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Vitrification as a Low-Level Radioactive Mixed Waste Treatment Technology at Argonne National Laboratory

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Vitrification as a Low-Level Radioactive Mixed Waste Treatment Technology at Argonne National Laboratory

Abstract

Argonne National Laboratory-East (ANL-E) is developing plans to use vitrification to treat low-level radioactive mixed wastes (LLMW) generated on-site. The ultimate objective of this project is to install a full-scale vitrification system at ANL-E capable of processing the annual generation and historic stockpiles of selected LLMW streams. This project is currently in the process of identifying a range of processible glass compositions that can be produced from actual mixed wastes and additives, such as boric acid or borax. During the formulation of these glasses, there has been an emphasis on maximizing the waste content in the glass (70 to 90 wt%), reducing the overall final waste volume, and producing a stabilized low-level radioactive waste glass. Crucible glass studies with actual mixed waste streams have produced alkali borosilicate glasses that pass the Toxic Characteristic Leaching Procedure (TCLP) test. These same glass compositions, spiked with toxic metals well above the expected levels in actual wastes, also pass the TCLP test. These results provide compelling evidence that the vitrification system and the glass waste form will be robust enough to accommodate expected variations in the LLMW streams from ANL-E. Approximately 40 crucible melts will be studied to establish a compositional envelope for vitrifying ANL-E mixed wastes. Also being determined is the identity of volatilized metals or off-gases that will be generated.

Introduction

Research activities at ANL-E produce radioactive, as well as low-level mixed radioactive waste (MLLW), *albeit* in very small quantities. Currently, ANL-E is shipping LLMW to the Hanford site packaged in 55-gal. drums with liners and an approved liquid absorbent, although it unclear whether this disposal option will be available in the future. Approximately 750 L of LLMW suitable for vitrification is currently stored and awaiting disposal. Future mixed waste production is expected to continue at varying rates. The stored and anticipated wastes need to be treated for ultimate disposal.

The commercial disposal options for mixed waste disposal are limited. The only operating commercial facility in the United States licensed to accept mixed waste for disposal is Envirocare's facility in Clive, Utah. While this facility is licensed under the Resource Recovery and Conservation Act (RCRA) Part B and has received wastes from the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) response actions and some clean-up projects of the Department of Energy (DOE), the facility is limited to accepting mixed waste with only normally occurring radioactive material, which is not covered under the Atomic Energy Act.

Section 105 of the Federal Facilities Compliance Act of 1992 (FFCA) is the main regulatory driver under which all DOE facilities are required to prepare an inventory of existing and planned mixed waste and to develop plans for mixed waste treatment. The DOE is required by section 3021(b) of the RCRA, as amended by the FFCA, to prepare plans describing the development of capacities and technologies for treating mixed wastes. The Act requires site treatment plans (STP) to be developed for each site at which DOE generates or stores mixed waste. The recently drafted ANL-E STP will provide information to other DOE sites with respect to common technology needs and mixed waste treatment options. Recent major DOE initiatives related to mixed waste treatment include the Mixed Waste Integrated Program (MWIP) and the Minimum Additive Waste Stabilization (MAWS) program, to develop and the investigate the use of vitrification as a mixed waste treatment technology [Bennet et al. 1994 (1); Pegg 1993 (2)].

There are several strategies for managing mixed wastes. If the waste is classified as a mixed waste because of a hazardous waste characteristic defined by the RCRA, then attempts are made to eliminate the characteristic prior to disposal in a non-hazardous waste facility (e.g. LLW facility). If the waste is classified as a mixed waste because it contains a listed material, then the waste must be disposed of in a hazardous waste facility. Additionally, if the waste falls under land ban restrictions, then it must be treated first. With respect to the radioactive component of the mixed waste, the Nuclear Regulatory Commision's 10 CFR 61 covers regulations for shallow land disposal of low-level radioactive waste.

This project has previously evaluated the feasibility of using vitrification to reduce the volume and stabilize some of the mixed waste streams at ANL-E [Mazer et al. (3)]. This report describes the results of an experimental study of crucible melts made with ANL-E LLMW. These test results have formed the technical basis for a decision to use vitrification as a mixed waste treatment option for some of the waste streams at ANL.

The objectives of the present study were to identify and produce glass formulations made with actual LLMW from ANL-E. These glass formulations were designed such that together they comprised a compositional envelope that could eventually be used by during the full-scale vitrification of LLMW. Several criteria were used to select glass formulations for inclusion in the compositional envelope:

1) The formulation melts at temperatures consistent with commercially available vitrification systems;
2) The melted mixture has a viscosity amenable to pouring at the melt temperature; and

3) The resultant waste form passes the TCLP, the regulatory basis for determining whether a material has the characteristic of being toxic and, therefore, hazardous.

The rationale behind identifying a compositional envelope, rather than a single glass composition, was to provide flexibility in handling the expected compositional variations in the ANL-E waste streams and to use a minimum of glass-forming additives. A compositional envelope will provide the eventual users of the full-scale vitrification system with greater flexibility to process compositionally unusual wastes and will not impose overly stringent waste processing requirements.

Experimental Methods

One of the most important variables in determining the vitrification compositional envelope is the composition of the LLMW streams to be treated. The waste streams identified for use in this study included Storage Tank Sludge (STS), Evaporator Concentrator Bottoms (ECB), and High Efficiency Particulate Air (HEPA) filter media. A fourth waste stream, LLMW soil, has also been identified as suitable for vitrification. This waste stream has not been incorporated in the present study but will be investigated in later studies. The nominal compositions provided for these waste streams are presented in Table 1. The radioactive component of these waste streams included a variety of radioactive elements (e.g., ^{232}U, $^{239/240}$Pu, ^{237}Np, ^{210}Po, ^{241}Am, ^{137}Cs, ^{60}Co), as well as metals (Ag, As, Ba, Cd, Cr, Hg, Se, or Pb) at levels above the EPA limits for hazardous materials, as determined with the TCLP.

The three waste streams were blended in two mixtures, designated SWA and SWB. The mixing ratios (by weight) for the STS:ECB:HEPA wastes were 4:1:1 (SWA) and 4:2.5:1 (SWB). These mixing ratios are estimated to be representative of the ranges of the annual generation of each of the waste streams. These mixing ratios have also been found to produce a chemical mixture that can be melted and result in a suitable glass product with a minimum of glass-forming additives. Each mixture was mechanically mixed to a degree believed to be representative of the full-scale vitrification process. In this way, the process could be evaluated for its tolerance of some inhomogeneities in the melter feed composition.

Based on the composition of SWA and glass chemistry, three glass forming additives were selected to produce acceptable glasses, borax ($Na_2B_4O_7 \bullet 10H_2O$), boric acid ($H_3BO_3$), and sodium carbonate ($NaCO_3 \bullet H_2O$). These additives were selected to lower the melting point of the glass yet keep the composition in the region known to form acceptable alkali borosilicate glasses.

All of the crucible melts were made using the wastes described in Table 1 and chemical-grade glass-forming additives. The melts were prepared in air in high-alumina (99% Al_2O_3) crucibles; these crucibles do not significantly interact with the molten glass during the short melt duration, 2 hours. Upon termination of the melt process, the glass was poured onto a graphite or stainless steel surface, neither of which significantly interacted with the melt.

Feeds for the crucible melts were prepared in the following manner. An unused high-alumina crucible was tared on a balance. The waste stream, either SWA or SWB, was added to the crucible according to the specifications of the formulation. The glass-forming additives were then added, and the mixture was blended to a degree representative of the conditions that may exist during full-scale vitrification.

Table 1. Chemical Compositions of ANL-E LLMW streams. All values are in weight percent.

Component	STS	HEPA	Soil	ECB
B_2O_3	0.0	8	0.00	0.2
SiO_2	53.1	60	53.92	0.2
Al_2O_3	8.1	5	18.43	
Na_2O	1.4	10	1.33	87.2
K_2O	1.6	1	1.13	
Li_2O	0.0		0.00	0.4
BaO	0.1	5	0.00	
Fe_2O_3	8.1		19.96	
CaO	21.6	5	1.56	0.8
MgO	2.1	3	1.92	2.0
NiO				0.1
ZnO	1.4	3		
CuO	0.9			0.1
MnO_2				0.1
Cr_2O_3	0.3			
TiO_2			1.06	
Cl			0.29	
S			0.41	
F				1.6
PO_4	1.3			7.4
Total	100	100	100	100

All melting was performed in an electric resistance furnace at 1100°C and the melts were held at that temperature for approximately two hours before removing the crucible from the furnace and attempting to pour out the melt. This temperature is comparable to that used in previously investigated commercial melters and reduces the tendency of volatile metals and radionuclides to be removed from the melt.

Results

Fifteen crucible melts (Table 2) were produced, characterized, and tested in this portion of this study. Ten melts were made with LLMW and additives. Five additional melts ("spiked melts") were made to determine the upper limits of hazardous metal contents in ANL-E LLMW, and still meet the selection criteria stated earlier. These spiked melts were made by doping with different amounts of each of the eight RCRA metals, as described in Table 3. These melts were based on the proven formulations WM-3, WM-5, WM-6, and WM-10. The volume reduction resulting from vitrification was estimated at about a factor of eight for these glasses.

Three melts (WM-4, WM-8, and WM-9) could not be poured from their crucibles. As described later, these glasses were subsequently tested with the TCLP to assess their leaching performance and evaluate whether vitrification had rendered these wastes non-hazardous.

Each of the glasses was characterized by scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS). These analyses provided a means of semi-quantitatively verifying the homogeneity and compositions of the glasses produced during crucible melting. In general, SEM/EDS analyses indicated that the compositions of the crucible glasses are approximately those of the glasses as formulated. The variations could be attributed to analytical error in the SEM/EDS system, volatilization of elements during melting, or variations in the compositions of the LLMW samples.

The results of TCLP testing of the crucible melts are presented in Table 4. The row labeled "Untreated HEPA" presents TCLP data for the HEPA sample blended in SWA. This row indicates how the unvitrified (as received) HEPA portion of SWA performed in a TCLP test (failed for cadmium because release was greater than 1 mg/L), and the results provide a measure of the effectiveness of vitrification in stabilizing the hazardous elements in this material. Also presented in this table is the leachant concentration limit that is used by the EPA to define whether a material is hazardous. The TCLP tests that were performed are considered to be modified TCLP tests, since the amounts of glass and leachant used were reduced proportionately to conserve glass. This is the only change that was made to the standard TCLP.

Table 2. Glass Formulations Produced for Compositional Envelope Development. All values are in weight percent. Glasses WM-18, WM-19, WM-20, WM-21, and WM-25 were spiked with hazardous metals and not used to define the compositional envelope.

				Glass-forming additives %		
Melt #	CMT ID	Waste Stream	Waste Stream	Boric Acid	Borax	Sodium Carbonate
1	WM-1	SWA	87	0	0	13
2	WM-3	SWA	80	10	7	3
3	WM-4	SWA	80	20	0	0
4	WM-5	SWA	72	25	3	0
5	WM-6	SWA	80	10	10	0
6	WM-7	SWA	90	5	0	5
7	WM-8	SWA	90	10	0	0
8	WM-9	SWA	85	10	5	0
9	WM-10	SWA	75	0	15	10
10	WM-15	SWA	85	4	11	0
11	WM-18	SWB	88	2	10	0
12	WM-19	SWB	78	7	15	0
13	WM-20	SWB	78	7	15	0
14	WM-21	SWB	87	2	11	0
15	WM-25	SWB	82	3	15	0

Table 3. Amount of Metals Spiked in Crucible Melts. Reagent grade oxides of each metal (Ag, As, Ba, Cd, Cr, Pb, Se and Hg) of each metal were added to each of the spiked melts.

Compositional Envelope Melt	Corresponding Spiked Melt	RCRA Metal Spike (mg/kg)
WM-3	WM-18	10,000
WM-5	WM-19	1500
WM-5	WM-20	8400
WM-6	WM-21	1200
WM-10	WM-25	1200

Table 4. Results of TCLP Testing of Formulations for ANL-E LLMW Glasses. All values in mg/L.

Test	As	Ag	Ba	Cd	Cr	Hg	Ni	Pb	Se
WM-1	0.11	0.003	0.35	0.004	0.030	0.230	1.30	0.0006	0.28
WM-3	0.020	<0.0002	1.00	0.006	0.080	0.050	6.00	0.070	0.11
WM-4	0.011	0.0003	5.10	0.0007	0.014	0.015	0.30	0.014	0.09
WM-5	0.003	0.0002	0.60	<0.0003	0.009	0.080	0.60	<0.002	0.01
WM-6	0.020	0.0001	0.30	0.0001	0.010	0.010	0.20	<0.002	0.03
WM-7	0.010	0.00007	0.20	0.0006	0.020	0.020	0.01	0.005	0.10
WM-8	0.007	0.0002	2.00	0.0003	0.070	0.010	0.60	0.050	0.04
WM-9	0.008	0.001	3.20	0.001	0.090	0.010	0.22	0.06	0.06
WM-10	0.009	0.0003	0.30	0.0010	0.020	0.004	1.00	0.040	0.01
WM-15	0.009	0.0003	0.30	0.0010	0.020	0.004	1.00	0.040	0.01
WM-18	1.862	0.0001	5.40	4.64	0.072	0.004	3.27	3.68	0.12
WM-19	0.833	0.0001	2.15	0.022	0.015	0.041	0.622	0.051	0.10
WM-20	2.400	0.0013	1.00	0.002	0.014	0.026	0.11	0.002	0.10
WM-21	0.140	0.0002	0.30	0.004	0.012	0.036	0.17	<0.0001	0.36
WM-25	0.320	0.0004	0.40	0.002	0.014	0.066	0.04	<0.0001	0.20
Untreated HEPA	<0.50	<0.02	0.23	4.89	0.48	0.6	-----	<0.50	1.37
TCLP Std.	5.0	5.0	100.0	1.00	5.0	0.2	-----	5.0	1.0

Discussion

The previous evaluations of ANL-E LLMW determined that the most promising glass compositions were sodium borosilicate glasses [Mazer et al. (1)]. Because these compositions have been studied extensively by others, it was not necessary to determine whether they could be vitrified, only to demonstrate vitrification with existing ANL-E LLMW streams. Figure 1 is a ternary diagram that is frequently used to display the region where alkali borosilicate glasses are known to form, as derived from the glass science literature [e.g., Jantzen et al. (4)] and previously investigated for ANL-E wastes [Mazer et al. (3); Mazer et al. (5)]. The symbol R is used to denote alkali metals. While Figure 1 cannot be used to precisely determine glass durability, processibility, or melting temperature, it can be used as a guide for studies of these properties. The eutectic melting point for the alkali borosilicate system is approximately 600°C, depending on the precise SiO_2 + Al_2O_3 composition considered. The eutectic point lies approximately where the value of $SiO_2+Al_2O_3:\Sigma R_2O:B_2O_3$ is 40:25:35. Melting isotherms extend approximately horizontally across the diagram for compositions with equivalent values of SiO_2 + Al_2O_3, and the isotherms increase with increasing SiO_2 + Al_2O_3.

Figure 1 plots the locations of the STS, ECB, and HEPA waste streams, showing their positions relative to the glass forming region. This study concentrated on identifying a practical compositional envelope within the known glass-forming region. While Figure 1 does indicate a region suitable for vitrification, the additional components and the SiO_2/Al_2O_3 ratio in the waste streams can greatly affect the boundaries of that region. Furthermore, the figure does not provide information about the melting temperature or viscosity of glasses in the region. For these reasons, it was necessary to experimentally demonstrate vitrification with actual ANL-E LLMW to confirm the expected properties of the melt and the final waste form.

Figure 1 also depicts the relationship between the individual waste streams and the composite waste feed SWA. The other composite waste stream SWB has a $SiO_2+Al_2O_3:\Sigma R_2O:B_2O_3$ ratio of 64:34:2. The mixture SWA lies in the glass-forming region, but the temperature where this melted material easily pours lies between 1200 and 1300°C.

For nearly all of the glasses in Table 4, the leachant concentrations for the eight RCRA metals are less than the EPA limit, and the glasses are therefore non-hazardous. In most cases, the glasses passed the EPA's limit for the TCLP by a relatively large margin. The exceptions were WM-1 which only met the TCLP limit for mercury, 0.2 ppm, and WM-18 which failed the test for cadmium. Test WM-1 produced a relatively viscous melt. If additional testing indicates that this glass composition does not retain mercury, it can easily be excluded from the compositional envelope. At this time WM-1 is marginally included in the compositional envelope. Test WM-18 suggests that melter feed compositions with Cd concentrations on the order of 10,000 ppm may not be sucessfully treated with vitrification.

A comparison of the TCLP results for the untreated HEPA filter with the TCLP results for glasses other than WM-20, WM-21, and WM-25 (these were made with other HEPA filter samples) suggests that Cd, Cr, Hg, and Pb are less leachable after vitrification. The approximate percentage of the HEPA filter sample in these glasses ranges from 12 wt% (waste loading 72%) to 15 wt% (waste loading 90%). The changes in the TCLP leachate results are greater than expected from the effects of dilution during blending and melting.

Three of the glasses, WM-4, WM-8, and WM-9, had viscosities at the melt temperature that did not allow them to be poured from the crucible. These melts are not included in the compositional envelope but may be useful if the final vitrification system is operated in a batch mode and does not require a continuous feeding and glass removal.

The spiked melt glasses all have acceptable viscosities and passed the TCLP and are now low-level wastes. These results suggest that vitrification can successfully treat mixed waste streams with concentration of RCRA metals greater than those typically encountered at ANL-E. The production and testing of additional crucible melts are expected to demonstrate that the entire compositional envelope can accommodate mixed waste streams with concentrations of RCRA metals greater than those typically encountered at ANL-E (<100 ppm per metal per waste stream). These analyses indicate that spiking the melts with ~10^3 ppm of each of the RCRA metals promotes the formation of multiple phases. Since the distribution of the phases appears to be relatively uniform, and the melts had viscosities that allowed them to be poured from the crucibles, these glasses are good candidates for inclusion in the compositional envelope.

The compositional envelope developed as a result of this study is depicted graphically in Figure 2. This is not the final compositional envelope since additional crucible melts are planned. These melts will be used to expand the compositional envelope beyond the existing boundaries and provide additional flexibility to the eventual users of the full-scale vitrification system.

Currently, ANL-E is in the process of finalizing the specifications for the vitrification system. This system is scheduled to be installed in late 1996, and operational in 1997. Our plans are to continue evaluating waste streams at ANL-E and identify and test those found suitable for vitrification. As noted in Table 1, a LLMW soil waste stream has already been identified, and studies are in progress to verify suitable glass compositions using this waste. Other potential LLMW streams include sludges, lab glass wastes, spent inorganic catalysts, and spent decommissioning abrasives.

Summary

The results of this study have identified a range of alkali borosilicate glass compositions that meet criteria identified at the start of the study: glasses that melt and are qualitatively viscous at 1100°C, and that pass the TCLP test. The glasses that make up the compositional envelope were produced with relatively small amounts (7 to 28 wt%) of glass-forming additives, and the glass-forming additives that were used (borax, boric acid, and sodium carbonate) are easily handled materials. The compositional envelope will become better developed at the conclusion of the next phase of crucible melting.

SEM analyses of the final waste forms indicate that most of the glasses that comprise the compositional envelope are homogeneous. This suggests that easily leached pockets of hazardous metals are not present in these glasses. The non-homogeneous glasses were spiked with RCRA metals, but still have characteristics that do not preclude them from the compositional envelope.

The results achieved in this portion of this program indicate that the identified compositional envelope will accommodate unusually hazardous waste streams. The spiked melts produced in this portion of the study provide compelling evidence that alkali borosilicate glasses are a robust waste form. Furthermore, the identified compositional envelope is broad enough to allow

ANL-E to potentially treat a wide variety of waste streams, not only streams similar to SWA or SWB.

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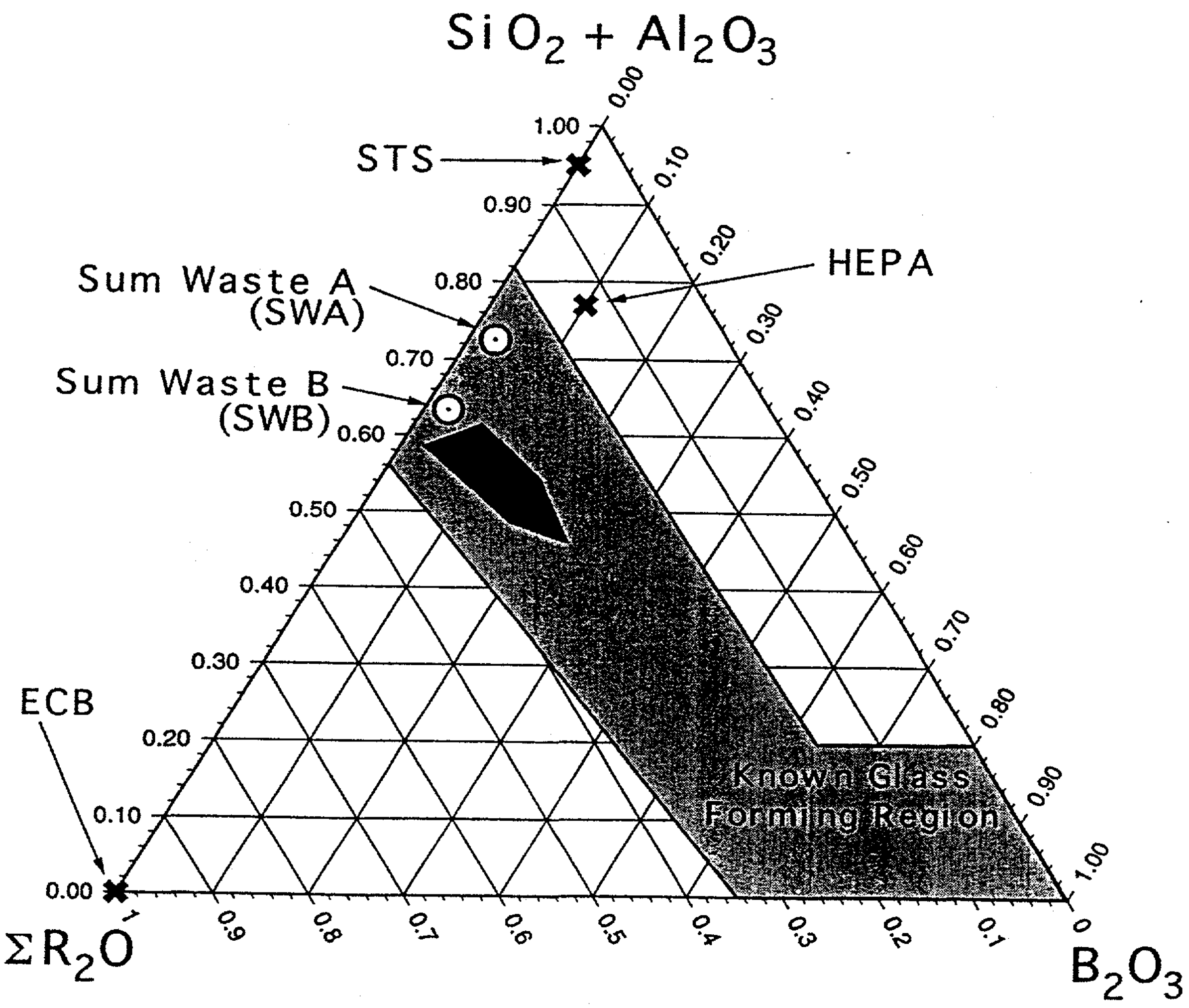
Figure 1. Ternary diagram of the alkali borosilicate system. Alkali elements are represented by the symbol R. The shaded region is the known glass-forming region for this system, as derived from the glass science literature. The cross symbols depict the individual waste streams studied; Storage Tank Sludge (STS), Evaporator Concentrator Bottoms (ECB), and High Efficiency Particulate Air (HEPA) filter media. The wastes have been mixed in their annual generation proportions of 4:1:1 (STS:ECB:HEPA) to form the point labeled SWA, and 4:2.5:1 to form SWB. The compositional envelope (dark gray area in glass-forming region) is described in the text and shown in detail in Figure 2.



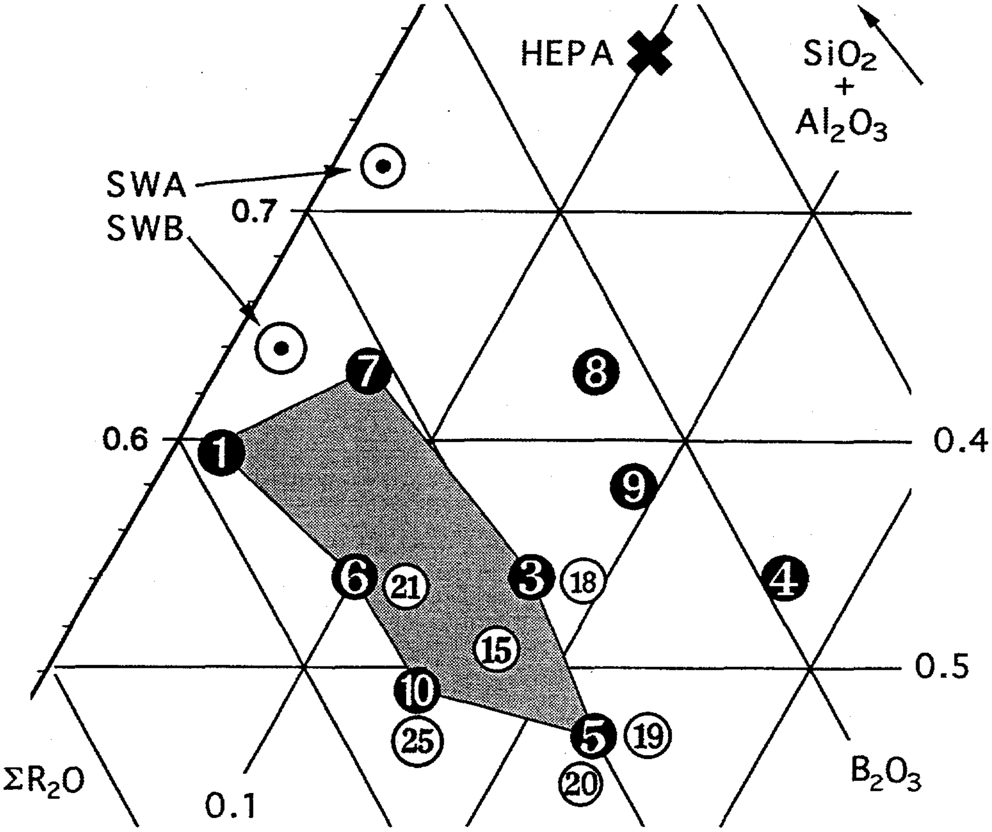


Figure 2. Section of the ternary diagram, shown in Figure 1, summarizing the work performed for compositional envelope development in this study. Each numbered point corresponds to a WM-formulation in Table 2. The formulations with white numbers and black backgrounds were made with LLMW, while the formulations with black numbers and white backgrounds contain added amounts of RCRA metals (see Table 3). Formulations WM-1, WM-3, WM-5, WM-6, WM-7, and WM-10 define the compositional envelope of glasses developed to this point (the region filled in with shading).