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Initial Experience to Determine the Solubility of Salts in Low-Level Mix Waste Glasses

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INITIAL EXPERIMENTS TO DETERMINE THE SOLUBILITY OF SALTS IN LOW-LEVEL MIXED WASTE GLASSES

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Abstract
Glass may be used to immobilize low-level mixed waste (LLMW) at the Savannah River Site because of its ability to accept a wide variety of components into its network structure. However, many common salts (sulfates, chlorides, phosphates, and chromates) present in the LLMW streams have limited solubility in glass. Processing and product problems may arise if the solubility of these salts is exceeded.

In an effort to determine the factors that most affect salt solubilities, a statistical screening experiment was performed. The screening experiment, a Plackett-Burman design, allowed efficient estimation of the effects of variables, such as the composition of the glass, the temperature of the melt, the duration of melting, and the cooling rate. Each of these factors, along with a combination of sulfate, chloride, phosphate and chromate concentrations, were examined to provide an estimate of the solubility of each salt.

The results of the screening experiment were interpreted to determine which variables should be further examined. The composition of the glass, especially the concentrations of boron, calcium and the alkalis, was found to have the greatest effect on the solubilities of the salts. This paper will discuss the results of the screening experiment and describe a path forward.

Introduction
Glass is an advantageous material for the immobilization of LLMW because of the ease of processing and its unique ability to accept a wide variety of waste elements into its network structure.[1] However, LLMW streams also contain a fraction of anionic species which have limited solubility in the glass and which may result in immiscible secondary molten salt phases.

Excess salts can form a water soluble surface layer on the glass, or they may separate from the glass product and concentrate radioactive cesium and strontium in a soluble salt phase. In either case, the corrosion rate of the melter refractory and melter electrodes can increase. The amount of material sent to the melter off-gas system and the leachability of radioactive elements may also increase.[2]

Previous work at the Savannah River Technology Center (SRTC) on High-Level Waste (HLW) has determined the factors which seem to affect the solubility of the salts in glass. These factors include the composition of the glass, the temperature of the melt, the duration of the melting and the glass cooling rates. A statistically designed experiment varied these factors, along with the concentration of sulfate, chloride, phosphate and chromate salts, to provide a basis for quantitative estimates of the solubility of each salt so that the proper controls may be placed on the vitrification process of LLMW.

Experimental

To efficiently identify which factors most affect salt solubilities, a Plackett-Burman screening design was used.[3] This design places a high and a low value for each variable into a statistical combination with all of the variables to be tested. As part of the screening experiments, the alkali, aluminum, iron, boron and calcium concentrations, as a function of silica, were varied. A total of twelve different combinations of the variables were tested. The glass composition of each trial is shown in Table 1.

Table 1 - LL/MW Compositions for Plackett-Burman Design
(Weight Percent)

Trial	Alkali	Al_2O_3	Fe_2O_3	B_2O_3	CaO	SiO_2
1	29.63	8.75	0.67	9.76	17.51	33.67
2	32.06	0.18	1.82	10.57	18.94	36.43
3	23.66	12.31	2.37	13.73	0.62	47.33
4	39.93	11.80	2.27	0.05	0.59	45.37
5	40.48	11.96	0.92	0.05	0.60	46.00
6	36.27	0.21	0.82	0.04	21.43	41.22
7	27.35	0.27	1.09	15.86	0.71	54.71
8	24.09	0.24	2.41	0.05	25.05	48.17
9	19.31	10.03	0.77	11.20	20.08	38.61
10	39.32	0.22	2.23	12.96	0.58	44.68
11	21.45	11.15	2.15	0.04	22.31	42.90
12	32.49	0.33	1.30	0.06	0.85	64.98

In addition to varying the chemical composition, the melt temperature, melt time and glass cooling rate were also varied as part of the screening experiment. For each of the trials listed in Table 1, the melt temperature was either 1050°C or 1300°C; the melt time was 1 hour or 2 hours; and the cooling rate was fast (air quenched) or slow (programmed cooled). Table 2 shows the statistical design of these variables for each trial.

Table 2 - LL/MW Variables for Plackett-Burman Design

Trial	Melt Temp (°C)	Melt Time (hrs)	Cooling Rate
1	1300	1	Air
2	1050	1	Air
3	1050	1	Prog
4	1050	2	Air
5	1300	1	Prog
6	1050	2	Prog
7	1300	2	Air
8	1300	1	Prog
9	1050	2	Prog
10	1300	2	Prog
11	1300	2	Air
12	1050	1	Air

For each of the twelve trials, nine crucibles, each with varying salt concentrations were vitrified. Table 3 shows the salt concentrations that were tested. Each sample was given a label which identified its composition (using the associated trial number) and the type and amount of salts added to it (using the sample codes listed in Table 3). For example, a label "L-1-S2" would represent the chemical composition and variables listed under Trial 1 (see Tables 1 and 2), with a sulfate concentration of 0.5 wt%. The "L" is an indication that the sample is a simulant of LLMW.

Table 3 - Salt Concentrations for Screening Experiments
(wt% in feed)

Sample Code	SO_4	NaCl	PO_4	Cr_2O_3
Baseline	0.0	0.0	0.0	0.0
S1	0.3	0.0	0.0	0.0
S2	0.5	0.0	0.0	0.0
S3	0.7	0.0	0.0	0.0
C1	0.0	0.5	0.0	0.0
C2	0.0	1.0	0.0	0.0
C3	0.0	1.5	0.0	0.0
AN	0.4	1.0	3.0	0.3
AH	0.7	1.5	4.5	0.6

Once the required chemicals were combined and placed in crucibles, the batches were vitrified at the appropriate time and temperature and cooled at the appropriate rate. If the trial did not produce a glass, it was noted and no further analyses were performed. For those trials that did produce a glass, the glass composition was analytically determined along with the composition of any salt layer that may have formed. The crystalline content of the glass was determined using X-Ray Diffraction and was confirmed by Scanning Electron Microscopy.

The glass durability was assessed by leaching the glass according to the Product Consistency Test (PCT).[4] The PCT is a crushed glass leach test that measures the releases of various elements, in 90°C ASTM Type I water over a period of seven days. Samples are run in triplicate and each test includes the appropriate blanks and standards. Although there is no current PCT acceptance criteria for LLMW glasses, these glasses were compared to the acceptance criteria for HLW glasses which states that the PCT release of the glass sample must be at least two standard deviations below the release of the Environmental Assessment (EA) glass.[5]

Results and Discussion

After vitrifying, none of the crucibles from trial 6 or trial 8 formed a glass. The baseline sample of trial 4 produced a glass, but as the salt content was increased, many of the samples did not. For trial 2, which was melted at 1050°C for one hour, only the crucibles which contained a combination of all of the salts, formed a glass. This was due to the presence of phosphate which has previously been shown to lower the melting temperature of a glass.[6] The remaining trials each produced a glass but the appearance and characterization of these glasses were quite different.

The first step in the characterization was a visual inspection of the glass to determine if a salt layer had formed. A numerical rating was assigned to each trial based upon the amount of salt that was present. Only two trials, 7 and 10, did not contain a salt layer on any of the crucibles and were therefore assigned the highest rating. Since trials 6, and 8 did not form a glass, these trials were assigned the lowest rating. The remaining trials were ranked in between. These ratings were interpreted to determine which factors most affect the formation of a salt layer. At an 80% confidence level, the results indicated that higher boron and lower calcium contents would be desirable to avoid the formation of a salt layer. Since the rating system was a subjective analysis, an 80% confidence level was not unexpected.

A more objective analysis was performed on the durability results. For each trial, the measured PCT responses for boron, calcium, sodium and silicon were averaged for each sample. The average PCT release was then normalized by the weight fraction of that element present in the glass. The normalized PCT release was then averaged over the nine salt concentrations to obtain an average for each trial. The average normalized release for each trial is shown in Table 4. The samples from trial 6 could not be analyzed due to the inability to grind the samples to the appropriate size. Grinding of the other samples that did not form glasses was possible, therefore, they were included in the testing with the glass samples.

Table 4 - Average PCT Results for Each Trial
(g/L)

Trial	Boron	Calcium	Sodium	Silicon
1	1.69	0.035	3.99	0.45
2	50.04	0.013	55.11	6.12
3	8.31	0.036	5.38	0.28
4	242.42	0.240	76.84	44.34
5	233.59	0.587	84.76	38.33
6	N/A	N/A	N/A	N/A
7	59.83	0.189	52.02	4.85
8	10.60	0.008	12.70	0.85
9	1.18	0.176	1.07	0.08
10	99.96	0.150	79.09	43.57
11	0.98	0.036	1.66	0.24
12	310.58	0.832	122.27	108.46
EA	16.70	N/A	13.35	3.92

Table 4 also shows the accepted values for the Environmental Assessment (EA) glass upon which the HLW glass acceptance criteria is based.[7] Since no criteria has been established for LLMW glasses, the PCT results of this study were compared to the EA glass. However, it should be noted that HLW will be vitrified into a borosilicate glass. Many of the glasses in this study contained low amounts of boron (boron is considered to be a conservative estimate of HLW glass durability). Since the PCT results were normalized by the fraction of the element present in the glass, glasses with low amounts of boron (trials 4, 5 ,8 and 12) could have misleading results. Since all of the trials contained similar levels of silicon, comparison of the silicon results may provide the best indication of the glass durability. Five of the trials would be considered acceptable using the HLW criteria for silicon.

The PCT results were interpreted based on the design of the screening experiment. The evaluation showed that a higher boron content corresponded to lower releases for all four of the studied elements while a higher alkali content correlated to higher release for boron and sodium. The sodium release was also affected by the aluminum and calcium in the glass - higher levels of both elements tended to decrease the amount of sodium released. In addition to higher amounts of boron, higher iron content corresponded to lower releases of calcium. The majority of these evaluations were performed using at least a 90% confidence level.

To determine the effect that the salts had on the glass durability, separate evaluations were performed on the samples with only sulfate salts (the "S" series, as shown in Table 3), the samples with only chloride salts (the "C" series), and the samples with a combination of the four salts (the "A" series). The average boron release of the three series for each trial is shown in Table 5. It should be noted that the results for the baseline sample (same composition, without any salt additions) have been included in the overall average but have not been included in the salt series averages.

Table 5 - Average Boron Release for each Salt Series
(g/L)

Trial	Overall Average	Sulfate Series	Chloride Series	Combination Series
1	1.69	1.85	1.27	2.07
2	50.04	41.83	36.92	80.70
3	8.31	7.05	8.03	11.96
4	242.42	89.00	366.58	349.75
5	233.59	260.02	109.42	296.38
6	N/A	N/A	N/A	N/A
7	59.83	62.54	70.54	38.67
8	10.60	15.19	3.68	17.88
9	1.18	1.22	1.27	0.93
10	99.96	100.86	103.79	92.92
11	0.98	1.15	0.83	1.08
12	310.58	280.71	320.37	270.80

The statistical evaluation of the boron releases for each salt series indicated that the composition had the largest effect but the melt temperature was also found to influence the results. A higher melting temperature, along with higher boron and lower alkali contents corresponded to lower boron releases. A summary of all of the findings related to the PCT results can be found in Table 6, along with the level of confidence used for the evaluations.

The crystalline content of some of the glass samples was determined using X-Ray Diffraction (XRD). Scanning Electron Microscopy (SEM) was used to confirm the XRD analysis. Samples containing the larger amounts of salts (the S3, C3 and AN or AH samples as shown in Table 3) were analyzed to determine if the salts had an effect on the formation of crystals. For those samples where crystals were detected, the largest percent of crystals detected was less than 3 wt%, and the average content was less than 1 wt%. Since only a small portion of the glass was used for the crystalline analyses and because no trends were observed, a statistical analysis was not performed.

Table 6 - Summary of Leachate Analyses

Analysis	Level of Confidence	Factor which Decreases PCT Release (Inc. Durability)
Average Boron	90% 80%	Low alkali content High boron content
Average Boron S Series	95% 90%	High boron content High iron content
Average Boron C Series	95% 95% 90% 90%	High boron content High melt temperature Low alkali content High calcium content
Average Boron A Series	99% 99% 99% 99% 99%	High boron content Low alkali content High melting temperature High calcium content High iron content
Average Calcium	95% 95%	High iron content High boron content
Average Sodium	98% 95% 95% 95%	High aluminum content Low alkali content High boron content High calcium content
Average Silicon	90%	High boron content

Conclusions and Path Forward

The screening experiment gave a strong start in determining the variables which increase the solubility of salts in LLMW glass. The factors which decreased the formation of salt layers on the top surface of the glass were a higher boron content and a lower calcium content. Since this experiment only tested two different values for each variables, further studies should be performed to determine the optimum concentrations of these elements and the solubility of the salts.

Because the durability study of this experiment used numerical values based on scientific data, this part of the experiment yielded results with a higher level of confidence than the salt layer analysis. In general, the results showed a higher level of boron and a lower level of alkalis improved the durability of glass. The other factors that also influenced the durability should be included in further studies to determine a more distinct relationship between the factors.

The composition of the glass was the factor that most affected the solubility of the salts. Therefore, future studies by SRTC will include glass formulations based on actual LLMW compositions since the screening experiment covered a broad range of compositions. The future studies will also include fluoride salts because fluoride is present in many LLMW. Quantitative salt solubility limits based on the specific glass composition can then be obtained.

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