TIME-TEMPERATURE-TRANSFORMATION STUDY OF SIMULATED HANFORD TANK WASTE (AZ-101) AND OPTIMIZATION OF GLASS FORMULATION FOR PROCESSING SUCH WASTE
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ABSTRACT

This paper presents the current results of a study for the optimization of the quality of the wasteform to be produced by vitrification of Hanford High Level Waste (HLW). A simulant of the content of Hanford Tank AZ-101 has been used for the experiments. A first phase of the research focused on the wasteform composition and showed that a high quality and chemical-resistant wasteform can be formed incorporating 60 weight % of dried waste into a borosilicate glass enriched with zinc oxide and boric acid and provided some indication about the heat treatment of the melt. A second phase of the study, still in progress, refines these findings. A detailed crystallinity survey of the waste form after various heat treatments has been performed, culminating in the development of a time-temperature-transformation (TTT) diagram. The results of the first phase of research and preliminary results from the second phase are described.

INTRODUCTION

This paper presents the preliminary results of a study on the formulation of High Level Waste (HLW) conducted under Department of Energy (DOE) contract DE-AC26-00NT40801 for Additional Tests of an Advanced Vitrification System. The work was performed by the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at Mississippi State University (MSU) and the Radioactive Isolation Consortium (RIC), LLC, together with the University of Missouri – Rolla (UMR).

The goal of the study is to optimize the process parameters so that the HLW vitrification procedure results in a high quality, high waste loading glass having the properties of chemical durability, thermal stability, and mechanical stability.

The work is focused on the in-can melter alternative being explored by the Office of River Protection (ORP) and DOE as part of a mission to accelerate the disposal of Hanford HLW. The target result is a borosilicate glass wasteform compliant with the current revision (Rev. 2) of the Waste Acceptance Product Specifications (WAPS) for Vitrified High-Level Waste Forms.[1]

All the waste loadings discussed in this paper, both from DIAL and VSL, were calculated in the following method (M-1):

Waste Loading (wt%)=[(mass of the glass)-((mass of glass formers added)+(mass of sodium oxide in the waste, expressed as Na_2O)+(mass of silicon dioxide in the waste, expressed as SiO_2))]/(mass of the glass)

The M-1 method is in accordance with the DOE Statement of Work and the DOE-approved RIC Detailed Test Plan.

Melter operation at temperatures of 1250°C or less has been previously performed at the GTS Duratek Waste Treatment Plant (WTP) and the Vitreous State Laboratory (VSL) of the Catholic University of America.[2,3] The waste loading achieved at VSL using the simulant most closely approximating the AZ-101 composition, HLW98-31,[4] is about 30% by weight, producing a wasteform having a density of 2.75 g/ml at 20°C.

This study was conducted with an upper temperature limit of 1450°C for the glass melting operation. The higher melter temperature was chosen because it would allow the incorporation of a larger waste percentage, thus limiting the volume of produced wasteform with respect to vitrification conducted at lower temperature and contributing to the acceleration of the disposal process.

In the study, a non-radioactive simulant the contents of the AZ-101 Hanford Tank , produced by NOAH Technologies, was used as a substitute for the actual radioactive waste. The recipe for the simulant was provided by DOE. The simulant is a complex slurry mixture of about 27 components and represents HLW that has been washed and is therefore low in Na and other elements producing soluble oxides that lower the melting temperature (flux). The simulant composition is not based entirely on the contents of Tank AZ-101. It also includes a substantial fraction of WTP process streams; cesium and technetium eluates and the Sr/Transuranic (TRU) precipitate, which is the origin of most of the Sr and Mn.

Before the experiments, the simulant was characterized at DIAL using Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), Atomic Absorption (AA), Ion Chromatography (IC) and Total Inorganic Carbon-Total Organic Carbon (TIC-TOC). The results of the analyses revealed that the material was near the target with the exception of a Pb deficiency. Upon remediation of Pb, the material was judged to be an acceptable simulant of the AZ-101 waste.

The target composition of the remediated simulant and the results of an analysis of its composition performed at DIAL are described in Table I.

Table 1. Simulant Analysis of Remediated AZ-101 simulant, Drum A, performed at DIAL.

Oxide	Target (wt. %)	Tolerance (%)	Tolerance (± wt .%)	DIAL Analyzed (wt. %)	Standard Deviation	Within Tolerance
Al2O3	*24.3*	*10.0*	*2*	*23.8*	*0.2*	*X*
As2O3	**0.13**	**15.0**	**0.02**	**0.13**	**0.03**	**X**
B2O3				BDL	NA	
BaO	**0.14**	**15**	**0.02**	**0.14**	**0.00**	**X**
CaO	0.81	15	0.1	1.14	0.01	
CdO	*1.22*	*15*	*0.2*	*1.23*	*0.01*	*X*
CeO2	0.27	15	0.04	0.25	0.01	X
Cr2O3	**0.14**	**15**	**0.02**	**0.09**	**0.01**	
Cs2O	0.27	15	0.04	0.28	0.02	X
CuO	0.09	15	0.01	0.09	0.01	X
Fe2O3	*34.1*	*10*	*3*	*32.9*	*1.8*	*X*
K2O	0.55	15	0.1	0.56	0.01	X
La2O3	*1.06*	*15*	*0.2*	*1.00*	*0.02*	*X*
MgO	0.21	15	0.03	0.28	0.01	
MnO	*9.94*	*10*	*1*	*9.4*	*0.2*	*X*
Na2O	*1.96*	*10*	*0.2*	*1.52*	*0.03*	
NiO	*1.76*	*10*	*0.2*	*1.95*	*0.03*	*X*
P2O5	**0.42**	**15**	**0.1**	**0.4**	**0.1**	**X**
PbO	**0.50**	**15**	**.08**	**0.54**	**.09**	**X**
SO3	0.82	15	0.1	1.6	0.2	
Sb2O5	**0.69**	**15**	**0.1**	**0.5**	**0.1**	
SeO2	**0.49**	**15**	**0.1**	**0.44**	**0.05**	**X**
SiO2	0.07	10	0.01	0.94	0.09	
SrO	*7.60*	*10*	*0.8*	*7.54*	*0.01*	*X*
TeO2	0.47	15	0.1	0.47	0.01	X
TiO2	0.21	15	0.03	0.28	0.01	
ZrO2	*11.7*	*10*	*1*	*12.6*	*0.1*	*X*

RCRA, and Target < 1 weight percent
Minor, Non-RCRA, and 0.1 < Target < 1.0 weight percent

Our study approached the problem of optimizing the HLW vitrification process parameters in two steps, discussed in detail in the two following sections of this paper.

The first step was aimed at determining the preferred waste form composition, so as to maximize the amount of waste incorporated in the glass while producing a high quality environmentally acceptable waste form. The parameters used to determine the waste glass quality were chemical durability, thermal stability, and mechanical stability. The results of the study suggested that the optimal composition be a borosilicate glass formulation including 60 weight % of dried waste (all the waste weight percentages indicated in this paper refer to a dry, calcine basis).

The second step involved the determination of the best thermal profile of the vitrification process, so as to prevent the formation of crystalline material and minimize the amount of leachants. This was accomplished by a time-temperature-transformation (TTT) study of the HLW glass for a glass formulation including 60 weight % simulated dried waste loaded material. The TTT work had the purpose of graphically demonstrating the pattern shape (TTT "nose" diagram) that bounds the initial formation of detectable crystallization with respect to time and temperature. Scanning Electron Microscopy (SEM) – Energy Dispersive Spectrometry (EDS) and X-Ray Diffraction (XRD)/Rietveld analyses supported the TTT study. This work is still in progress.

The preliminary results obtained from the two parts of our effort are described below.

OPTIMIZATION OF GLASS FORMULATION

The initial scoping melts performed for this study ranged from 45-65 weight percent dry AZ-101 waste loading. Borosilicate melts loaded with large amounts of AZ 101 waste are relatively refractory, as the washed HLW simulated by the NOAH compound has very little flux. For this reason, the upper temperature limit of 1450°C was chosen for the glass melting operation.

The vitrification process used was the following.

The simulant material was dried in a kiln. The drying procedure used throughout the work consisted in placing the material in a 300°C oven overnight. We found that the weight of the material stopped decreasing after 4 hours of permanence in the oven. The dried material was mixed into a slurry when simulating the actual melter process.

Glass compositions containing 45, 50, 55, 60, and 65 dry weight % of HLW simulant were prepared. Duplicate samples were prepared for each composition, so that each batch included two identical samples. The samples were placed in two identical alumina crucibles, and each pair of samples was melted simultaneously in a resistance furnace at 1450°C for at least 2.5 hours. One crucible was quickly removed from the furnace and air cooled by placing it onto a room temperature steel plate. The other sample remained in the furnace, which was cooled to 600°C at the rate of 1°C per minute and held at that temperature for 24 hours. The power to the furnace was then turned off and the sample was allowed to cool down inside the furnace. The air-cooled samples yielded amorphous material, while all heat treated glass showed evidence of crystallization. X-ray diffraction analysis showed the crystals to be transition metal-rich spinel.

The ASTM C-1285 Product Consistency Test (PCT)[5] and Toxicity Characteristic Leaching Procedure (TCLP)[6] methods were performed on the all the samples. As expected, all the PCT results were 20 times or more lower than the Savannah River Site (SRS) Environmental Assessment (EA) glass values, that represent the maximum allowed values.

The Cd released during the TCLP proved to be the limiting factor, as it was closest to the minimum Universal Treatment Standards (UTS) acceptable levels. All other RCRA species were significantly below the UTS regulatory levels.

All samples, air-cooled and heat-treated, were determined to satisfy the UTS criteria. However, for a waste loading above 50-55 weight percent, the release of Cd and other RCRA species increased. It was also noted that for each waste loading tested the heat-treated sample had a higher Cd release as compared with the air cooled sample.

Some chemicals ("trim" chemicals) were used in a first set of experiments to perform fine adjustments of the glass properties. The trim chemicals included small amounts of silica, SRS frit 200, sodium carbonate, and boric acid.

The experiments were repeated with no trim chemicals, and the results were reproduced. It was therefore assumed that the trim chemicals used in the first set of experiments did not produce any significant effect.

In a third set of experiments the glasses were reformulated using the same waste-loading percentages, but with different batch additives. The added chemicals in this case were silica, boric acid and zinc oxide. These formulations also yielded amorphous material for the air-cooled samples. It was found that these glasses were more chemically durable,as shown by the PCT and the TCLP tests. Cadmium content in the TCLP leachate still determined to be the waste-loading limiter for AZ-101 glass.

The TCLP data for the amount of Cd leached for the different weight percentages of waste loaded for this third set of experiments are illustrated in Fig. 1 below.
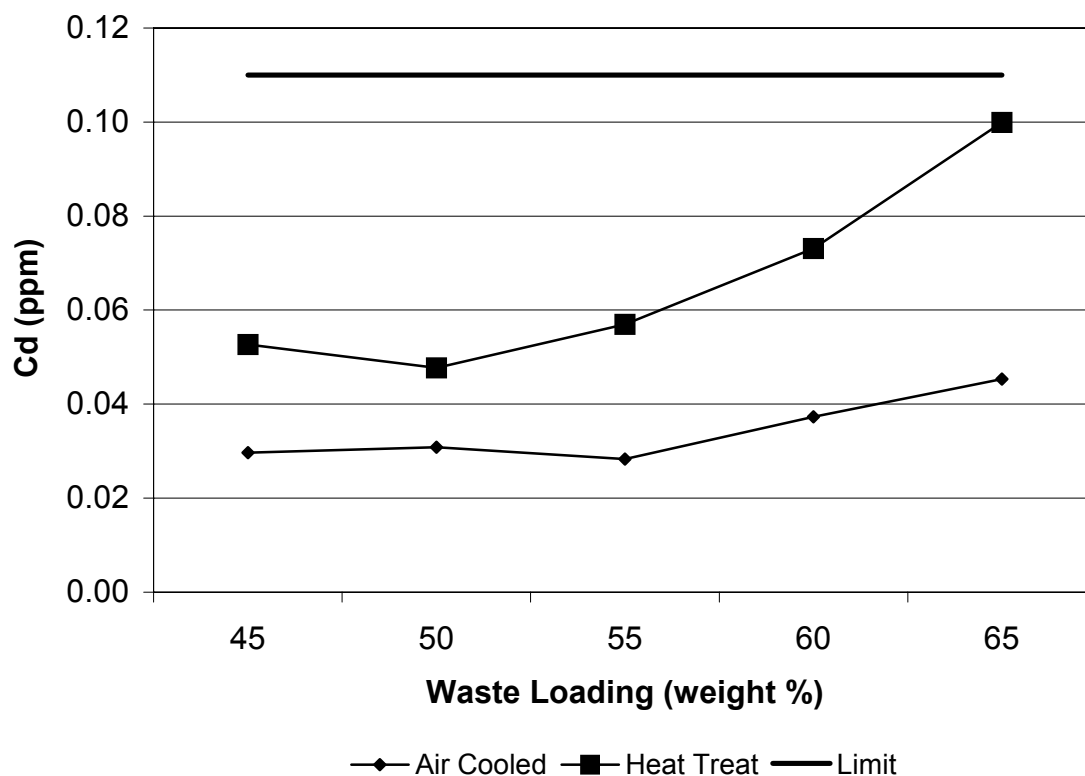
Fig. 1 - Cd concentration vs. Waste Loading

From the results shown in Fig. 1, it was decided that the 60 weight % waste loading provided a safely low level of leached Cd together with a reasonably high amount of waste incorporation.

Fig. 1 also shows that the post-melting heat treatment of the wasteform plays an important role in minimizing the amount of chemicals, in particular Cd, leached from the glass.

In view of the results shown in Fig. 1, the borosilicate waste glass composition containing silica, boric acid and zinc oxide, and 60 weight % waste simulant was chosen as the optimal composition to be used in the determination of the heat process parameters. The oxide weight composition of this glass as measured at DIAL is shown in Table 2.

Table 2 – Oxide weight composition of the glass containing 60 weight percentage of dry waste simulant used in the second part of the study.

Oxide	Wt % (normalized to 100 g)
Al2O3	16.87
As2O3	0.07
B2O3	6.11
BaO	0.08
CaO	0.73
CdO	0.69
CeO2	0.15
Cr2O3	0.16
Cs2O	0.17
CuO	0.05
Fe2O3	20.66
K2O	0.37
La2O3	0.60
MgO	0.16
MnO	5.60
Na2O	1.04
NiO	1.14
P2O5	0.20
PbO	0.32
Sb2O5	0.30
SeO2	0.00
SiO2	29.94
SO3	0.37
SrO	4.52
TeO2	0.14
TiO2	0.16
ZnO	1.92
ZrO2	7.49

Fig. 1 also shows that the post-melting heat treatment of the wasteform plays an important role in minimizing the amount of chemicals, in particular Cd, leached from the glass.

Air cooling of a large amount of radioactive melt is obviously an unpractical and hard-to-control procedure, so a controlled heat treatment process capable of reproducing or improving on the air cooling process results must be found. This issue was addressed in detail in the second phase of our research, discussed below.

TIME-TEMPERATURE-TRANSFORMATION STUDIES OF HLW SIMULANT GLASS
The HLW simulant glass formulation studied in this set of experiments was a borosilicate glass loaded with 60 weight % AZ-101 waste simulant having the weight oxide composition shown in Table 2.

The intent of the study was, as discussed above to determine the types and amount of crystallinity generated when the chosen melt composition was heat treated in different ways, study the effect of crystallization on waste form durability, and determine the pattern shape (TTT "nose" diagram) that bounds the initial formation of detectable crystallization with respect to time and temperature. This information will define a controlled heat process to produce a high quality wasteform.

A 36-point experiment was planned to generate the TTT diagram. Identical batches of the HLW simulant glass were melted, then isothermal heat treatments of the melt were performed. The temperature range selected for each heat treatment was located between the liquidus temperature and the glass transition temperature of the glass studied. The highest temperature selected was 1200°C, and the lowest temperature 500°C. The remaining four temperatures (640, 780, 920, and 1060°C) were 140°C increments between these points. The lengths of the isothermal heat treatments ranged from 0.75 hours, increasing by multiples of 4, to as long as 768 hours (32 days). Thus, the heat treatments lasted 0.75, 3, 12, 48, 192, and 768 hours.

The experiment was conducted as follows. Identical batches of the glass formulation were placed in 250cc alumina crucibles and melted at 1450°C. The crucibles were then placed in a pre-heated furnace at the appropriate temperature for the specified length of time and cooled down in the furnace. The cooled waste form was removed by sacrificing the crucible to recover the glass.

The glass produced was broken up and visually examined for uniformity. The break-up process was videotaped to preserve evidence of the fracture modes. Fragments of the glass were then prepared for analysis.

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) were performed to detect the formation of crystalline phases. Specimens randomly selected from different areas of the wasteform were mounted in epoxy, then ground and polished to a 1 μm or better finish. These cross-section specimens were then characterized using a SEM equipped with a light element EDS detector. As a standardization method, a sample of cast AZ-101 waste glass (previously characterized by dissolution followed by spectroscopic analysis) was mounted alongside the samples to be studied, allowing comparative EDS spectra to be gathered under identical conditions.

SEM examination of the samples was used to detect presence of crystals in the glass. The identification of the different crystalline phases was performed through chemical analysis of the composition by EDS. Qualitative XRD analyses were performed to determine to the crystalline phases and were complemented by Rietveld analysis of the spectra. A TTT diagram was constructed, using the percent crystallinity determinations resulting from the Rietveld analyses, as complemented by the SEM-EDS analysis of the spinel compositions. The Rietveld analysis provided a relative uncertainty of about 10% for the zircon and zirconia weight percentage. The

uncertainty in the spinel phase is considered somewhat higher because of the variability of the spinel composition across the glass matrix.

The Rietveld method requires knowledge of the crystallography for relevant crystalline phases, including standards. Multiple peaks were used for the quantitative crystallization analysis. A known quantity of NIST traceable alumina was added to all samples prior to XRD analysis. A check of the Rietveld analysis was provided by analyzing a mixture of 1) a NIST traceable material (pure zirconia, for instance) with a crystal structure similar to a crystal phase identified by qualitative XRD and 2) a sample of crystal-free, water quenched waste glass. This was performed in the range of expected crystal concentrations to determine the accuracy of the methodology for this system.

Fig. 2 shows the results of Rietveld analysis for a crystalline sample treated at 1060°C for 192 hours. The NIST-traceable material was Cr-doped aluminum oxide.
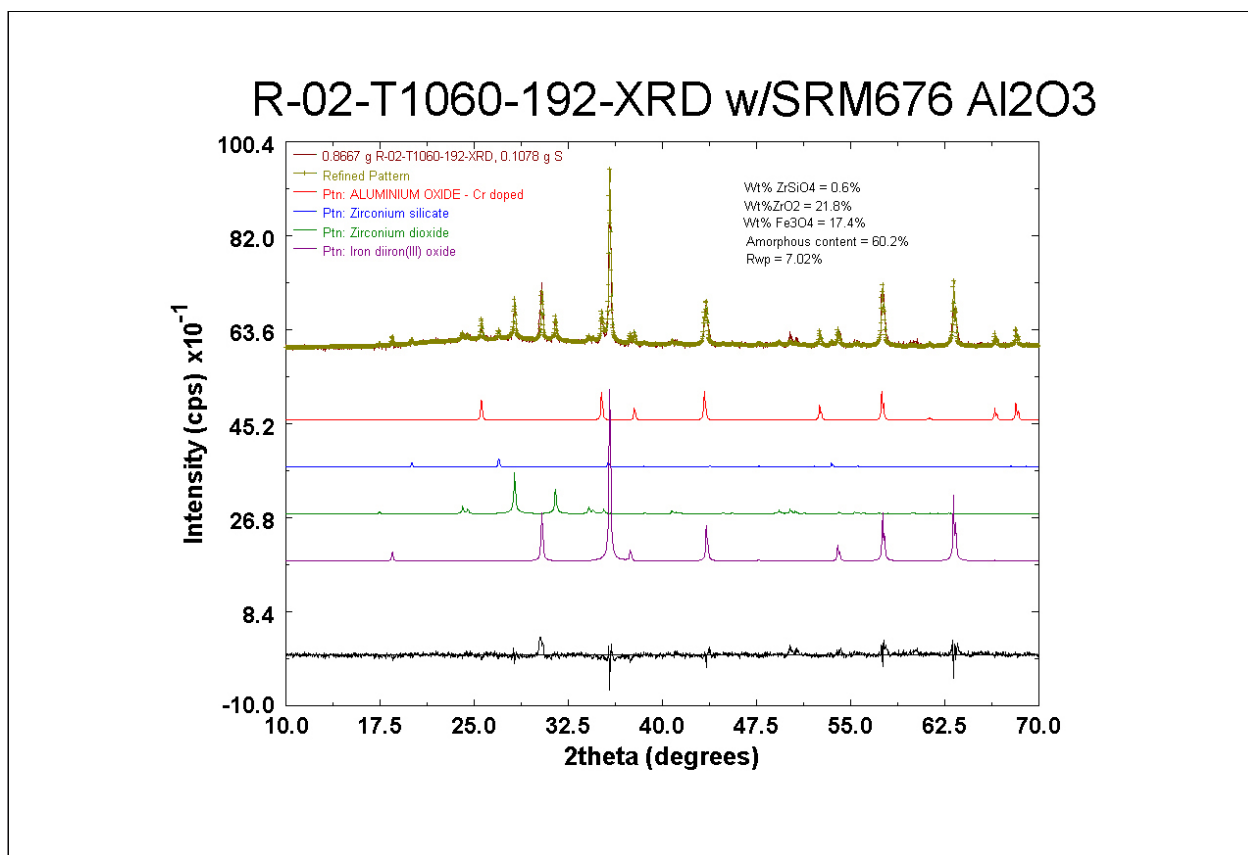

Fig. 2 –Results of Rietveld analysis from a wasteform treated at 1060°C for 192 hours.

To aid in characterization of the crystalline phase formations within glasses, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) is being performed. Specimens randomly selected from different areas of the wasteform are mounted in epoxy, then ground and polished to a 1 μm or better finish. These cross-section specimens are then characterized using a SEM equipped with a light element EDS detector. As a standardization

method, a sample of cast AZ-101 waste glass (previously characterized by dissolution followed by spectroscopic analysis) is mounted alongside the samples to be studied, allowing comparative EDS spectra to be gathered under identical conditions.

Fig. 3 below shows a SEM Backscattered Electron Image (BEI) photography of a wasteform produced by heat treating at 1200°C for 192 hours. The dark gray areas represent the amorphous matrix, while the two lighter grey areas and the white spots correspond to different crystalline phases. The different phases are labeled with the letters A, B, C, and D.
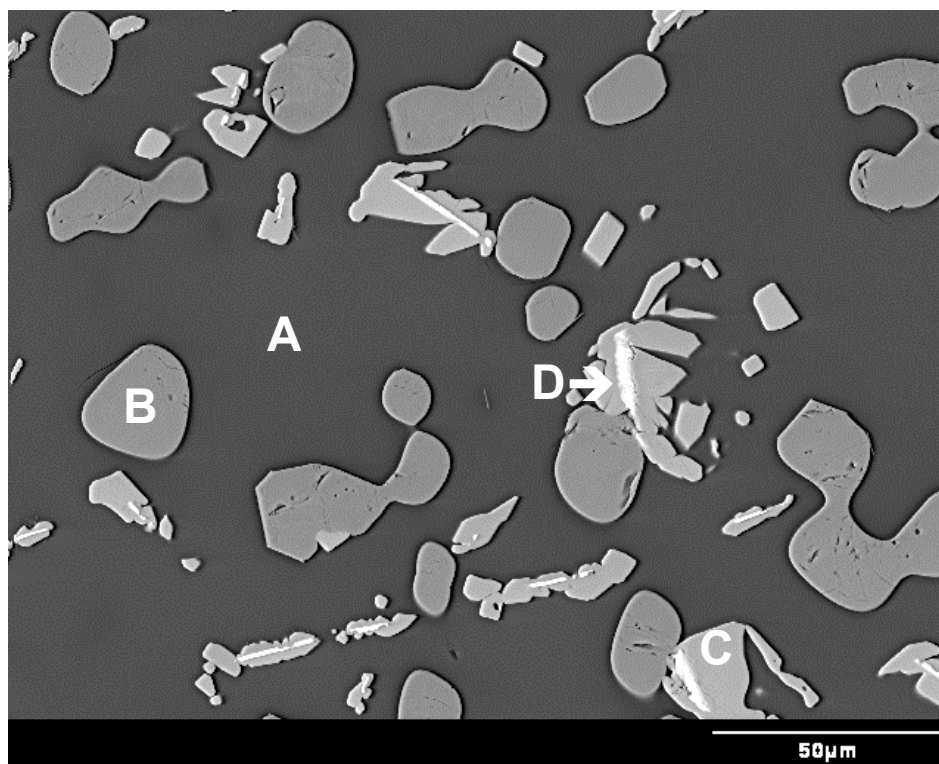

Fig. 3 - Backscattered electron image at 500x of a wasteform treated at 1200°C for 192 hours.

Table 3 shows the EDS compositions for the different areas shown in Fig. 3.

Table 3– Composition of the various crystalline phases in Fig. 2

A: Matrix Phase	B: Dark Gray Phase:	C: Medium gray Phase:	D: White Phase:
SiO_2 - 48 wt%	Fe_2O_3 - 58 wt%	ZrO_2 - 59 wt%	ZrO_2 - 78 wt%
Al_2O_3 - 20 wt%	Al_2O_3 - 15 wt%	SiO_2 - 31 wt%	SiO_2 - 10 wt%
Fe_2O_3 - 12 wt%	MnO - 6 wt%	all others < 2 wt%	Al_2O_3 - 3 wt%
SrO - 5 wt%	NiO - 6 wt%		all others < 2 wt%
ZrO_2 - 5 wt%	SiO_2 - 4 wt%		
CaO - 4 wt%	ZnO - 4 wt%		
CdO - 3 wt%	all others < 2 wt%		
all others < 2 wt%			

Thus, phase A was identified as the glass base, phase B as iron spinel, phase C as zircon, and phase D as zirconia. These identifications are consistent with the XRD analysis.

The TTT diagram shown below in Fig. 4 was constructed based on the Rietveld results obtained so far. Crystal phase boundary lines indicate the detection limit, 5 volume percent (±2 volume percent), and 15 volume percent (±2 volume percent). The dashed lines indicate approximately in which conditions the different crystalline forms are observed.
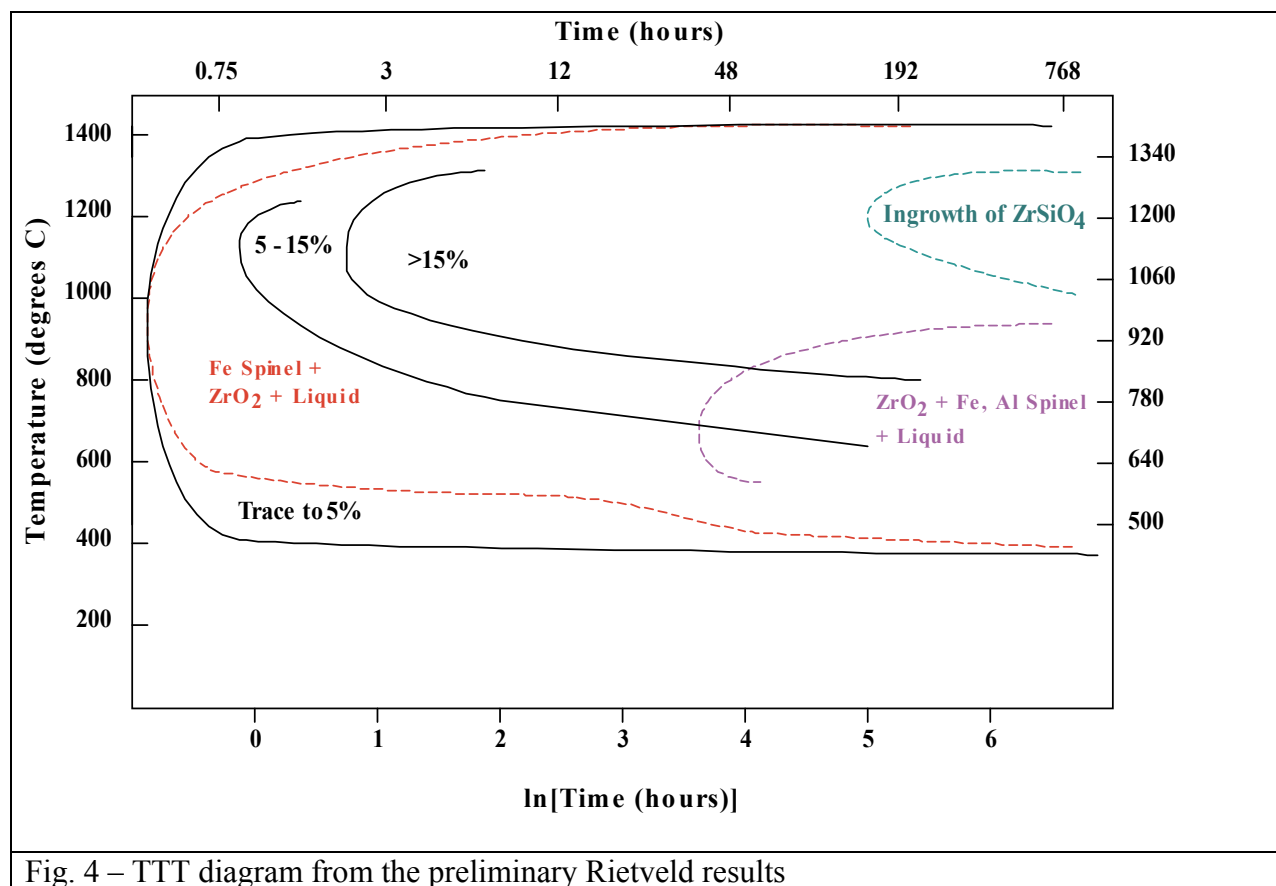
Fig. 4 – TTT diagram from the preliminary Rietveld results

Thus, by optimizing the melt cooldown procedure, it is possible to produce a low crystallinity wasteform. This wasteform incorporates up to 60% waste (dry weight) and has a density of 3.2 g/ml at 20°C, compared to 30% by weight waste incorporation and density of 2.75 g/ml at 20°C of wasteforms produced at lower melter temperatures.[3]

The 60% waste loaded wasteform (as produced and cooled in a 5 inch diameter crucible) has a significantly higher inherent crystallinity than lower waste loading forms. The samples produced during this project contain on the order of 5+ volume percentage of high-Fe spinel and a lower concentration of zirconia as compared with about 0.1 volume percentage of high Fe spinel crystals at the glass-crucible interface in the wasteform generated at lower temperature.[3]

The impact of the thermal treatments on waste form durability (as measured by the results of PCT and TCLP tests) is also under study. For the PCT, the concentration of elements reported as required by the Waste Acceptance Procedure Standards (WAPS) is being measured and plotted (in normalized release units). As with the bench-scale PCT, data for all species will be obtained and release rates reported. For the TCLP, the response from all UTS species present in the waste will be measured and plotted. Finally, the relative durability (PCT) and TCLP response will be plotted on time-temperature graphs to provide a direct visual correlation of heat treatment and product acceptance.

CONCLUSIONS

Our preliminary results show that 60% dry weight of AZ-101 simulant can be incorporated in a borosilicate matrix to produce a highly durable (as determined by the PCT method) wasteform.

The borosilicate wasteforms generated were processed at or below 1450°C. This concentration of the AZ 101 waste does lead to considerably higher crystal contents. Significant quantities of zirconia, zircon and predominately transition metal-rich spinel were identified. Heat-treated samples contained crystal contents as high as 30+ weight percent, but the chemical durability was not found to change appreciably as a function of crystallinity.

A TTT diagram was produced indicating the heat treatment time/temperature relationship with the various crystalline phases. Spinel was observed in all samples. Zircon formation was limited to high temperature and long-term heat treatments.

The study was performed as part of the development of Advanced Vitrification System (AVS), a variable temperature, in-can, inductively heated melter system currently being developed for high-level waste processing.

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[1] Waste Acceptance Product Specification for Vitrified High-Level Waste Forms, US Department of Energy, Office of Environmental Management, EM-WAPS Rev. 02, Washington, DC, December 1996.

[2] W.K. Kot, H. Gan, and I.L. Pegg, *Physical and Rheological Properties of Waste Simulants and Melter Feeds for RPP-WTP HLW Vitrification*, Final Report, VSL-00R2520-1, Rev. 0, Prepared for GTS Duratek, Inc. and BFNL, Inc., by the Vitreous Stale Laboratory, the Catholic University of America, Washington, DC 20064, October 31, 2000.

[3] W. K. Kot and I.L. Pegg, *Glass Formulation and Testing with RPP-WTP HLW Simulants*, Final Report, VSL-00R2540-2, Rev. 0, Prepared for GTS Duratek, Inc. and BFNL, Inc., by the Vitreous Stale Laboratory, the Catholic University of America, Washington, DC 20064, February 16, 2001, provided to DIAL by the DOE.

[4] HLW98-31 was identified as the simulant most closely approximating the AZ-101 composition because it is the only formulation of AZ-101 simulants that has the same ratio of Fe_2O_3 to MnO ratio as given in the DOE simulant target composition. The Fe_2O_3 to MnO ratio should not change as the glass forming compounds are added. Both the VSL and the DIAL simulants are reasonably close to the target composition.

[5] American Society for Testing and Materials (ASTM) Designation C 1285-97.

[6] Toxicity Characteristics Leaching Procedure, Test Method 1311, in "Test Methods for Evaluating Solid Waste, Physical Chenical Methods," EPA Publication SW-846.