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COPPER SOLUBILITY IN DWPF, BATCH 1 WASTE GLASS - UPDATE REPORT (U)

by R. F. Schumacker

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

Other Authors:

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CC: E.W. Holtzscheiter, 773-A
N.E. Bibler, 773-A
J.T. Carter, 704-T
L.F. Landon, "
C.T. Randall, "
J.C. Marek, "
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R.A. Jacobs, "
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To: M.J. Plodinec, 773-A

From: R.F. Schumacher, 773-42A

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**Copper Solubility in DWPF, Batch 1 Waste Glass -
Update Report (U)**

SUMMARY

The "Late Washing" Step in the processing of precipitate will require the use of additional copper formate in the Precipitate Reactor to catalyze the hydrolysis reaction. The increased copper concentration in the melter feed increases the potential for metal precipitation during the vitrification of the melter feed. This report describes recent results with a conservative glass selected from the DWPF acceptable region in the Batch 1 Variability Study.

There appeared to be two major regions of copper concentration and redox ratio where this glass did not precipitate metallic copper and change the color of the normally black glass. When the copper level was less than about 0.40 wt% elemental copper in the glass, the glass did not show evidence of copper precipitation up to the DWPF redox limit of 0.33 ($\text{Fe}^{2+}/\Sigma\text{Fe}$). When the redox ratio was below about 0.07, the glass did not exhibit any signs of copper precipitation up to levels of 1.10 wt% elemental copper in the glass. In addition, when the elemental copper concentration was near 0.50 wt%, the glass redox limit for copper metal formation approached 0.10. Outside of these control regions copper may precipitate and form the small, one micron, copper crystals which may color the glass brown. It should again be stated that the glass chosen was a conservative case and glasses closer to the target glass would be less prone to the copper precipitation.

INTRODUCTION

With the adoption of a "Late Washing" step to remove the nitrites from the precipitate material and the processing of irradiated precipitate, it will be necessary to increase the amount of copper added to the Precipitate Reactor (PR). The copper acts as a catalyst for the separation of the precipitate material into an aqueous phase (PHA) and an organic benzene phase. The catalyst operating parameters could produce a copper concentration in the PHA as high as 1050 ppm (operating range - 850 to 1050 ppm). The resulting PHA is then combined with washed sludge and glass frit to form the melter feed. When the amount of copper in the PHA is combined with the copper already present in the sludge, an elemental copper level in the glass of about 0.40 wt% is expected.

The chemistry of copper in glass is complex¹ and has been quite useful in producing various glass colors in the commercial glass industry. Copper is the first member of the triad Cu-Ag-Au and occurs in glass in both ionic form and as colloidal or macroscopic metal particles. The Cu^{2+} ion produces blue to green color in glass. A state of equilibrium between ionic and metal species may be established in glass and under increasingly reducing conditions this equilibrium may lead to metallic copper: $\text{Cu}^{2+} \Rightarrow \text{Cu}^+ \Rightarrow \text{Cu}^0$. Increasing the redox condition produces a ruby red color after complete disappearance of the bivalent copper. The final color depends on the copper concentration and on the size and shape of the metal particles, so that the following variations of glass color may be created:

- colorless glass, produced by rapid cooling (Cu^+)
- copper ruby, formed by colloiddally dispersed Cu particles in equilibrium with Cu^+
- haematinon, an opaque glass of red brick color due to small metallic copper particles.

When sulfur is present in the glass, the copper may form copper sulfides such as Cu_2S .

It was previously shown in the Batch 1 variability study that under very reducing conditions the copper tended to precipitate from the glass, forming sulfides or copper alloys which settle to the bottom of the crucible². When this occurs in a Joule-heated electric melter this conductive material may form a low resistance, non-heating electrical path which creates melter operational problems. It was found that the metallic precipitation was glass composition dependent, and particularly influenced by the ferric oxide level in the glass as well as the glass redox ratio. While examining a wide range of mixtures of Batch 1 PHA, Sludge, and SRL Frit 202, it was observed that the color of the glass was either black or a mixture of black and chocolate brown. In addition, some of the crucibles had small metallic shot at the bottom which were later identified as copper-nickel alloy, copper sulfide (Cu_2S), and small inclusions of ruthenium³.

Additional microscopic and scanning electron microscopic investigation of the chocolate brown portions of the glasses identified dispersions of small particles of precipitated copper. These dispersions of one micron metallic particles were causing the brown coloration of the glass.

Previous experiments by Schreiber⁴ with additions of 1% metal oxides to SRL 131 frit measured the redox ratios of various ion pairs. Examination of Figure 1 shows that at the current DWPF redox limit of 0.33 ($\text{Fe}^{2+}/\Sigma\text{Fe}$) the oxygen fugacity is about -log 6. Following the dashed line to the right, the percentage of copper ions in the reduced cuprous state is about 80%. Of the 80% cuprous ions in the glass approximately 1% would be in the metallic state. Schreiber's investigation examined only one component additions so there were no interactions with other elements. Also please note that the results of Schreiber were extrapolated in Figure 1.

Reference: "Oxidation-Reduction Chemistry of Nonmetals in a Reference Borosilicate Melts", Schreiber, 29.1-14, H.D. et al, *Advances in the Fusion of Glass*, Ed. Bickford, D.F. June 1988, American Ceram. Soc. Westerville, Ohio

Figure 1. The Percentage of Reduced Couple Compared to the Oxygen Fugacity for 1% Additions to Frit 131.

After studying the previous references and experimental evidence, the amount of elemental copper in the glass was initially limited to 0.30 wt% of the glass⁵. This limitation applied up to the current redox ratio of $\text{Fe}^{2+}/\Sigma\text{Fe} = 0.33$.

Ramsey, et.al.⁶ after examining sealed crucible melts of doped pilot operation feed, found that it may be possible to predict the redox ratio of the glass from the difference between the analyzed formate and nitrate levels in the melter feed. The use of this relationship eliminates the need for the more difficult slurry vitrification and redox measurement⁷. Table 1 presents the redox values obtained for the three analyzed formate minus nitrate regions.

Table 1
Factors for Predicting Redox Ratio for Glass from the Formate and Nitrate
Concentration in Moles.

[F - N] (Moles)	Redox Ratio (Fe ²⁺ /ΣFe)
< 0.90	<0.10
0.90 to 1.70	0.10 - 0.60 *
>1.70	~0.60

$$* \text{ Fe}^{2+}/\Sigma\text{Fe} = -0.83 + 0.89 [\text{F}-\text{N}]$$

[F - N] = Formate - Nitrate Concentration in Moles for a Slurry with 45% Solids

It should be mentioned that while simple crucible melts do not exactly reproduce the complex melting conditions experienced in the cold cap of the DWPF Melter, they are the best guides available at present. Additional trials with IDMS-PX4 melter feed and increased copper and formic acid concentration are under way in the 774 Research Melter at this time. The purpose of the present effort was to investigate the limits of copper solubility with respect to the glass redox ratio of the waste glass.

EXPERIMENTAL

During the Batch 1 Mixture Study it was found that glasses with higher levels of PHA and lower levels of sludge were more prone to the precipitation of copper metal alloys. In order to be conservative, Glass No.8 with 12.5 wt% PHA, 25 wt% sludge, and 62.5 wt% Frit 202, as shown in Figure 1, was selected as a base glass for additional experimentation. Glasses closer to the target glass would be less prone to precipitation of copper. A number of additional scoping studies were undertaken prior to the present investigation using copper acetate and copper oxide as the source of the copper for the batch. Concerns over the homogeneous distribution of the copper oxide in the batch and redox considerations with the copper acetate, prompted this investigation which employed copper nitrate as the copper source. Copper nitrate is both soluble in water and acts as an oxidizer in glass.

Three 1200 gram batches of Glass No. 8 were prepared by weighing reagent materials as shown in attached Table 2. After weighing, the raw batch was mixed in mortar & pestle with additions of 90% formic acid, deionized water, and small amounts of copper nitrate (Cu(NO₃)₂·2.5 H₂O). The 1200 gram master batch was dried at 90 to 105°C and split into 12 equalized samples of about 100 grams each. Specific additions of 90% formic acid and copper nitrate were made to each of these samples and the batch re-mixed. The copper nitrate is very soluble and should be distributed evenly throughout the mixture. These samples were again dried at 90 to 105°C.

Figure 1. The Batch 1 Ternary Mixture Study with Individual Glasses Numbered. The Outlined Region is an Approximation of the DWPF Operating Region.

Portions of these samples were placed in numbered 100 ml dense alumina crucibles and the lid sealed by coating the contact area with a slurry of the batch. The crucibles were placed in a programmable molybdenum disilicide furnace and heated to 1150°C at $10^\circ\text{C}/\text{min}$. At about 950°C the crucible lids were pressed down to promote sealing of the crucible. The glass was melted for one hour at 1150°C and the sealed crucibles removed from the furnace. The crucibles were allowed to cool to room temperature.

The crucibles were opened, the condition of the seal observed, and the glass was inspected for color (black or brown). Any precipitation of metallic particles at the bottom was also noted. Pieces of the glass were submitted for determination of the glass redox ratio.

RESULTS AND DISCUSSION

The results of thirty six vitrifications of Glass No. 8 with varying concentrations of elemental copper and formic acid additions are presented as Table 3. Included in Table 3 is the crucible number, elemental copper concentration in weight percent, the formic acid concentration in moles/kg, a visual description of the glass, and the glass redox ratio. The results are reported in three sections indicating the three 1200 gram batches employed.

Table 3
Glass No. 8 with Levels of Copper Nitrate and Formic Acid

NB No. E-51767-145	Cu Wt%	Formic Moles/Kg	Description	Redox Ratio Fe ²⁺ /ΣFe
- 1	0.4	2.39	Black, No Brown, No Metal	0.237
- 2	0.5		Black, Brown???, No Metal	0.197
- 3	0.6		Black, Little Brown, No Metal	0.233
- 4	0.7		Black, Brown, No Metal	0.214
- 5	0.4	1.59	Black, No Brown, No Metal	0.086
- 6	0.5		Black, No Brown, No Metal	0.088
- 7	0.6		Black, No Brown, No Metal	0.055
- 8	0.7		Black, No Brown, No Metal	0.056
- 9	0.4	0.80	Black, No Brown, No metal Foam	0.025
- 10	0.5		Black, No Brown, No metal Foam	0.019
- 11	0.6		Black, No Brown, No metal Foam	0.022
- 12	0.7		Black, No Brown, No metal Foam	0.068
<u>E-51767-153</u>				
- 1	0.4	6.36	Black, Little Brown, No Metal	0.106
- 2	0.5		Black, Brown, No Metal	0.109
- 3	0.6		Black, Brown, No Metal	0.144
- 4	0.7		Black, Brown, No Metal	0.077
- 5	0.4	4.77	Black, No Brown, No Metal	0.066
- 6	0.5		Black, Little Brown, No Metal	0.180
- 7	0.6		Black, Brown, No metal	0.219
- 8	0.7		Black, Brown, No metal	0.364
- 9	0.4	3.18	Black No Brown, No Metal	0.102
- 10	0.5		Black, Streaks Brown, No Metal	0.104
- 11	0.6		Black, Brown, No Metal	0.130
- 12	0.7		Black, Brown, No Metal	0.206
<u>E-57158-4</u>				
- 1	0.8	4.77	Black Top, All Brown Inside, No Metal	0.274
- 2	0.9		Black Top, All Brown Inside, No Metal	0.190
- 3	1.0		Black Top, All Brown Inside, No Metal	0.211
- 4	1.1		Black Top, All Brown Inside, No Metal	0.310
- 5	0.8	3.18	Black Top, Streak Brown. No Metal	0.136
- 6	0.9		Black Top, Streak Brown. No Metal	0.128
- 7	1.0		Black Top, Streak Brown. No Metal	0.186
- 8	1.1		Black Top, 70%Brown No metal	0.145
- 9	0.8	1.59	Black, No Brown, (Air Leak) Foamed	0.052
- 10	0.9		Black, No Brown, (Sealed) Foam	0.046
- 11	1.0		Black, No Brown, (Air Leak) Foam	0.058
- 12	1.1		Black, No Brown, (Air Leak) Foam	0.057

From the results presented in Table 3 it was possible to prepare a map of the regions of brown glass and regions of black glass. The brown glass region was caused by the precipitation of small copper crystals. Some of the highly oxidized glasses appeared to foam during vitrification in the crucible but produced black glass. These black and brown colored glasses are presented in Figure 2 and tend to form regions of similar color.

Figure 2. Regional Map Comparing Levels of Elemental Copper to the Redox Ratio for Glass No. 8.

Extensive experimental evidence with the various experimental melters and crucible melts has shown that when the copper level was less than 0.30 wt% elemental copper in the glass, the glass was observed to be glossy black up to the current DWPF redox limit of 0.33 $\text{Fe}^{2+}/\Sigma\text{Fe}$. Evidence from this study suggests that when the redox ratio was below about 0.07, the glass remained glossy black up to a copper level of 1.10 wt% elemental copper in the glass. In addition when the elemental copper concentration was near or below 0.50 wt%, the glass redox limit for copper metal formation approached 0.10 $\text{Fe}^{2+}/\Sigma\text{Fe}$. Beyond these approximate regions copper precipitated and formed the small, one micron, copper crystals which colored the glass brown. It should again be stated that Glass No. 8 was conservative and glasses closer to the target glass would be less prone to the copper precipitation.

CONCLUSIONS

The following conclusions were drawn from this investigation:

1. When the glass redox ratio was equal to or less than 0.07 and had an elemental copper concentration equal to or less than 1.0 wt% in the glass - the glass was free from metallic copper precipitation.
2. When the elemental copper concentration in the glass was approximately 0.50 wt% it was possible to extend the redox ratio limit to 0.10 without initiating copper precipitation in the glass.

QUALITY ASSURANCE

This task was conducted in response to the specific objective in the "Task Assignment for the DWPF Batch 1 Variability Study"⁸ and was controlled according to the "Batch 1 Variability Study" task plan⁹ and the controls established in the Glass Technology Procedures Manual¹⁰. Specific information on tests and the resulting data was included in two notebooks^{11,12}. A records package covering the copper solubility effort is being prepared.

ACKNOWLEDGEMENTS

I wish to acknowledge the consistent efforts of Roberta Hooks in performing all of these tests and organizing the analyses under the severe time constraints placed on this task. I also wish to acknowledge the very rapid response time from the ADS for their determinations of glass redox ratio, formate-nitrate concentrations, copper concentrations and the SEM-microscopy efforts. I especially appreciate the input from W.G. Ramsey on the formate-nitrate relationship and the slurry redox test.

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11. Notebook No. E-51767, DPSTN-4649, Last Entry 7/30/92.
12. Notebook No. E-57158, WSRC-NB-89-29.

ATTACHMENTS

Table 2

OXIDE	FORM WT	SLUDGE INPUT WT%	PHA INPUT WT%	FRIT 202 WT%	GLASS COMP WT%	SLUDGE +PHA WT	RAW MATERIAL	FORM WT	BATCH 12 Gms.	ACTUAL WEIGHT	OXIDE	WEIGHT Gm.	WEIGHT %	Moles in Glass	Mole % Oxide
Ag2O	231.76	0.000	0.000	0	0.000	0.000	Al2O3	101.94	52.38	52.383	Al2O3	52.383	4.366	0.043	3.13%
Al2O3	101.94	16.861	1.200	0	4.365	4.365	BaCl2*2H2O	244.28	3.10	1.946	BaO	1.946	0.162	0.001	0.08%
BaO	153.36	0.243	0.811	0	0.162	0.162	2(H3BO3)	123.66	78.06	43.958	B2O3	43.958	3.663	0.124	9.09%
B2O3	69.64	0.000	29.305	8	8.663	3.663	CaCO3	100.09	22.32	12.504	CaO	12.504	1.107	0.020	1.44%
CaO	56.08	4.389	0.076	0	1.107	1.107	CaF2	78.08	1.08	0.777	CaO	0.777			
Cr2O3	152.02	0.356	0.017	0	0.091	0.091	Na2Cr2O7*2H2O	298.00	2.14	1.094	Cr2O3	1.094	0.091	0.001	0.04%
Ce2O	281.81	0.007	0.995	0	0.126	0.126	2(CsCl)	336.72	1.81	1.514	Ce2O	1.514	0.126	0.000	0.03%
ClO	79.57	0.185	3.801	0	0.521	0.521	Cu(NO3)2*5H2O	232.60	18.29	6.257	ClO	6.257	0.521	0.007	0.48%
Fe2O3	159.70	44.123	0.807	0	11.132	11.132	Fe2O3	159.69	133.58	133.580	Fe2O3	133.580	11.133	0.070	5.09%
H2O	216.61	0.000	0.000	0	0.000	0.000	K2CO3	138.20	82.98	56.553	K2O	56.553	4.713	0.050	3.65%
K2O	94.19	0.392	36.918	0	4.713	4.713	MgO	40.32	1.07	1.071	MgO	1.071	0.089	0.033	2.43%
Li2O	29.88	0.000	0.000	7	4.375	0.000	MnO2	86.94	26.97	26.969	MnO2	26.969	2.248	0.026	1.89%
MgO	40.32	0.354	0.006	2	1.339	0.089	2(Nd(NO3)3*6H2O)	876.78	16.96	6.509	Nd2O3	6.509	0.542	0.002	0.12%
MnO2	86.92	8.911	0.157	0	2.247	2.247	Na2CO3	105.99	106.54	65.994	Na2O	65.994	5.500	0.143	10.90%
Na2O	61.99	12.767	18.462	6	9.250	5.500	Na2SO4	142.04	6.44						
NiO	74.69	2.647	0.047	0	0.668	0.668	NO	74.71	8.01	8.012	NiO	8.012	0.668	0.009	0.65%
P2O5	141.96	0.095	0.028	0	0.027	0.027	2(Na3PO4*12H2O)	760.24	1.75	0.327	P2O5	0.327	0.027	0.000	0.01%
PbO	223.21	0.407	0.007	0	0.103	0.103	PbO	223.19	1.23	1.232	PbO	1.232	0.103	0.000	0.03%
PbO	122.70	0.000	0.000	0	0.000	0.000	RuCl3*1-3H2O	207.40	0.55	0.294	RuO2	0.294	0.025	0.000	0.01%
PuO2	274.00	0.000	0.000	0	0.000	0.000	SiO2	60.06	12.63	12.626	SiO2	12.626	1.052	0.819	59.80%
PuO2	134.90	0.000	0.000	0	0.000	0.000	Sr(NO3)2	211.63	0.59	0.291	SiO2	0.291	0.024	0.000	0.02%
PuO2	133.08	0.097	0.002	0	0.025	0.025	TiO2	79.90	10.82	10.824	TiO2	10.824	0.902	0.011	0.82%
SiO2	60.06	4.175	0.067	77	49.177	1.052	ZrO	1.37	0.93	0.933	ZrO	0.933	0.078	0.001	0.07%
SiO	103.63	0.096	0.002	0	0.024	0.024	ZrO2	123.22	4.26	4.259	ZrO2	4.259	0.355	0.003	0.21%
ThO2	264.12	0.000	0.000	0	0.000	0.000				449.901		37.495			
TiO2	79.90	0.000	7.216	0	0.902	0.902	Frit 202	750.00		750.000		62.505			
UO2	270.07	0.000	0.000	0	0.000	0.000									
Y2O3	225.84	0.034	0.001	0	0.009	0.009	Total	1344.48		1199.90		100.00	1.369		
ZrO	81.37	0.308	0.006	0	0.078	0.078	Yield	0.89							
ZrO2	123.22	1.407	0.025	0	0.355	0.355									
Nd2O3	336.54	2.148	0.043	0	0.542	0.542	Formic Acid(20%)	46.03	72ml						
Total	100.002	99.999	100	100	100.000	37.500	Formic Acid(10%)	46.03	36ml						
						Organic	xxx	0.00							
F	0.168	0.015	0	0	0.044	0.044	F2	38.00	0.53						
Cl	1.326	0.058	0	0	0.339	0.339	Cl2	70.91	1.28						
SO3	0.737	0.945	0	0	0.302	0.302	SO3	80.07	3.63						
NO3							NO3	62.01	12.50						
Sludge		0.250	ALK +B/ Si =		0.679										
PHA		0.125	Viscosity =		23.882	Poise									
Frit		0.625													
Total		1.000													

C (Formic Acid) = Approx.1.0 wt%

-8.000

TABLE 2. GLASS NO. 8 TYPICAL WEIGH SHEET

**DATE
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4 / 19 / 93