.12	0.12	nd	nd						
P2O5	2.43	2.06	5.00	242		3		yes-b	AG-30-35	Bottom 1 mm same as contol; rest opaque greenish-gray (PO4)
PbO	5.25	0.04	nd	nd						
SiO2	34.14	3.11	5.00	161	2.78	3	47	yes	AG-16-28	Same as control w/small bubbles -- disappear w/> time or temp.
V2O5	0.12	0.11	1.00	893		4			AG-32-37	Same as control w/small bubbles -- disappear w/> time or temp.
	100.00	13.62								
Special Cases:										
-5% Al2O3 + =mole% SiO2					2.86	3		yes	AG-15-27	Same as control w/small bubbles -- disappear w/> time or temp.
-10% Al2O3 + =mole% SiO2					2.79	3		yes	AG-23-32	Same as control w/small bubbles -- disappear w/> time or temp.
-2.5% NaO2 + 3.75%CaO					2.80	3		yes	AG-24-33	Same as control w/small bubbles -- disappear w/> time or temp.
SO3 Saturated			Saturated	na	2.74	3	26	yes	AG-17-28	Same as control w/small bubbles -- disappear w/> time or temp.
-25% Additives					2.79	4		yes	AG-28-35	Same as control w/small bubbles -- disappear w/> time or temp.
+25% Additives					2.78	4		yes	AG-29-35	Best looking glass in series

*a Visual Viscosity was determined by looking at a glass while it was poured and giving it a number between 1 and 10.
1 appears to pour like water. 10 it is solid like and cannot be racked out of the crucible. The startup glass was given a 3 as a standard.

*b This glass appears that it would be a good glass in the melter, but upon cooling it degrades.

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Rod F. Gimpel 04/23/96

Sizing Melters Per Glass Formulations

Scenario	Silos 1 & 2 Separate tons	Silo 3 Separate tons	All Silos Blended tons	Total tons	Relative melter rate Silos 1 & 2	Relative melter rate Silo 3	Melter Rate tons/day	Silos 1 & 2 Separate tons	Silo 3 Separate tons	All Silos Blended tons	Total years
Dry wastes in	10,613	3,918	14,531	14,531							
Glass Out:											
1. C4A-03 & C4C-08 (see note)	13,421 73.65%	4,801 26.35%	--	18,222 100.00%	2.4	2.3	25	1.96 73.65%	0.70 26.35%	--	2.66 100.00%
2. C4A-03 mod. & C4C-08 (not demonstrated)	14,823 75.53%	4,801 24.47%	--	19,624 100.00%	2.6	2.3	27	2.02 75.53%	0.65 24.47%	--	2.68 100.00%
3. C4D-15	--	--	18,468 100.00%	18,468 100.00%	3.0	3.0	31	--	--	2.16 100.00%	2.16 100.00%
4. C4D-01	--	--	20,227 100.00%	20,227 100.00%	3.4	3.4	35	--	--	2.09 100.00%	2.09 100.00%

Note: The C4A-03 glass is probably too viscous for operation in pilot melter and product forming. Therefore, Scenario 2 is presented. This made a good looking glass in the FERMCO Laboratory.

Basis: All based on a melter of the same physical dimensions. The relative performance is the minimelter's performance for that glass on a tonnes/day basis. No relative melter rate is available for the C4A-03 mod, formula . Therefore, similar numbers as for C4A-03 are used. All based on 1250^C operation. 75% uptime on melter. The C4A-03 rate was 2.7 at an average 1265^C. Therefore, approx. rate = 2.7 + (1250 -1265) x 0.02 = 2.4. The C4D-01 glass was run at 2.9 t/day rate at 1235^C . Therefore, 2.9 + (1250-1235)*0.02 = 3.2. However, the maximum rate was not determined (e.g., was not cold cap limited at 2.9). Therefore, use 3.4.

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4.10 Modeling Sulfates In The Surrogates

4.10.1 General Sulfate Discussion

Originally, it was assumed that a "sulfate is a sulfate", and what goes into making a glass is of little importance since most chemical constituents thermally breakdown in the molten glass. Therefore, most (if not all) of the sulfate surrogates used by PNL, FERMCO, and VSL, was calcium sulfate which resulted in sulfate layers. FERMCO did use barium sulfate in Silo 1 and Silo 2 stimulants. In retrospect, a better sulfate to use may have been magnesium sulfate to simulate Silo 3 wastes and barium sulfate to simulate Silos 1 and 2. Table 19 gives the melting and decomposition characteristics of the most common constituents sulfates in the silos. This Table is relevant to the scenarios described in the following Subsections.

Sulfates Melting and Decomposition Characteristics

Table 19

4.10.2 Silo 3 Sulfate

Since the most common metal constituent in Silo 3 is magnesium. Magnesium sulfate thermally decomposes at 1124°C, whereas, calcium sulfate decompose above 1400°C and barium sulfate (which may be the main sulfate in Silo 1 and 2) decomposes at >1580°C. This anomaly was just recently noted at FERMCO, and may be used to explain the enigma discussed in the PNL report[1], and summarized in this exert below:

> *Initially, sulfate was thought to be an issue only with the Silo 3 material (with 15 wt% SO_3 in the waste material); however, during the treatability test it was found that the glass formulation for the Silo 3 material readily promoted the decomposition of sulfate in the Silo 3 waste without added reductant. A separate phase was not observed in the Silo 3 melts despite the very high initial sulfate concentration. On the other hand, melts with the K-65 material were found to form significant salt layer on the surface of the glass, even though the concentration in the waste was much lower (about 3 wt%).*

Therefore, it is possible that the sulfate studies may have been modeled incorrectly. For example, the heat above the molten glass in the melter, alone, may be enough to destroy most of the sulfates in Silo 3. This assumes the magnesium sulfate does not enter into chemical reactions with the chemicals, such as sodium, prior to destruction. Recent laboratory melts using magnesium sulfates surrogates indicates

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[1] Final Report of Vitrification Development for Fernald CRU-4 Silo Wastes, Battelle - Pacific Northwest Laboratory, April 1994, page 10.

Decomposition Temperatures of Sulfates

Compound	Melting Point, °C	Decomposition Temperature, °C	Behavior
$Al_2(SO_4)_3$	–	770	Low temperature decomposition.
$BaSO_4$	1580	>1580	Melts without decomposition.
$CaSO_4$	1450	Graduated	Some decomposition before melting, but slow.
$Fe_2(SO_4)_3$	–	480	Low temperature decomposition.
Li_2SO_4	860	~ 860	Decomposition is not far above melting temperature.
$MgSO_4$	–	<1124	Decomposes before melting.
Na_2SO_4	884	Graduated	Volatilization and decomposition both take place, however, both are slow at lower molten glass temperatures. Increases with temperature.
$PbSO_4$	1170	< 1170	Decomposes noticeably below the melting point.

Information from:

The Chemical Rubber Company (CRC) Handbook of Chemistry and Physics, 51th Edition, and

High Temperature Properties and Decomposition of Inorganic Salts, "Part 1. Sulfates," October 1, 1966, K. H. Stern and E. L. Weise, Institute for Basic Standards, National Bureau of Standards, Washington, D.C.

that this does not happen because the sulfate is rapidly destroyed at lower temperatures.

Early laboratory crucible melts (using surrogates and actual K-65 wastes) resulted in molten salt layers on the surface of the glass. This sulfate layer was presumed to be predominantly sodium sulfate (because of the sodium flux added to the mix) which has a lower melting point than the glass. Increased temperatures ($\geq 1350°C$) and/or elemental carbon added to the glass melt resulted in significant reductions of the sulfate layer. These techniques resulted in the sulfate being reduced to the metal oxide and SO_x gases which leave the glass melt. The elemental carbon is a strong reducing agent and did produce some metallic lead or lead sulfide nodules. Later, it was discovered that excess amounts of calcium added to the crucible melt appeared to increase the destruction of the sulfate (even at lower temperatures) without the need for carbon (unfortunately, this did not appear so apparent with melts done at FERMCO and VSL)

4.10.3 Silos 1 and 2 Sulfate

Sulfate was formulated in the surrogate Series A glass as calcium sulfate at VSL and PNL (Fernald used barium sulfate). Whereas, it may actually be barium sulfate in Silo 1 and 2 because barium was used as a "getter" to remove radium as radium sulfate in the uranium extraction process which the Silo residues came from. If this is so, the sulfate may actually be more stubborn to handle and destroy in Silos 1 and 2 than simulated in the minimelter runs. This could explain why the PNL studies showed that Series C and D melts did not form sulfate layers and the Series A and B melts did. Barium sulfate was used in the Fernald laboratory studies (and is scheduled to be used in the Pilot Melter Series A campaign). Crucible melts at Fernald frequently showed sulfate layers for Series A melts. And again none of the crucible melts at the VSL showed a sulfate layer. Further studies are presently being performed at the Fernald Laboratory to determine if the possibilities described in this paragraph are true. If they are determined to be true, the processing rates for the Series A glass will probably be slower than expected and a reductant (urea) may need to be used to regain lost processing rate.

4.10.4 Sulfate Summary

If the sulfate in Silo 3 is actually magnesium sulfate and the sulfate in Silos 1 and 2 actually barium sulfate, then actual production rates for (1) the Series C and Series D glasses may be produced at faster production rates than the minimelter runs predict and (2) the Series A glass may run at a slower production rate than the minimelter runs predict. The author thinks the later is more true than the former because the Series C and D glasses are already performing at higher optimal rates. However, the poisoning effect of the barium sulfate could hamper the production rate of the Series A and B glasses.