This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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EVALUATION OF GLASS FROM THE DWPF MELTER

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ABSTRACT

The Defense Waste Processing Facility (DWPF) melter has operated for over eight years with more than six years of radioactive operations. For each sludge batch of waste processed a sample of the radioactive glass is analyzed. In conjunction with the pour stream sampling of Sludge Batch 2, a sample of the glass in contact with the pour spout insert was also collected for analysis. The samples were evaluated for chemical composition, crystal content and redox. This paper was prepared in connection with work done under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

INTRODUCTION

Two glass samples from the Defense Waste Processing Facility (DWPF) were characterized for chemical composition, crystal content and redox. The two glasses consisted of a pour stream sample taken while filling canister S01753 during processing of sludge batch 2 (SB2) and a sample from an Inconel™ pour spout insert recovered during insert removal/replacement and consisted of material that had spalled off the insert during cooling. To provide some comparative data, the analysis of SME batch 224[*] (processed shortly before or during the sampling of the pour stream) and the Savannah River Technology Center (SRTC) Tank 40 qualification sample are included.

SAMPLE ANALYSIS

Visual Observation

The two samples were placed in the SRTC Shielded Cells, removed from their primary containers, and photographed, Figure 1. The pour stream sample was contained in a platinum sampling boat and appeared dark with a reflective surface. The insert sample consisted of small thin flakes that were matte and dark

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[*] The Slurry Mix Evaporator (SME) is the vessel where the frit is added to the modified sludge prior to being transferred to the melter feed tank.

gray to black with textured surfaces that had a gritty appearance. The pour stream sample was removed from the boat using an extractor provided by DWPF-Engineering to contain the glass during impact. The pour stream sample was 40.7 grams and the insert sample was 20.2 grams.

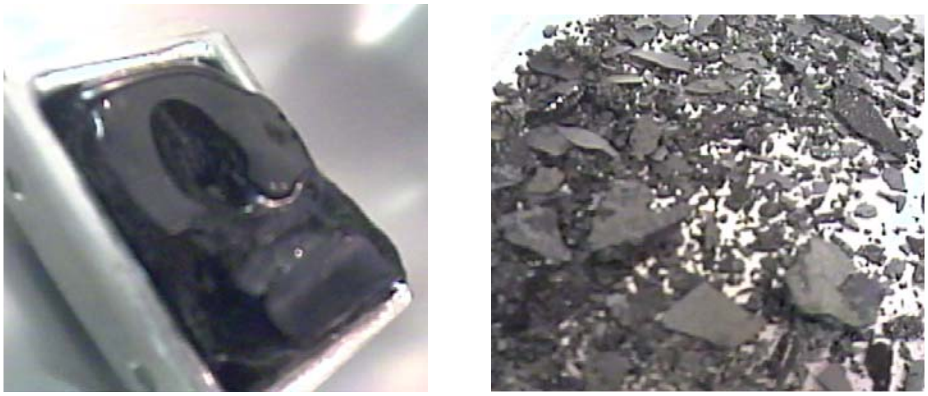

Figure 1. A) Dark and reflective pour stream sample, 40.7 grams and B) Dark gray and matte insert sample, 20.2 grams.

Chemical Composition

Samples were prepared for chemical analysis by pulverizing a portion of the glass in an agate vial with agate balls. The pulverized sample was sieved using a 100-mesh (149 µm) sieve. The –100-mesh sample was used for the dissolutions. The glass samples were dissolved by two methods[†] to account for all of the elements of interest. To provide a gross representation of the expected composition of the pour stream sample, the analysis of SME batch 224 was converted to oxides. Table I shows the composition of the two DWPF samples as well as the composition of the SRTC Tank 40 qualification sample and the measured composition of the vitrified SME batch 224. As expected, the composition of the pour stream sample resembles those of the SRTC Tank 40 qualification sample and SME batch 224. The composition of the insert sample was different from the other samples in that it was deficient in aluminum, boron, calcium, lithium, sodium, uranium, and silica. The insert sample was enriched in chromium, iron, and nickel with respect to the other samples. The low sum of oxides for the insert sample is a result of incomplete dissolution of the sample. The dissolution procedures are tailored for glass analysis and, while aggressive, is not designed for the dissolution of all ceramic materials. Table II presents the ratio of the major components of the pour stream sample to the other compositions from Table I. It can be discerned from Table II that the pour stream sample was close in composition to both the SRTC Tank 40 qualification and the SME batch 224 compositions (a ratio of 1 would indicate identical compositions

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[†] ADS-2502 – Sodium Peroxide/Sodium Hydroxide Dissolutions of Sludge and Glass for Elemental and Ion Analysis.
ADS-2227 – Acid Dissolution of Glass and Sludge for Elemental Analysis.

for an analyte). These results were expected given that the SRTC Tank 40 qualification sample is intended to be representative of Sludge Batch 2 (Tank 40). Applying the DWPF process to a sample of Sludge Batch 2 produced the SRTC Tank 40 qualification sample. The glass from SME batch 224 was vitrified and analyzed in the DWPF analytical laboratory during the processing of Sludge Batch 2. It is also apparent that the composition of the insert sample is significantly different from that of the pour stream (and SRTC TK 40 and SME batch 224) sample. The ratio of the major non-spinel forming components (Al, B, Ca, Li, Na, Si, U) is approximately 0.5, indicating that the sample is 50% glass and 50% other materials (Probably from the Inconel™ pour spout insert. The components are the same, nickel, chromium and iron, but the ratios do not precisely match).

Table I. Compositions of Pour Stream, Insert and Qualification Glasses (in wt%; NM-not measured).

	Pour Stream	**Insert**	**SRTC TK 40**[1]	**SME batch 224**
Al_2O_3	4.22	2.12	4.27	4.36
B_2O_3	7.31	3.30	8.21	7.37
CaO	1.39	0.62	1.30	1.25
Cr_2O_3	0.06	21.44	0.33[a]	0.09
CuO	0.07	0.06	0.09	0.03
Fe_2O_3	12.29	21.05	11.80	12.08
La_2O_3	0.02	0.01	0.16	0.00
Li_2O	3.29	1.70	3.51	3.21
MgO	2.35	2.18	2.49	2.27
MnO	2.14	3.09	1.38	1.42
Na_2O	11.38	5.45	11.9	10.19
NiO	0.54	7.03	0.60	0.55
SiO_2	48.73	23.05	53.1	49.42
TiO_2	0.05	0.11	0.08	0.05
U_3O_8	3.57	1.99	2.98	3.43
ZnO	0.09	0.18	NM	NM
ZrO_2	0.09	0.04	0.13	0.08
Sum	98.59	94.00	102	95.80

[a] Sample prepared in stainless steel grinder for sludge batch 2 qualification.

Table II. Ratio of Major Components of the Pour Stream Sample to the Insert Sample.

	Insert / Pour Stream	SRTC TK 40/ Pour Stream	SME batch 224/ Pour Stream
Al_2O_3	0.50	1.0	1.0
B_2O_3	0.45	1.1	1.0
CaO	0.45	0.94	0.90
Cr_2O_3	360	5.5[a]	1.5
Fe_2O_3	1.7	0.96	0.98
Li_2O	0.52	1.1	0.98
MgO	0.93	1.1	0.97
MnO	1.4	0.64	0.66
Na_2O	0.48	1.1	0.90
NiO	13	1.1	1.0
SiO_2	0.47	1.1	1.0
U_3O_8	0.56	0.83	0.96

[a] Sample prepared in stainless steel grinder for sludge batch 2 qualification.

Analysis for Noble Metals, Am-241 and Selected U-235 Fission Products in the Two Samples

The solutions that resulted from acid dissolution of the two samples were analyzed by Inductively Coupled Mass Spectroscopy (ICP-MS) for noble metals and gamma emitters to gain more detailed information about the composition of the samples. Isotopes selected were the gamma emitters detected, noble metals resulting from neutron fission of U-235, and a sampling of other U-235 fission products. Concentrations in weight percent along with the respective concentrations measured in the SRTC Tank 40 qualification sample are given in Table III. The ratios of the concentrations in respective glasses are given the last two columns of the Table III. The isotopes Co-60, Cs-137, Eu-154, Eu-155, and Am-241 were measured by gamma counting. All others were measured by ICP-MS.

The concentrations measured in the pour stream sample for most of the isotopes were nearly equal to their respective concentrations in the SRTC Tank 40 sample, Table III. Agreement is expected as the Tank 40 Qualification sample originated from the same material as the feed for the pour stream sample. This indicates that mixing in Tank 40 was sufficient to get a representative sample for the SRTC qualification demonstration For the gamma emitters, the agreement was within 20% or better. For some of the isotopes analyzed by ICP-MS the agreement was not as good. For the noble metals, isotopes of Ru and Pd were 40 to 50% higher in the pour stream than the SRTC Tank 40 sample. To the contrary, the noble metal Rh-103 had a concentration 64% less in the pour stream sample than that in the SRTC Tank 40 sample. These differences can be attributed to analytical error associated with the low concentrations of these isotopes in the glass. The measured concentrations in the samples were in some cases close to the sensitivity of the ICP-MS method; thus their relative error could be large (in some cases 30-50%).

Most of the concentrations of the radioisotopes measured in the insert sample were less than those measured in the pour stream sample. The Insert/Pour Stream column of Table III indicates that the ratio of differences was 0.4 to 0.6 as indicated by the major components in the sample that do not typically participate in spinel formation (see Table II). However, six isotopes had higher concentrations in the insert sample compared to the pour stream samples. These were Co-60 measured by gamma counting and the noble metals measured by ICP-MS. As shown in Table III, the concentration of Rh was significantly higher in the insert sample compared to the pour stream. The reason for these higher concentrations in the insert is not immediately apparent.

Table III. Comparison of Some Isotopic Concentrations (wt.%) of the SRTC Tank 40, Pour Stream, and Insert Glasses.

Isotope	SRTC Tank 40	Pour Stream	Insert	Insert/ Pour Stream[a]	Pour Stream/ Tank 40[b]
Co-60	1.50E-07	1.54E-07	5.05E-07	3.3	1.0
Tc-99	2.28E-04	2.75E-04	9.68E-05	0.35	1.2
Ru-101	2.13E-03	2.97E-03	7.02E-02	24	1.4
Ru-102	1.99E-03	2.89E-03	6.69E-02	23	1.5
Rh-103	1.71E-03	6.22E-04	1.78E-01	286	0.36
Ru-104	1.41E-03	1.91E-03	4.48E-02	24	1.4
Pd-105	1.34E-04	2.07E-04	3.35E-04	1.6	1.5
Cd-112	9.83E-03	1.06E-02	6.51E-03	0.61	1.1
Cs-137	8.93E-05	1.03E-04	4.55E-05	0.44	1.2
La-139	5.55 E-03	6.54E-03	3.72E-03	0.57	1.2
Nd-143	5.96 E-03	6.10E-03	3.29E-03	0.54	1.0
Eu-154	8.47E-07	8.45E-07	3.94E-07	0.47	1.0
Eu-155	2.36E-07	2.52E-07	1.45E-07	0.57	1.0
Am-241	2.74E-04	2.85E-04	1.17E-04	0.41	1.0

[a] Ratio should be ~0.47 by dilution of the glass components by insert material

[b] Ratio should be ~1.0 as the Tank 40 sample should be representative of the pour stream.

REDOX Analysis

To prepare samples for redox analysis, portions of the pour stream and insert materials were pulverized in an agate vial with agate balls. The Environmental Assessment (EA) glass was prepared alongside the pour stream and insert samples as a control. EA glass is reported to have a redox ratio (Fe^{2+}/Fe^{tot}) of ~ 0.18[2]. The dissolution of the samples was conducted so as to maintain the redox of the iron in the glass[3]. Not all of the dissolutions could be performed on the same day as they were measured. Therefore, some of the samples were prepared a day in advance. Previous research has indicated that the redox state of the dissolved material is stable when diluted with boric acid solution[3]. Using the method in Reference 3, dissolution of all three of the insert samples was incomplete. Incomplete dissolution is not a problem in a homogeneous glass because the redox value is a ratio. However, if there is selective dissolution of phases that contain disproportionate amounts of Fe^{2+} and Fe^{3+}, the results become meaningless. Table IV shows the results of the redox analysis. The measured redox ratio of the EA glass was greater than expected. For the amount of EA glass used (20 - 32 mg) the typical absorbance value for Fe^{tot} is 0.5 - 0.6. The average measured redox of the pour stream sample was 0.21. SME batch 224 had a predicted redox of 0.19. The relatively low absorbance of Fe^{tot} in the insert sample that had significantly more iron (Fe_{insert}/ $Fe_{pour\ stream}$ =1.7), which indicates that there were undissolved iron compounds in the insert samples. One explanation is the formation of iron-rich spinel in the insert sample. Spinels are not as readily dissolved as glasses and may not have been completely taken into solution.

Table IV. Redox of Pour Stream Sample (PSS) and Insert Sample (IS).

Sample	**Fe^{2+}/Fe^{tot}**	**Average**
EA-1	0.31[a]	
EA-2	0.37[a]	
EA-3	0.23[b]	0.30
PSS-1	0.23[a]	
PSS-2	0.20[b]	
PSS-3	0.19[b]	0.21
IS-1[c]	0.24[b]	
IS-2[c]	0.19[b]	
IS-3[c]	0.27[b]	

[a] prepared one day before analysis
[b] prepared day of analysis
[c] Sample only partially dissolved

Contained Scanning Electron Microscopy

For contained scanning electron microscopy with energy dispersive spectroscopy (CSEM/EDS), the samples ranged from eight to twelve milligrams to minimize the interference of radiation with the detector and personnel exposure. The small size of the samples limits the representative nature of the analysis. The CSEM analysis of the pour stream sample revealed uniformity across the entire sample. The insert sample viewed at 1000x appeared to have more surface texture than a typical glass sample. However, there were no ambiguous inclusions using SEI mode, Figure 2, although when the image viewed using the backscatter electron imaging (BSI) mode, several distinct features became apparent, Figure 3.

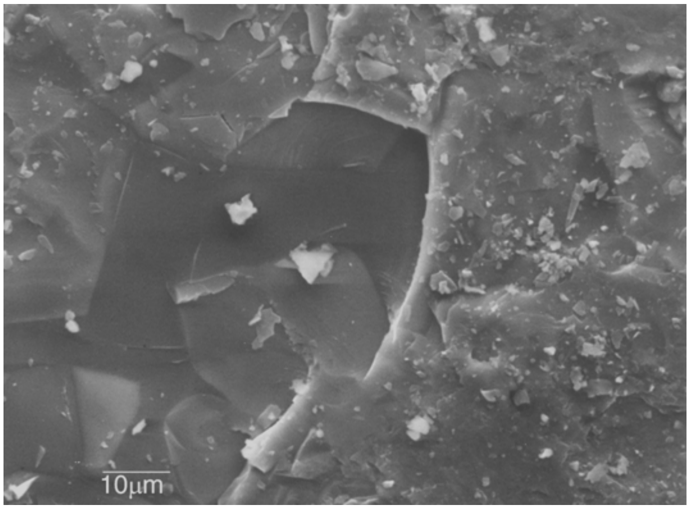

Figure 2. Micrograph of the insert sample, 1000x.

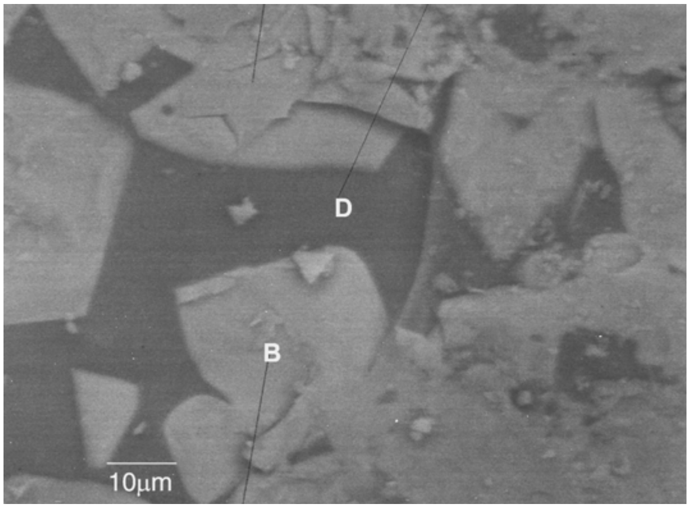

Figure 3. Micrograph of the image in Figure 3 using the BSI mode, 1000x.

EDS analysis of the insert sample revealed that there are at least three distinct compositional regions. One region, as indicated by spot "B" in Figure 3, is predominantly chromium and iron. The darker region of the photo, spot "D", has the components of a typical DWPF glass. Spot "C", not shown in Figure 3 (from a separate micrograph), is almost entirely chromium. Figure 4 is the EDS spectra for spots "B", "C", and "D". In the evaluation of the two insert samples, the majority of the material was represented by one of the three compositional regions

"B", "C", or "D". A fourth region, represented by a twenty-micron diameter region, indicates the presence of a sodium chromium sulfate. This has been detected in previous analysis of pour spout regions[4].

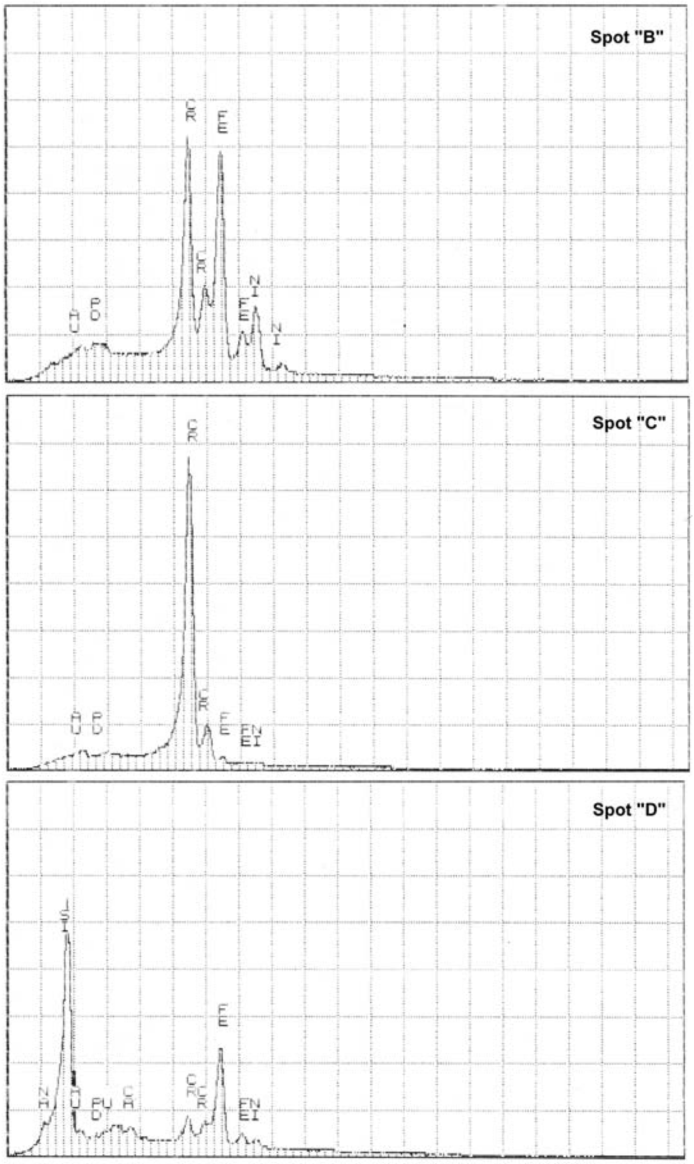

Figure 4. EDS spectra from the insert sample showing the chromium and iron rich region (spot "B"), the predominantly chromium region (spot "C", and the glass region (spot "D").

Contained X-ray Diffraction Analysis (CXRD)

In agreement with the SEM results, the XRD pattern of the pour stream sample was typical of a borosilicate glass and free of any indicators of crystalline matter.

The XRD analysis of the insert sample indicated the presence of three distinct phases. Along with the amorphous hump associated with a glassy phase, a spinel phase and a chromium oxide phase (eskolaite[‡]) were identified. The spinel phase resembles trevorite[§] with chromium partially substituting for iron and iron partially substituting for nickel. This reasoning is based on the EDS spectrum of spot "B". Figure 5 shows the XRD patterns of both the pour stream sample and the insert sample to demonstrate the differences between the two samples. With only 0.06 wt % Cr_2O_3 in the pour stream, the Inconel™ insert is most likely the primary source of the chromium for both the eskolaite and the trevorite.

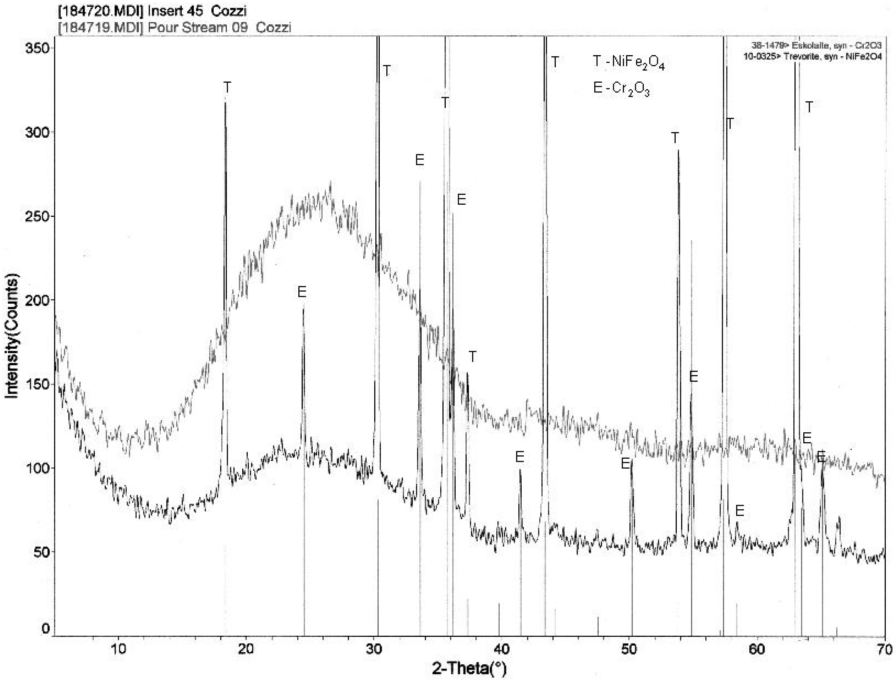

Figure 5. Overlaid x-ray diffraction patterns of the pour stream and insert samples.

CONCLUSIONS

Pour Stream Sample

Visual observation of the pour stream sample it sample to be typical of a DWPF-type glass (opaque and reflective). Compositional analysis by ICP-ES demonstrated a correlation among the pour stream sample and both the SME batch 224 and the SRTC Tank 40 qualification sample. Agreement of concentrations between the pour stream sample and the SRTC Tank 40 qualification sample was also observed for Am-241 and most of the measured U-235 fission products. However, agreement between many of the noble metal

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[‡] Eskolaite. International Centre for Diffraction Data (ICDD) card 38-1479 Cr_2O_3

[§] Trevorite ICDD card 10-0325 $NiFe_2O_4$

concentrations was poor. The average measured redox of 0.21 in the pour stream sample matches well with the predicted redox value of 0.19 for SME batch 224. CSEM analysis revealed an amorphous sample with no indication of inclusions or crystalline material. The spectrum from the CXRD analysis reinforced the amorphous nature of the sample.

Pour Spout Insert Sample

The sample was received as small, thin dark gray flakes with a matte, grainy finish. Compositional analysis of the insert sample revealed significantly greater quantities of transition elements (Cr, Fe, Mn, Ni, and Zn) and reduced amounts of other components (Al, B, Li, Na, Si and several radioactive isotopes) as compared to the pour stream sample. Samples for redox analysis were not dissolved completely and were therefore not meaningful. CSEM analysis identified four distinct compositional regions ("glass", transition metals, high chromium, sulfate salt). CXRD analysis confirms the presence of an amorphous phase, a spinel phase, and a chrome oxide phase. CSEM indicated that the sulfate content was minimal and would not be discernible by CXRD. It can be hypothesized from the compositional ratios and the CXRD results that the insert sample is comprised of approximately 50% glass and 50% crystalline material. At the temperature of the insert in the pour spout, approximately 1100°C, Inconel™ rapidly oxidizes to form a protective chrome oxide layer. Under typical operation, glass moving over the insert will not significantly react with the Inconel™. However, glass that has spattered onto the insert, out of the path of the pour stream, is given substantial opportunity to incorporate not only the oxide coating, but also a portion of the underlying Inconel™. The amount of material (pour spout insert and spattered glass) involved should not affect normal melter operations.

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