LEACH-RESISTANT GLASSES FROM THE FERNALD SURROGATES WITH REDOX CONTROL FOR PRACTICAL MANUFACTURING

Douglas H. Davis and David M. Bennert, COGEMA Inc./ Toledo Engineering Co., Inc., Toledo, Ohio;
Gary Stegen, COGEMA Engineering Corp., Richland, Washington; Elisabeth Nicaise, SGN, France.

ABSTRACT

Under contract to Fluor Daniel Fernald (FDF), treatment of Silos 1 and 2 surrogates by Joule-heated vitrification was successfully demonstrated. Development of glass formulas from these high lead, high-sulfate wastes presented processing challenges due to the need for high resistance to leaching at high waste loading while controlling the formation of molten salts and precipitated metals.

Glasses were developed from surrogates representing Silo 1 (S1), Silo 2 (S2), and a combined demonstration surrogate (S0). Each surrogate required an independent glass meeting a.) 50% of the characteristically hazardous waste limits, (commonly called TCLP) and b.) UTS standards. Approaches included low levels of alkali, and high levels of alkaline earth and alumina. The glass developed for the Joule-heated demonstration was an alkali-lime-silica glass at 90 wt.% waste loading, meeting 50% of the characteristically hazardous waste limits. Key components of this glass were 9.5 wt.% alkali (16 mol%), 12 wt.% alkaline earth, 9 wt.% alumina, 9.5 wt.% PbO, and 4 wt.% BaO. UTS-compliant glasses were prepared at 50% waste loading, and yielded data indicating practicality of even higher waste loading. Of over 60 discrete glasses, 98% met current regulatory limits. The data demonstrates the robustness of vitrification to accept waste and process variation while producing a high-quality wasteform.

A batch redox safety zone developed allowed melting with neither separated salts nor precipitated metals. Changes between different alkalis and increased alkaline earth reduced the excess salts. Lower waste loading was effective in controlling salts and metals but was not considered economical. To eliminate the sulfate layer, reductants were added to the batch to decompose sulfates. For the final demonstration glass, only 0.1 wt.% C was required to prevent molten salt separation during crucible melting, and metals were precipitated only after 0.4 wt.% reductant addition, a good "safety zone" for crucible melting. The glass r
edox target for the commercial cold-top melter was $0.15 - 0.20$ wt.% Fe^{+2}/Fe^{total}. This glass in the cold-top melter achieved the target redox levels with only 25% of the reductant required in the crucible tests.

INTRODUCTION

A Proof-of-Principle Test demonstration of Joule-heated vitrification technology for hazardous and radioactive waste treatment was successfully performed for DOE contractor, Fluor Daniel Fernald (FDF) at the Clemson Environmental Technologies Laboratory (CETL). [a]

As part of this contract, suitable glass recipes had to be developed based on the FDF-specified surrogates for the Silos 1 and 2 wastes at the DOE site in Fernald, OH. Three surrogates were specified, S1 and S2 being simulations of Silos 1 and 2. A surrogate S0 was designed by FDF to be used for a 72-hour Proof of Principle Trial (POPT) melting demonstration. Critical differences between the surrogates for glass development are shown in Table I where the three surrogates are used in the same base glass. The high lead content makes durability an issue, in addition to metal precipitation. The predicted SO_3 content in all cases is more than will be

retained by the glass, with 0.5 wt.% common for soda-lime glasses. The probability of separated molten salts is a processing issue.

Table I
Critical Differences Between Surrogates Specified for Development

	S1 Surrogate	S2 Surrogate	S0 Surrogate
Glass	S1-U1-1	S2-U1-1	S0-U1-1
Wt.%Waste Loading	$\cong 90$	$\cong 90$	$\cong 90$
Wt.% PbO	9.25 **Basis**	5.09 **45% less PbO**	9.46 **2% more PbO**
Wt.% SO$_3$	3.83 **Basis**	2.53 **34% less SO$_3$**	2.70 **30% less SO$_3$**

CHALLENGES FOR RECIPE DEVELOPMENT

The wasteform specifications imposed by FDF did not represent a technical challenge to vitrification, with the exception of resistance to leaching. Several processing requirements were also stipulated by us as on Table II.

Table II
Requirements Placed Upon the Wasteform

By FDF Contract	
RCRA Characteristics	None
Liquids Present	None
Compressive Strength	Retracted as a Requirement
Dusting / Particulate	1% 1 micron, 15% 200 micron
Appearance	Uniform and Homogeneous
TCLP Leaching Results	1) Less than 50% RCRA Characteristic Limits 2) Less than UTS Limits
Self-Imposed	
Processing Temperature	1300 $^{\circ}$C
Viscosity	Log 2 viscosity less than 1350 $^{\circ}$C
Salt Generation	No secondary drainage
Metals Precipitation	None

Glass Resistance to Leaching

The over-riding challenge was to meet the standard for glass leaching resistance. The contract required development of glass recipes for each surrogate sufficiently resistant to leaching that the treated waste no longer exhibited RCRA hazardous waste characteristics. For a safety margin, leaching at less than 50% of current characteristically hazardous waste limits was required. Additional glass recipes were required for each surrogate that demonstrated leaching at less than the UTS limits, as future regulation could impose this more restrictive limit. With the high barium and lead levels of the surrogates, the challenge was to obtain leach resistance and still maintain high waste loadings. Since the POPT work was a cost competition against other treatments, such as cementation, the inherent volume reduction of vitrification needed to be maximized.

Problems in obtaining the required leach resistance were seen only in reaching the more restrictive UTS Pb leaching limits (0.75 ppm Pb versus 5-ppm current characteristic waste limits). TCLP leaching data shown in the following tables will only be for lead. The other components of a characteristically-hazardous waste leached at only a small fraction of their limit.

The same is true for the glasses in the UTS series. Glasses passing the current characteristically hazardous waste limit were readily achieved over a wide range of composition. Following the very first screening tests, all the remaining glasses (109 out of 112 total) passed current regulatory limits and would not be considered hazardous.

Redox-Related Salts and Metals Control

Molten Salt Layer

An additional challenge dealt with balancing two factors in processing, molten salt segregation and metals precipitation. Glasses made from these surrogates would normally produce a molten layer of salts on the melt surface, due to salt concentrations well beyond expected solubility in the glass. A layer of molten salts on the melt surface would aggravate refractory corrosion.

One option was to drain these salts from the surface using a proprietary drain design. This would create a secondary salt stream high in barium and lead, however, in addition to a sulfate-containing secondary stream already coming from the emissions control system. A second option was to increase the glass SO_3 solubility. This would, however, increase the reboil potential of the glass, making the melter operation more difficult. A third possible action was to decompose the waste sulfates by adding reductant to the batch. Adequate additions of reductant should eliminate the sulfate layer, sending the SO_2 up the stack to the emissions system.

Metals Precipitation

Over-reduction of these glasses, however, needs to be avoided. Reduction of the metal oxides to elemental metal or sulfides would be expected to lead to refractory drilling, contamination of molybdenum used in electrodes and drains, and possible short-circuiting of the Joule-heating circuits. Testing confirmed that molten lead had essentially no effect on molybdenum, but introduction of lead sulfide would give catastrophic damage to Mo.

The reducing capability of the mixed batch was the controlling factor on both the metals and the salts. As will be seen, the molten salts could be controlled and eliminated by greater reduction of the batch. Too much reduction, however, would lead directly to precipitation of metals out of the glass. The boundaries of the "safety zone" between salts and metals were the critical data necessary for moving to the demonstration melter.

PROCEDURES

Surrogate Preparation

A batch formulation for surrogates was supplied by Fluor Daniel Fernald as shown in Table III. Following chemistry validation, surrogates were prepared at 30 wt.% moisture to approximate silo conditions and tests were performed to ensure matching of the physical properties of the silo wastes. These included moisture content, pH, in-situ density, plastic limit and lead leaching. Discrepancies from the plastic limit targets led to increased fumed silica at the expense of coarse silica. Lower than expected lead leaching was corrected by a 24 wt.% reduction of magnesium phosphate. Surrogates were prepared in large quantities (5 kg) for weighing accuracy. The dry mixes were homogenized dry and wetted to a paste consistency to prevent dusting of hazardous ingredients, to lock in homogeneity, and to allow representative sampling for individual melts.

Glass Melting Procedures

The surrogate was mixed with glass additives, as required, and further wetted to maintain the paste-like consistency. This increased the bulk density of the powdery mixes, increasing glass

yield nearly 10-fold to over 250 grams, adequate for both TCLP leaching test sampling and analytical work. The large quantity of glass facilitated observations of effects, such as sulfate separation.

Table III
Batch Preparation Sheet for FDF SO Surrogate

Soluble Components	FDF-Supplied Component Value	Dry wt.%	LOD wt.%	Chem H$_2$O %	Target Wt- 3 kg
Na$_2$HAsO$_4$-7H$_2$O	0.17	0.17	38.43	40.385	7.82
Na$_2$CrO$_4$	0.27	0.27	0.69		7.45
Na$_2$SeO$_3$	0.1	0.10	0.06		2.74
NaNO$_3$	1.03	1.04	0.09		28.26
V$_2$O$_5$	0.09	0.09	0.11		2.47
Insoluble					
BaSO$_4$	8.18	8.25	0.05		224.31
Fe$_2$O$_3$	2.52	2.54	0.09		69.13
Mg$_3$(PO4)2-5H$_2$O	1.457	1.47	1.37	25.502	53.60
NiO	0.43	0.43	0.04		11.79
PbO	5.67	5.72	0.01		155.42
PbCO$_3$	6.6	6.66	0.32		181.48
PbSO$_4$	2.65	2.67	0.03		72.65
Coarse SiO$_2$	18.096	18.26	0.02		496.08
Fine SiO$_2$	18.9	19.07	0.06		518.33
Fumed SiO$_2$	10.944	11.04	2.12		306.45
ZnO	0.01	0.01	0.1		0.27
Tributyl Phosphate	0.92	0.93			25.22
Kerosene	0.92	0.93			25.22
Diatomaceous Earth	1.83	1.85	5.25		52.94
Feldspar	18.32	18.49	0.07		502.47
BentoGrout	8.618	8.70	7.7		255.91
Surrogate + Bento Grout	107.73	108.70			3000

Melts were made at 1300°C for 90 minutes using an electrically heated furnace. Fused silica crucibles allowed insertion of full crucibles at heat. Melts were removed and examined for molten salts after 60 minutes and re-inserted for the remainder of the melting period. Most of the glass melts were cast into graphite molds and cooled slowly over several hours to keep the 4-inch pucks intact. This allowed chemical removal of the residual salts without materially effecting results of the TCLP leaching test. To quantify the amount of salt in some experiments, melts were cooled in the crucible (ambient cooling), and then the crystallized salts were chipped off and weighed. Where reduced phases were expected (metals, sulfides), the glass was broken out of the crucibles in small pieces and examined for metallic beads. Techniques for crucible melting have been extensively discussed in literature. Our procedures were chosen to maximize collection of data and samples. We accept some discrepancy between the "intended" and the actual glass. Judgements must be made on the glasses actually produced.

For S1 and S2 melt work and UTS development, high-alumina crucibles were used to minimize crucible corrosion. These alumina crucibles could not be inserted directly at melting temperatures, and the alternative of heating up the crucibles and batch from room temperature was considered too slow. Instead, empty crucibles were preheated to 1200°C, transferred to the

Deltech furnace and brought to melting temperature. Mixed batch was then charged into the crucibles with the crucibles remaining in the furnace.

Sample Preparation for TCLP Leach Tests

An advantage of vitrification is that waste is <u>not encapsulated</u>, but <u>incorporated</u> into the glass. The TCLP leaching procedure is set up to deal fairly with encapsulated wastes, requiring the entire sample be crushed to less than 9.5 mm. The normal vitrification product, however, would be large cast blocks or cylinders and, even with no special cooling, the resultant pieces would be quite large. The crushing step of the TCLP procedure gives an exaggerated surface area per unit weight and a leaching value not representative of the final wasteform. All the following leaching data complies with the standard procedure (all fines submitted), but it should be borne in mind that actual vitrified waste would be subject to only a fraction of predicted leaching losses.

All of the following TCLP leaching data is reported as only the leached values of lead (Pb). A number of samples were tested for all of the RCRA characteristically hazardous material, and even more for both lead and barium. All of the characteristic components except lead were so low as to have no influence on the experimental work.

Use of Sugar as Batch Reductant

Sugar was used in both the crucible melts and the large-scale demonstration. Use of sugar solutions in the crucibles assisted in distributing the small reductant addition. In the large-scale demonstration trial, the use of sugar avoided the difficulty of keeping fine carbon distributed in the slurry. Based on melt observations and the final glass redox, both sugar and activated carbon showed similar efficacy at a ratio of 2.4 gm sugar to 1 gm carbon. Reductant use is expressed as the equivalent carbon and as a weight percentage of the glass being produced.

Determination of Sulfate Solubility

All glass compositions tested were evaluated for their effect on molten salts and metals. Data on the sulfate solubility is a series of "snapshots in time", consisting of observations on the presence of a residual salt layer, not actual sulfate solubility, as shown on Table IV. The empirical data used is the relative amount of salt present during and after melting, and the presence of any precipitated metals.

Table IV
Variation of Redox with Glass S0-1-10

Weight % Equiv. Carbon Reluctant	Salts Present?	Metal Present?	TCLP Leaching Ppm Pb	Glass Redox wt.%Fe^{+2}/ΣFe
0.0	Yes-Heavy Amount	None	2.0, 2.0	0.03
0.1	Yes-Heavy Amount	None		0.10
0.2	Yes-Moderate Amount	None	1.9	0.18
0.3	**Yes-Minor Amount**	**Yes**		**0.19**
0.4	None	Yes		0.20

EXPERIMENTAL RESULTS

Control of Molten Salts - Influence of Glass Composition

The discussion of glass composition is restricted slightly due to proprietary considerations. The specific mixture of alkaline oxides, plus the identity of oxide additives A and B, are held as proprietary.

The glass composition itself significantly influences the apparent solubility of SO_3. As shown on Table V, larger percentages of CaO at the same level of reductant gave significantly less molten salt collection on the surface. This could indicate a greater solubility, but SO_3 content was not being measured directly. The data only indicated that a salt layer was, or was not, present when observed. With changes in batch composition, both the solubility of SO_3 in the glass, and the chemistry and volatility of the molten salt on the glass surface would be changed. In the case of increased alkaline earth additions to the glass, the decrease in molten salt was almost certainly due to an actual increased solubility, since $CaSO_4$ is a reasonably stable liquid.

Table V
Effect of CaO on Molten Salts and Precipitated Metals

Weight % Equiv. Carbon Reluctant	Glass S0-D1-10 Alkali Ratio = 1, **4.2.wt.% CaO**			Glass S0-D3-1 Alkali Ratio = 1, **9 wt.% CaO**	
	Salts Present?	**Metals Present?**		**Salts Present?**	**Metals Present?**
0.00	**Yes – Heavy Amount (5.7 gm salts)**	**None**		**Yes – Minimum (4.6 gm salts)**	**None**
0.063					
0.10	**Yes – Heavy Amount**	**None**		**None***	**None**
0.125					
0.20	**Yes – Moderate Amount**	**None**		**None***	**None**
0.250					
0.30	**Yes – Minimum Amount**	**Yes**		**None****	**Yes**
0.40	**None***	**Yes**		**None ****	**Yes**

* -- Indicates that there were no salts present after melting, but some salts during the melting process.
** - Indicates no salts observed during melting, as well as after.

On the other hand, as shown on Table VI, an increase of the molar ratio of the two alkali additives (total alkali maintained at 16 mol %) also showed a significant decrease in the amount of observed salts. However, this increase in molar ratio alkali resulted in a less stable alkali sulfate. Therefore, in this case, the decreased salt presence would be largely due to a very rapid volatilization and liquid loss.

Table VI
Effect of Alkali Ratio on Molten Salts and Precipitated Metals
(Parallel entries valid comparisons for alkali ratio)

2 : 1 Alkali Ratio				**1 : 1 Alkali Ratio**		
Exp. #	Salts Present?	Metals Present?		Exp. #	Salts Present?	Metals Present?
0170	**Yes-minimum amount**	**None**		**0182**	**Yes-medium amount**	**None**
0180	**None ***	**None**		**0183**	**Yes- medium amount**	**None**
0171	**Yes-minimum amount**	**None**		**0184**	**Yes- medium amount**	**None**
0181	**None***	**None**		**0185**	**Yes- medium amount**	**None**

* -- Indicates there were no salts present after melting, but some salts during the melting process.

Analysis of the demonstration glass from a crucible melt showed 0.35 wt.% SO_3. This same batch formula fed to the continuous cold-top melter was analyzed numerous times at 1.2 wt. %. SO_3. The final sulfate solubility was achieved by the combination of the composition changes, the cold cap on the all-electric melter, and a 100-150°C lower melting temperature in the continuous tank. The high sulfate solubility in the continuous melter was a benefit, but it did yield a glass that needed to be processed carefully since reboil and foaming was always possible from temperature variation.

Sulfate solubility increased significantly through adjustment of the oxide composition and then through process differences in the continuous melter, including the cold cap and lower temperatures. The measured solubility increased from less than 0.5 wt.% SO_3 up to 1.2 wt.%, but this did not eliminate the salt layer. Therefore, use of a batch reductant was required.

Need For an Operational Safety Zone

Data from one of the early sets of melts demonstrated that a safe operating zone between the elimination of molten salts and the appearance of precipitated metals was not normally to be expected. On Table IV above, with increasing reductant addition to the batch, the molten salts present on the melt surface do, indeed, decrease and, eventually, disappear after reaching a 0.4 wt.% addition. However, metal droplets began to appear in the cast glass after only 0.3 wt.% reductant addition. With this glass, it would not be possible to eliminate a molten salt layer on the surface without accepting the probability of molten metal at the bottom of the melter.

Determination of a Leach Resistant Demonstration Glass – S0-TCLP-Compliant (50% of characteristic limits)

Initial Scoping Series
Based on literature review (1-7) and prior experience with the DOE Transportable Vitrification System (TVS) operations, the lithia-soda-lime-silica glass system was selected. The borosilicate system was reserved for later needs, hoping to avoid devitrification concerns.

Additives to the waste initially included lithia, soda, lime and alumina. Both soda and lithia were added to the surrogate waste, maintaining a set molar ratio. This gave the strong fluxing effect of the lithia and the durability improvement from the mixed alkali effect (5,6,7). $CaCO_3$ was used to maintain the total RO content (CaO+MgO+BaO+PbO) at 10-12 mol%. Alkali decreases were countered by alkaline earth increases to keep melt viscosity low. From an initial set of melts, only the lowest alkali glass (17 mol %) and the high- Al_2O_3 glass (10 wt.%) achieved both the desired viscosity and leaching resistance.
Additional melts were based on the 10 wt.% Al_2O_3 S0-D1-10 glass, the most leach resistant of the initial series. All were at 78 to 80 wt.% waste loading based on oxide derivation. [b] An additional glass additive (A) was chosen from a group of metal ions that combine with excess sulfur in the glass structure to form stable compounds under reducing conditions (3,5,8,9,10). While Additive A did not show an obvious benefit in suppressing salt formation, it did show some benefit in leach resistance. Another refractory additive (B) was used with the direct intention of increasing leach resistance.

Tests that included increased alkaline earth content, major additions of iron oxide, and incorporation of Additive B did not demonstrate significant improvements in leach resistance. Only an increase in the alkali molar ratio to 3:1 gave better leach resistance than the S0-D1-10 glass. The increase in alkali ratio also aided in the suppression of excess salts. Additional melts confirmed that the 2:1 alkali ratio also was beneficial in both areas, avoiding some potential devitrification problems and added cost from the 3:1 ratio.
Other melts showed that decreased waste loading in the glass rapidly improved resistance to leaching, at a rate greater than the decrease of waste loading. However, lower waste loading was avoided, if possible, due to its effect on increasing the total operating cost.

There was repeated confirmation that more highly reduced glasses are more resistant to leaching. Table VII shows a partial comparison of the effects of different levels of sugar added as reductants to the formulation series.

Table VII
Effect of Batch Redox on Leach Resistance

0.2 wt. % Equivalent. Carbon as sugar					0.3 wt. % Equivalent. Carbon as sugar			
Experiment.	Salts Present?	Metals Present?	TCLP ppm Pb		Experiment.	Salts Present?	Metals Present?	TCLP ppm Pb
0170	**Yes-minimum amount**	**None**	2.1		0180	**None***	**None**	1.8
0171	**Yes-medium amount**	**None**	1.9		0181	**None***	**None**	1.6
0184	**Yes-Medium Heavy amount**	**None**	2.0		0185	**Yes-medium amount**	**None**	1.3
0182	**Yes-medium amount**	**None**	2.1		0183	**Yes-medium amount**	**None**	1.9

* -- Indicates there were no salts present after melting, but some salts during melting.

The oxide composition of the glass chosen for the Demonstration Glass is shown in Table VIII. Additional glass data is shown in Table IX.

Table VIII
Composition of Glass S0-D5B-2 (Recommended Demonstration Glass)
(Waste Loading – 90 wt. % from Silica Source (FDF) – 83 wt.% from Oxide Source [b])

Oxide	Predicted (wt.%)	Measured (wt.%)
$Li_2O + Na_2O$	8.81*	6.69
K_2O	0.68	0.68
P_2O_5	0.82	0.86
SiO_2	52.55	58.2
Al_2O_3	9.00	9.32
CaO	6.51	6.58
MgO	0.94	0.72
BaO	4.16	4.21
PbO	9.48	9.56
Additive A	1.51	Not measured
Fe_2O_3	2.20	Not measured
SO_3	2.70*	0.35
Cr_2O_3	0.10	Not measured
NiO	0.34	0.34
SeO_2	0.05	Not measured
As_2O_3	0.08	Not measured
V_2O_5	0.07	Not measured
Total Alkali	9.50 wt.%, 15.21 mol %	
Total Alkaline Earth	22.6 wt.%, 15.43 mol%	

* - Does not compensate for volatility losses or losses due to reaction with sugar

Table IX
Demonstration Glass S0-D5B-2 Properties From CELS Analyses

Property	Value
0-300 Expansion	96.9 x 10^{-7}/°C
Density	2.836 gm/cc
Liquids temperature	1020°C
Devitrification Phase	Spinel
Annealing Point log n = 13	476°C
100 Poise Temp.	1327°C

Defining the Redox Safety Zone

The optimization of composition above did provide glasses with minimal molten salts present during melting. This provides part of the safety zone representing operational leeway between the amount of reductant required to eliminate the salt formation and that larger amount required to cause unwanted metals precipitation.

Table X shows the redox safety zone that exists for this particular glass within a range of batch reductant levels. At a reductant addition of 0.1 wt.% equivalent carbon, no separated salts were seen even during melting and no metals were seen in the resulting glass. The same was true for carbon additions of 0.2 and 0.3 wt.%. At a reductant addition of 0.4 wt.% carbon, there were still no molten salts, but deposits of lead metal were detected in the resulting glass. This shows the upper limit of reductant that should not be approached.

Table X
Effect of Reductant Level on Molten Salts and Precipitated Metals

Glass	Wt.% Waste Loading	Wt% Carbon Equivalent.	Redox value Wt.% Fe^{+2}/ Fe^{total}	Salts Present?	Metals Present?	Predicted Melter Operating Status
S0-D5B	83.9	0.1	0.135	None*	None	Good
S0-D5B	83.9	0.2	0.166	None**	None	Good
S0-D5B	83.9	0.3	0.188	None**	None	Good
S0-D5B	83.9	0.4	0.217	None**	Yes	Bad

*Salts not present at casting, but present during melting.
**- Salts not seen during melting.

This defines the redox safety range in crucible melts of this glass. However, the glass was developed for use in the continuous, all-electric cold-top melter. In a cold-top melter, reductants are much more effective due to atmosphere retention and protection against early "burn-out". This difference is significant since, for rapid data gathering, we used open crucibles with an ambient furnace atmosphere. Therefore, the specific reductant weight added to the crucible melts is not directly transferable to the cold-top, continuous melter operation.

What can be transferred to the cold top, continuous melter, however, is the glass redox level (wt.% Fe^{+2}/Fe^{total}) that a particular amount of reductant produced in the crucible melt. The amount of reductant to reach this level in the cold-top melter must be determined empirically, but is often only 20 to 25% of that required in an open, oxidized-atmosphere crucible. Therefore, the recommendation from this crucible-based development study was that the glass (SO-D5B) be

used in the demonstration melter with adequate reductant to give a measured redox value of <u>ABOVE 0.135</u>, but <u>BELOW 0.217</u>.

A sugar addition to the glass batch slurry of only 0.1 wt.% equivalent carbon was adequate to place the redox in the cold-top, continuous melter within the operating safety zone.

GLASSES COMPLIANT WITH CURRENT CHARACTERISTIC LIMITS FOR SI AND S2 SURROGATES

The S0 POPT demonstration glass was the baseline glass for the S1 and S2 glasses, modified to accommodate differences in the surrogate compositions. This initial adaptation of the S0 glass met the contract-specified leaching requirements of 50% of the characteristically hazardous waste limits as shown on Table XI.

Table XI

<u>Glass Compositions Passing Currently Characteristically-Hazardous Waste Limits (TCLP) for S0, S1, and S2 Surrogate Wastes</u>

	S0 Surrogate Glass S0-D5B-2 83 wt. % Waste Loading (Oxide) 1.5 ppm Pb Leaching		S1 Surrogate Glass S1-U1-1-S3 79 wt. % Waste Loading (Oxide) 2.1 ppm Pb Leaching		S2 Surrogate Glass S2-U1-1-S3 79 wt. % Waste Loading (Oxide) 1.5 ppm Pb Leaching	
Oxide	**Wt.%**	*Mol %*	**Wt.%**	*Mol %*	**Wt.%**	*Mol %*
$Li_2O + Na_2O$	**8.81**	*14.72*	**8.94**	*15.01*	**10.01**	*16.25*
K_2O	**0.68**	*0.49*	**0.58**	*0.42*	**0.62**	*0.43*
SiO_2	**52.55**	*59.33*	**50.98**	*57.72*	**55.05**	*60.37*
P_2O_5	**0.82**	*0.39*	**0.39**	*0.19*	**0.34**	*0.16*
CaO	**6.51**	*7.87*	**6.03**	*7.32*	**6.03**	*7.09*
MgO	**0.94**	*1.58*	**1.18**	*1.99*	**0.52**	*0.85*
BaO	**4.16**	*1.84*	**5.05**	*2.24*	**3.37**	*1.45*
PbO	**9.48**	*2.88*	**9.25**	*2.82*	**5.09**	*1.50*
Additive A	**1.51**	*1.26*	**2.01**	*1.68*	**2.01**	*1.63*
Al_2O_3	**9.00**	*5.99*	**9.05**	*6.04*	**9.03**	*5.83*
Fe_2O_3	**2.20**	*0.93*	**2.22**	*0.95*	**4.94**	*2.04*
Cr_2O_3	**0.10**	*0.04*	**0.02**	*0.01*	**0.01**	*0.01*
As_2O_3	**0.08**	*0.02*	**0**	*0*	**0.06**	*0.02*
NiO	**0.34**	*0.30*	**0.34**	*0.31*	**0.28**	*0.25*
SO_3 *	**2.70**	*2.29*	**3.83**	*3.25*	**2.53**	*2.08*
SeO_2	**0.05**	*0.03*	**0.06**	*0.04*	**0.05**	*0.03*
V_2O_5	**0.07**	*0.03*	**0.07**	*0.03*	**0.06**	*0.02*
R_2O	**9.48**	*15.21*	**9.53**	*15.43*	**10.63**	*16.69*
RO	**22.60**	*15.43*	**23.52**	*16.05*	**17.02**	*12.52*

* - Does not compensate for volatility losses or losses due to reaction with sugar.

RECIPE DEVELOPMENT TO MEET UTS LEACHING LIMITS

First UTS Glass Series – Variation in Waste Loading

One obvious approach was to decrease waste loading. The only UTS-listed component approaching the proposed leachability limit is lead, and all lead comes from the waste. This first UTS series began with the three TCLP glasses shown on Table XI. These glasses were decreased in waste loading in 10 wt.% increments down to 30 wt.%. To reduce waste loading while maintaining the key glass characteristics, a dilution "glass" system was used. This dilution composition was selected so that increasing additions would maintain the approximate level of total R_2O, total RO (CaO+ MgO+ BaO+ PbO+ Additive A), and the specific level of Al_2O_3 and

additive A. Since the surrogates provided Na_2O, but no Li_2O, manipulation was required to maintain the overall alkali mole ratio at 2.0 for the various waste loadings. Also, as the contribution of BaO, PbO, and MgO from the waste decreased, CaO was increased to maintain the RO content.

Basis for Reductant Additions – Equivalent Reduction Between Surrogates
It was felt that considerations should be taken to control the final glass redox as both surrogate type and waste loading was varied. Four levels of sugar additions were planned for each glass batch, but sugar is only one of the components influencing final glass redox. The sugar addition for each surrogate was reduced in proportion to waste loading, since the redox reactions (oxidation or reduction) in the glass melting process all occur with waste components and not with any of the batch additives.

Reductant level was also varied between surrogates as S0 = 1, S2 = 1, S1 = 1.3. Components involved in redox reactions were present at different concentrations in all three surrogates. Redox reactions were considered for iron oxides, sulfur oxides, and sodium and potassium oxides. Based on the concentrations of the above oxides and the expected redox equilibrium's, the equivalent sugar addition required would be approximately equal for the S0 and S2 surrogates, and 1.3 times greater for the S1 surrogate.

The effect of the organic compounds in the surrogate was ignored in the calculations. If these organics had been reacting with waste species, substantial oxidant additions (rather than reductants) would have been required to achieve the 0.15 glass redox ratio. These organics were decomposing or evaporating and burning in the plenum.

Table XII presents the leaching data obtained from these experimental series. Those glass melts which were seen to be UTS-compliant are printed in bold.

Table XII
Results on Leach Resistance of the U1 Series – S0, S1, S2 Surrogates

Surrogate.	Wt. % Waste Loading	Wt. % Equivalent Carbon	TCLP ppm Pb UTS limit=0.75	Regulatory Limits Passed	Salts Present?	Metals Present?
S0	80	0.2			None**	None
S0	50	0.2	1.24	TCLP	None**	None
S0	40	0.2	0.89	TCLP	None**	None
S0	30	0.2	**0.4**	**UTS**	None**	None
S1	79	0.2			Yes-Moderate Amount	None
S1	79	0.3	2.14	TCLP	Yes-Minimum Amount	None
S1	70	0.3	0.95	TCLP	Yes-Minimum Amount	None
S1	60	0.1	2.14	TCLP	Yes-Heavy Amount	None
S1	60	0.1	2.21	TCLP	Yes-Moderate Amount	None
S1	60	0.3	1.33	TCLP	Yes-Minimum Amount	Yes
S1	50	0.1	0.76	TCLP	Yes-Heavy Amount	None
S1	50	0.1	1.54	TCLP	Yes-Moderate Amount	None
S1	50	0.3	0.99	TCLP	Yes-Minimum Amount	Yes
S1	40	0.1	**0.53**	**UTS**	Yes-Minimum Amount	None
S1	30	0.1	**0.7**	**UTS**	Yes-Minimum Amount	None
S2	79	0.3	1.49	TCLP	Yes-Minimum Amount	None
S2	70	0.3	1.22	TCLP	Yes-Minimum Amount	None
S2	60	0.1	0.97	TCLP	Yes-Minimum Amount	None
S2	50	0.1	0.96	TCLP	Yes-Very Minimum	None
S2	40	0.1	0.82	TCLP	None**	None
S2	30	0.1	**0.58**	**UTS**	None**	None

*=Salts not present at casting, but present during melting.
**Salts not present during melting.

As seen again in this study, greater batch reduction improves the leach resistance of the resulting glass. If all the experimental melts were at higher batch reductions, i.e. 0.2 wt.% and preferably 0.3 wt.%, all three surrogates should pass UTS standards at a waste loading of 40 wt.%.

Second UTS Glass Series – Variation in Composition

UTS-compliant glasses discussed above, available at 40 wt.% loading, met contract requirements but gave poor economics.

A second series of melts were carried out at 50 wt.% waste loading, using only the S1 surrogate provided by FDF; the most severe in terms of providing an acceptable glass. It was assumed that

recommended formulas for S1 glasses could then be safely applied to S0 and S2. This second UTS series was set up as a matrix of melts to show the effect on durability and processability of five variables, i.e. wt.% Additive A, wt.% Additive B, Molar alkali ratio, wt.% Al_2O_3, and wt.% reductant. The starting point for this matrix was the 50% waste-loaded glass from the previous UTS series, i.e. molar alkali ratio = 2, 9 wt.% Al_2O_3, 8.4 wt.% CaO, 2 wt.% Additive A, 0 wt.% Additive B, and log_{10} viscosity = 2 at 1300^oC.

This data is difficult to evaluate in tabular form, so the trends from the matrix will be described and those compositions meeting UTS Standards listed. The change in alumina (Al_2O_3) from 9 down to 6 wt.% showed no effect on glass leaching resistance, allowing lower alumina and higher levels of other components. Changes in the molar alkali ratio showed only a minor effect on leachability, but a significant difference in the excess molten salts. Increases in Additive B gave significant improvements in leach resistance, especially at high levels of additive A, and additive A itself, in general, improved leach resistance. Increased batch reduction showed a marked effect on resistance to leaching, even where reduced metal was present after melting. In addition, the added reductant had a strong effect on the residual molten salts. Reductant addition will be maintained at as high a level as is possible within the acceptable bounds of processing in a continuous melter. Three glasses of the S1-U2 series passed the UTS maximum leaching standards at a 50 wt.% waste loading of S1 surrogate. These are shown in Table XIII.

Table XIII
Glasses from S1-U2 Matrix Passing UTS Durability Standards (0.75 ppm for Pb)

Glass	TCLP ppm Pb	Matrix Point	Wt.% Waste Loading	Alkali Mole ratio	Al_2O_3 Wt.%	CaO Wt.%	Equivalent Carbon Wt.%	Add.A Wt.%	Add. B Wt.%
S1-U2-10	0.58/0.73	2	50	2	9	8.4	0.3	2	6
S1-U2-8	0.60	7	50	2	9	4.8	0.2	7	3
S1-U2-14	0.65	17	50	3	9	4.8	0.3	7	6

The S0, S1 and S2 UTS-compliant glasses are in the following composition range:
- 50 wt% waste loading,
- 9.2 - 10 wt% total R_2O at Alkali Molar Ratio of 2,
- 20.2 - 21.6 wt% total RO,
- 9 wt% Al_2O_3,
- 0.2 - 0.3 wt% C equivalent batch reductant,
- 4 - 7 wt% Additive A, and 3 - 6 wt% Additive B

SUMMARY – DURABILITY OF THE FDF-SURROGATE GLASSES

The high-sulfate, high-lead wastes from Fernald Silos 1 and 2 presented challenges in achieving high durability while controlling molten salts and precipitated metals. Glasses were developed for each of three surrogate formulations, both at 50% of the current characteristically hazardous waste leaching limits (commonly called TCLP), and at the lower UTS standards. By the use of high levels of alkaline earth and alumina, glass formulations were developed that required only low levels of alkali.

The glass developed for the demonstration surrogate S0 was a lithia-soda-lime-silica glass at 90 wt.% waste loading (SiO_2-based). This glass contained 9.5 wt.% alkali (16 mol%), 12 wt% alkaline earth, 9 wt.% alumina, 9.5 wt.% PbO, and 4 wt.% BaO. This glass formula had a usable

redox safety zone, whereby the excess molten salts layer could be eliminated by a 0.1 wt% C batch addition, but metal precipitation was not observed until addition of 0.4 wt% C. The corresponding range in glass redox (0.15 to 0.2) was used to guide the reductant batch addition for the continuous, cold-top melter demonstration.

Similar formulations compliant at 50% of the current characteristically hazardous waste leaching limits were developed for the S1 and S2 surrogates. UTS-compliant glasses were demonstrated with 50 wt.% waste loading.

The data presented on this formulation development demonstrates the inherent robustness of vitrification, i.e. the ability to accept waste and process variation while producing a high-quality product. Over 60 discrete glass compositions were melted and tested, covering a significant range of oxide composition. Of these glasses, 98% met current regulatory limits, allowing disposal or storage of these waste glasses to be determined by their low-level radioactivity alone.

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FOOTNOTES

[a] These tests were performed by Cogema, Inc./Toledo Engineering Co., Inc. for Envitco, Inc. under contract number 98WO002240, as issued by Fluor Daniel Fernald, acting under the U.S. Department of Energy Contract No. DE-AC24-92OR21972. The data presented summarizes the results reported to Fluor Daniel Fernald by Envitco, Inc., Final Report Submittal, May 4, 1999. The Final Report appears in

the Revised Feasibility Study Report for Remedial Actions at Silos 1 and 2, Report No. 40730-RP-001, December, 1999, U.S. Department of Energy, Fernald Environmental Management Project.

[b] The most widespread formula for waste loading is the percentage of the oxide composition of the glass that is derived from the waste. Fluor Daniel Fernald expressed waste loading as the percentage of silica in the glass that is derived from waste. For the S0-D5B glass used in the Demonstration Run, the oxide-derived waste loading was 83 wt.%, compared to $\approx$ 90 wt.% based on the silica-derived calculation.