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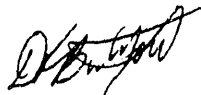
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CONTROL OF HIGH LEVEL RADIOACTIVE WASTE-GLASS MELTERS - PART 5: MODELLING OF COMPLEX REDOX EFFECTS (U)

by



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CONTROL OF HIGH LEVEL RADIOACTIVE WASTE-GLASS MELTERS- PART 5: MODELLING OF COMPLEX REDOX EFFECTS

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ABSTRACT

Slurry Fed Melter (SFM) are being developed in the United States, Europe and Japan for the incorporation of high-level radioactive waste in borosilicate glass for permanent disposal. The high transition metal, noble metal, nitrate, organic, and sulfate contents of these wastes lead to unique melter redox control requirements. Pilot waste-glass melter operations have indicated the possibility of nickel sulfide or noble-metal fission-product accumulation on melter floors, which can lead to distortion of electric heating patterns, and decrease melter life. Sulfide formation is prevented by control of the redox chemistry of the melter feed.

The redox state of waste-glass melter is determined by balance between the reducing potential of organic compounds in the feed, and the oxidizing potential of gases above the melt, and nitrates and polyvalent elements in the waste. Semiquantitative models predicting limitations of organic content have been developed based on crucible testing. Computerized thermodynamic computations are being developed to predict the sequence and products of redox reactions and in assessing process variations. Continuous melter test results have been compared to improved computer staged-thermodynamic-models of redox behavior. Feed chemistry control to prevent sulfide and moderate noble metal accumulations are discussed.

DISCUSSION

The durability and processing properties of the Defense Waste Processing Facility (DWPF) glass product will be kept within the necessary operating ranges by controlling the chemical composition of the melter feed. The glass redox state will be controlled by limiting the total formate to total nitrate ratio of the melter feed transferred from the Slurry Mix Evaporator (SME) to the Melter Feed Tank (MFT). During the course of normal operations there may be occasions when it is desirable or necessary to change the amount of organics going to waste glass melter.

Examples are coal contained in some of the waste, cleaning of equipment with oxalic acid or organic cleaners, cleaning of equipment with caustic or KOH (which are most easily neutralized with formic acid), overbatching of formic acid to the SRAT/SME, or passage of a slug of high boiling point organics from the precipitate hydrolysis process.

Limitations on organic to the melter consist primarily of fusion and Fe(II)/Fe(III) determination of a small sample of SME product prior to forwarding the product to the melter feed tank, and monitoring of % of the Lower Explosive Limit (LEL) in the melter offgas. The Fe(II) / Fe(III) determination is a conservative check on the amount of organic distributed evenly in the feed, since there is essentially no oxidation by air in this test. The monitoring of the % LEL integrates the reactions between the organics, the oxidants, the combustion conditions, and dilution air.

The primary concerns in the waste glass melter with respect to organics in the melter feed include:

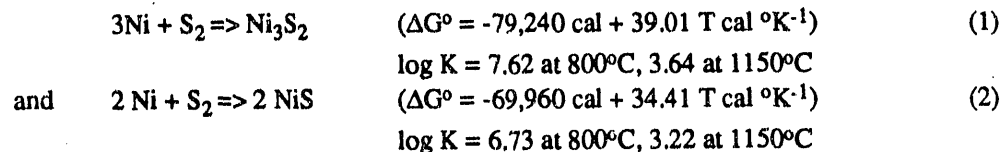
- 1) Preventing nickel sulfide precipitation in glass.
- 2) Minimizing noble metal settling in the melter.
- 3) Providing sufficient oxidant to promote combustion of volatiles.
- 4) Maintaining the offgas system below 60% of Lower Explosive Limit.

PREVENTION OF NICKEL SULFIDE ACCUMULATION IN THE MELT

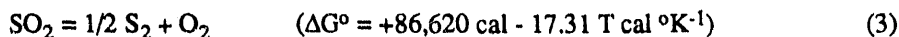
The precipitation of nickel sulfide in the melter could result in shorting of the bottom electrodes of the melter. The electrical response of the melter has been reported based on a 2 dimension physical model [6]. This analysis will focus on the chemical conditions which will result in formation and retention of a nickel sulfide phase. With current feed, the nitrates and formic acid are closely balanced, and only slightly reducing, with a glass Fe(II) / Fe(III) of about 0.05 .

If all the nickel contained in blended waste-melter feed were precipitated as nickel sulfide, it could accumulate at the maximum rate of 4.75 cm/y . Nickel sulfide precipitates at a slightly higher oxygen fugacity than iron sulfide, so this also precludes the possibility of iron sulfide, which could accumulate up to 12.59 cm/y under extremely reducing conditions.

Nickel sulfide can have varying stoichiometry at melter temperatures. The Gibbs Free Energies for two stoichiometric sulfide reactions have been tabulated [11]:



In both cases the sulfide would be in its standard state, and it is conservative to assume that the nickel is also in its standard state. (Dissolution of the nickel oxide and sulfur in the glass would tend to drive the reactions to the left, reducing the tendency to precipitate nickel sulfide.) Therefore, the sulfides will not precipitate if the sulfur is not reduced:



Since SO_2 will escape if its partial pressure is above 1 atmosphere, it is conservative to assume SO_2 in its standard state. Then S_2 will form (in its standard state) when:

$$\Delta G^\circ = +86,620 \text{ cal} - 17.31 \text{ T cal } ^\circ\text{K}^{-1} = -4.574 \text{ T log } (p_{\text{O}_2}) \quad (4)$$

$$\text{or } \log (p_{\text{O}_2, \text{atm}}) < -18937 / \text{T} + 3.784 \quad (5)$$

For example, when $\log (p_{\text{O}_2}) < -13.86$ at 800°C , or < -9.52 at 1150°C , nickel sulfide precipitation is possible. The solution for equation 3 has also been published as a graph with corresponding $\text{H}_2 / \text{H}_2\text{O}$ and CO / CO_2 reducing agents [12]. The limiting values are

$$\text{H}_2 / \text{H}_2\text{O} > 1/100 \text{ at } 800^\circ\text{C}, > 1/20 \text{ at } 1150^\circ\text{C} \quad (6)$$

$$\text{and } \text{CO} / \text{CO}_2 > 1/200 \text{ at } 800^\circ\text{C}, > 1/10 \text{ at } 1150^\circ\text{C} \quad (7)$$

That is, when gas ratios in equilibrium with glass exceed these values nickel sulfide precipitation can not be precluded. Or, in other words, waste glass with nickel sulfide precipitates can be considered to be in equilibrium at 1150°C with a mixture of 5% H_2 / 95% H_2O , or 10% CO / 90% CO_2 .

Schreiber has directly evaluated the $\text{Ni}(0)$ to $\text{Ni}(\text{II})$, $\text{Ni}(\text{II})$ to $\text{Ni}(\text{III})$ and S^\ominus to SO_4^\ominus reactions for redox species in SRL Frit 131 [4]. In his case, standard state could be considered to be 0.5 wt% of the redox specie, and the oxygen fugacities read at the 50% reduced position. Sulfate is effectively reduced at 1150°C when $p_{\text{O}_2} < 10^{-9.5}$ atm, which corresponds almost exactly to the results of the normal standard state calculations of Equation 5 above. To provide some margin for composition variations, and errors in the $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$ determination it is therefore reasonable to establish an absolute limit of

$$p_{\text{O}_2} > 10^{-8} \text{ atm at } 1150^\circ\text{C} \quad (8)$$

$$\text{or } \text{Fe}(\text{II}) / \text{Fe}_{\text{total}} < 0.50 \text{ for a sample fused at } 1150^\circ\text{C} \text{ in a closed crucible,}$$

$$\text{or } \text{Fe}(\text{II}) / \text{Fe}(\text{III}) < 1.0 \text{ for a sample fused at } 1150^\circ\text{C} \text{ in a closed crucible.}$$

This is much more reducing than where waste melter have been normally operated, and the effect of sustained reducing conditions on melter electrodes and other components are unknown. Direct measurements of melting glass show that the melt is normally very reducing in its early stages [1,3], which indicates that the effect on melter materials is probably not severe. However, Reference 3 also indicates that the melter relies upon the final 100 to 150°C in the melting process to eliminate any sulfide formed, and test melters have frequently been idled under oxidizing conditions. It is therefore prudent to establish **Preliminary Operating Goals** to preclude nickel sulfide accumulation:

$$p_{\text{O}_2} > 10^{-6} \text{ atm at } 1150^\circ\text{C} \quad (9)$$

$$\text{or } \text{Fe}(\text{II}) / \text{Fe}_{\text{total}} < 0.25 \text{ for a sample fused at } 1150^\circ\text{C} \text{ in a closed crucible,}$$

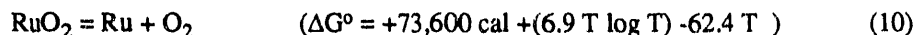
or $\text{Fe(II)} / \text{Fe(III)} < 0.33$ for a sample fused at 1150°C in a closed crucible.

This Operating Goal could be relaxed to levels closer to those of the absolute limit, but only after demonstration of the analytical methods in the actual facilities, and after sustained operation of pilot sized melter under the proposed conditions.

NOBLE METAL PRECIPITATES

Ruthenium is the predominant noble metal fission product in DWPF melter feed. Ruthenium is a concern because neither it nor its dioxide dissolve in waste glass [12], and both have high densities and high electrical conductivities. Thus, ruthenium and other noble metals tend to settle to the bottom of waste glass melter and short circuit the bottom electrodes. The electrical effects of this have been summarized in Reference [6].

Since ruthenium and ruthenium dioxide have negligible solubility in waste-glass, it is possible to closely predict ruthenium redox behavior using standard state equilibrium calculations for waste glass melting.



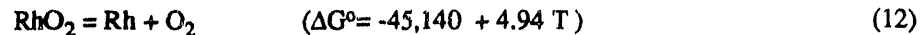
Since both RuO_2 and Ru are in their standard states:

$$-4.574 \text{ T} \log (p_{\text{O}_2}) = +73,600 + (6.9 \text{ T} \log \text{ T}) - 62.4 \text{ T} \quad (11)$$

$$\text{or} \quad \log (p_{\text{O}_2}) = -16,090/\text{T} - (1.51 \log \text{ T}) + 13.64 \text{ (atm, } ^\circ\text{K)}$$

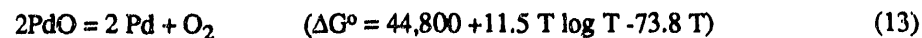
Therefore, if $\log (p_{\text{O}_2}, \text{ atm}) < -5.94$ at 800°C, or < -2.43 at 1150°C, then the ruthenium is in equilibrium with the glass as Ru(0) , rather than as the oxide. This corresponds to a low $\text{Fe(II)} / \text{Fe(III)} = \text{Fe(II)} / \text{Fe}_{\text{total}}$ of > 0.03 . Thus, in most instances the Ru in DWPF glass will be as Ru(0) , but could tend to oxidize to RuO_2 during melter idling. This should also be true of the WVDP and HWVP melts, since both use reducing agents. However, the PNC and the German and Japanese melter feeds are nitric acid based and will not go reducing, their glasses therefore contain RuO_2 .

Rhodium is the next most common noble metal present in SRS high level radioactive waste. It is not oxidized in waste glass:



$$\log K = \log (p_{\text{O}_2, \text{ atm}}) = +7.92 \text{ at } 800^\circ\text{C}, +5.86 \text{ at } 1150^\circ\text{C}$$

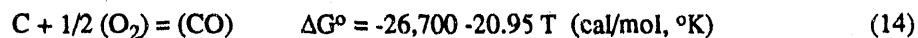
Palladium is also present in the DWPF feed. As with the other noble metals, there is little tendency for it to be dissolved in the glass, and it is found as round particles. It is less likely to be oxidized than ruthenium, and the oxide is not stable at normal melter conditions:



$$\log K = \log (p_{O_2, atm}) = -0.63 \text{ at } 800^\circ\text{C}, +1.32 \text{ at } 1150^\circ\text{C}$$

CARBON AS A REDUCING AGENT

Pure carbon is a powerful reducing agent, capable of carbothermic reduction of most metal oxides to the metal. It is produced by pyrolysis of formates or sugar [1]. With excess carbon:



$$\Delta G^\circ = + 52,840 \text{ cal} + 42.7 T = -4.574 T \log K = -4.574 T \log ([p_{O_2} * [C]] / p_{CO}^2)$$

Since $[C] = 1$:

$$\log (p_{O_2} / p_{CO}^2) = -11,550/T - 42.7 \quad (\text{e.g. } -50.8 \text{ at } 1150^\circ\text{C}) \quad (16)$$

When there is insufficient carbon present to complete the reaction, less reducing mixtures of CO/CO₂ are produced:



$$\log p_{O_2} = -17 \text{ at } 800^\circ\text{C}, -10 \text{ at } 1150^\circ\text{C} \text{ if } 10 p_{CO} = p_{CO_2}$$

Carbon is a less powerful reducing agent when water vapor is present. This is the result of the "water gas shift", where water oxidizes part of the CO to CO₂, and H₂ is liberated.



In this case the oxygen fugacity is limited by the formation and decomposition of water:



$$\log p_{O_2} = -16 \text{ at } 800^\circ\text{C}, -10 \text{ at } 1150^\circ\text{C} \text{ if } 10 p_{H_2} = p_{H_2O}$$

Thus, equilibrium thermodynamics indicates that waste glass with nickel sulfide precipitates can be in equilibrium with carbon almost completely oxidized to CO₂, and hydrogen almost completely oxidized to water. X-ray diffraction analysis of partially melted waste glass samples indicates that carbonaceous reducing agents tend to pyrolyze or dehydrate below about 500°C [1]. Most of the transition metals in waste are not reactive at this low a temperature, and are therefore not directly influenced by most of the hydrogen in the reducing agents.

RELATIVE EFFECT OF REDUCING AGENTS IN WASTE GLASS

The preceding calculations are based upon equilibrium thermodynamic calculations. They indicate the general trends that can be foreseen, and set limits on the strength of reduction that is

necessary to cause certain reactions, as for example the precipitation of nickel sulfide. There are two general ways in which such calculations can be misleading. First, there is the question of reaction kinetics: a portion of the reducing agents may volatilize and escape the glass before they are effective as reducing agents. This general method is accepted in the glass industry for prediction of redox with relatively small amounts of redox species under stable operating conditions [16,17].

The second concern is the actual reaction path that is followed: It is possible in specifically designed apparatus to fully react the weak reducing agents first, when they are most effective, and then sequentially react the stronger reducing agents. This is analogous to a counterflow chemical reactor, and can be more effective in reducing the glass than a simultaneous reaction of all of the reducing agents. Based upon a comparison of the water gas shift reaction to the sulfur/SO₂ reaction, hydrogen will be thermodynamically almost as effective a reducing agent as carbon or carbon monoxide. Thus, the major question is how effective the reducing agents are, and if the efficiency of their reductions varies in waste-glass melters.

A sequence of closed crucible fusion tests has been conducted to determine the relative strength of typical waste glass reducing agents. Tests are plotted in Figure 1, showing the resulting glass Fe(II) / Fe_{total} ratio versus the weight percent of reducing agent added to the feed. The reactions are not linear for carbon, phenyl boric acid (PBA) or sodium formate, even though iron was the only other redox specie in these tests. The general conclusion is that at high reducing agent concentrations the incremental additions are less effective.

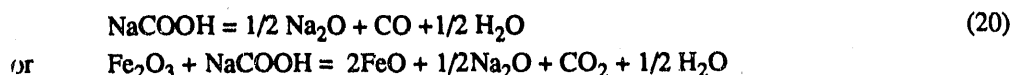
Figure 2 includes the data of Figure 1, replotted versus Fe(II) / Fe(III) ratio. In this case good linear response is seen for all the reducing species in the range of interest of $0 < \text{Fe(II)} / \text{Fe(III)} < 0.8$, corresponding to oxygen fugacities from air to 10^{-10} atm. Additional lines are based on tests with formic acid and an experimental organic Cs resin by C.M. Jantzen.

Values for formic acid were derived by digesting realistic hydroxide sludge with various amounts of formic acid, and then fusing mixtures of the digested sludge and frit. The line for formic acid does not pass through the origin, because volatilization, the acid/base reactions, and aqueous reduction reactions [e.g. Mn(IV) \rightarrow Mn(II)] consume some of the formic acid. The slope of the formic acid and sodium formate curves are similar, indicating that once the formic acid feed preparation reactions are complete the two reducing agents are about equally effective on a per unit weight basis. However, if the two were equally effective on a molar basis the slope of the formic acid line in Figure 1 would be expected to be 1.5 times that of the sodium formate line. This probably resulted from volatilization of part of the formic acid during feed preparation, since most of the excess formic acid is expected to have reacted with the frit to produce sodium formate during the final stages of the feed preparation. For Cs Resin tests realistic calcined sludge was used instead of powdered Fe₂O₃ and frit in the crucible tests. In this case it would be expected that MnO₂ in the feed would cause an offset similar to the one seen in the formic acid case, but none is apparent. It therefore has to be assumed that the MnO₂ in the Cs resin tests converted to MnO during calcination of the simulated sludge, and did not influence the results.

Based upon a graphical solution of the difference between the existing nominal Fe(II) / Fe(III) ratio of 0.05 in the DWPF glass, and the Operating Goal discussed earlier, approximately 0.2 wt% Carbon, or 1.2 wt % HCOOH, or 1.0 wt% NaCOOH, or 1.2 wt% KCOOH, or 0.7 wt% phenyl boric acid, or 2.8 wt% Cs Resin, all on a dry weight basis relative to the glass, could be added to nominal melter feed and sulfide formation could still be avoided. This would leave a margin of about twice these amounts between melter operations and the absolute nickel sulfide limit. Even this is conservative, because air flowing through the melter tends to further oxidize the glass.

STOICHIOMETRY OF REDUCING AGENT REACTIONS

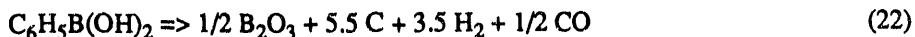
The data indicates that for normal contents of NaCOOH the reactions are about 75% efficient relative to the theoretical reaction:



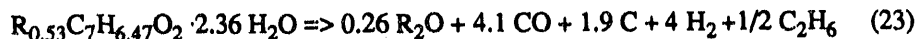
where 2 moles of ferrous iron are produced per mole of NaCOOH. This reduction efficiency drops to about 50% in the range where nickel sulfide precipitates. Similarly, carbon is about 80% efficient by



at relatively oxidizing conditions, but drops to 45% efficient at conditions where nickel sulfide precipitates. Phenyl boric acid could decompose to yield



where the carbon is about 100% efficient, and the hydrogen is about 70% efficient at normal oxygen fugacities, decreasing to 10% H₂ efficiency at very reducing conditions. The cesium resin has relatively little effect on the glass, because it contains its own supply of oxygen. On heating it can be considered to decompose to:



The carbon can then be considered to be about 85% efficient, and the C₂H₆, CO and H₂ may be evolved at low temperatures and are less than 10% efficient in reducing the glass at typical oxygen fugacities. Under very reducing conditions the carbon is about 45% efficient, and the remainder of the reducing agents have no effect on glass redox.

NITRATES AS OXIDANTS

Nitric acid will tend to boil off, with the extent of its redox reactions depending upon concentration. Nitrate salts can be high-active-oxygen-content oxidizers, decomposing at high temperature (e.g. 900°C) according to the reaction:



When nitrates are mixed with simple organic fuels (esp. carbohydrates), nitrate decomposition may stop at the nitrite stage of decomposition [14]:



Nitrates which remain after organic combustion will thermally decompose as the surrounding batch is heated, or can float on the glass, forming low density molten salt layers near the glass surface. Because of the various reaction routes that the nitrates can follow, it is not possible to predict a priori what the extent of their effect will be in a melter. The best available information is for the interaction of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and nitrates [15]:

$$(M \cdot \log(C / (\text{NO}_3^- \cdot f))) + B = \log(\text{Fe}^{++}/\text{Fe}^{+++}) \quad (26)$$

Where M & B are empirical constants for a given melter and leakage rate, C = g/L carbon (by LECO analyzer), NO_3^- is g/L nitrate, f is weight fraction solids in the feed (with iron about 10% of the solids), and $\text{Fe}^{++}/\text{Fe}^{+++}$ is the ferrous/ferric ratio of the product glass. Based on West Valley data [14]:

$$\log[\text{Fe(II)}/\text{Fe(III)}] = 3.24 \log[C / (f \cdot \text{NO}_3^-)] + 0.175 \quad (27)$$

for $\text{Fe}^{++}/\text{Fe}^{+++} = 0.33$ (the Upper Operating Goal discussed above):

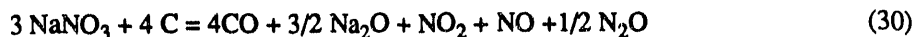
$$C / (f \cdot \text{NO}_3^-) = 0.63 \quad (28)$$

solving for C:

$$C \text{ (g/L)} = 0.25 \cdot \text{NO}_3^- \text{ (g/L)} \quad (29)$$

or $C \text{ (moles)} = 0.77 \text{ NO}_3^- \text{ (moles)}$

Indicating that on average 1.3 mol carbon is being reacted / mol nitrate. Ignoring the water in the sugar, this corresponds to an approximate stoichiometry of:



Neither the formate pyrolysis reactions or the nitrate oxidation reactions are believed to be stoichiometric, but using coefficients that are based on the available experimental information:

$$[\text{FeO}] \cong [\text{COOH-TOTAL}] + 1.6 [\text{C TAR, PBA}] - 2 [\text{NO}_3^-] - 2\text{MnO}_2 \quad (31)$$

The amount of FeO, i.e Fe(II), that can be tolerated in the melter is limited by $0.33 < \text{Fe(II)} / \text{Fe}_{\text{total}}$ to avoid nickel sulfide precipitation, (or $\text{Fe(II)}/\text{Fe(III)} < 0.5$). The redox buffering capacity of the iron in the glass was calculated from physical properties of the melter feed, typically 0.113 mol usable Fe (III) buffer per liter of melter feed: $1250 \text{ g/l} \cdot 0.45 \text{ solids} \cdot 0.10 \text{ Fe}_2\text{O}_3 / 79.85 \text{ g Fe}_2\text{O}_3 / \text{mol Fe (III)} \cdot 0.16 \text{ Fe(II)} / \text{Fe}_{\text{total}}$ (at centerline) = 0.113 mol useable Fe (III) buffer per liter of melter

feed. Thus, if iron, carbon from aromatics, nitrate and formate are considered to be the major redox species present then the first equation leads to the conclusion that:

$$[\text{COOH-TOTAL}] + 1.6 [\text{C TAR, PBA}] - 2 [\text{NO}_3^-] < 0.113 \text{ (molar)} \quad (32)$$

to avoid excessively reducing conditions in the melter. These coefficients and their resulting limits should be checked using pilot scale melters.

IMPROVED THERMODYNAMIC REACTION MODEL OF GLASS MELTING

A melter redox model has been developed based on the melt chemistry in the cold cap. It assumes that all chemical events occurring in the cold cap are at equilibrium and, therefore, such effects as transport resistance and chemical kinetics are ignored. The present model can be considered as an extension to the model developed earlier based on the same chemical equilibrium concept [3]. A series of five melting tests were made at the Battelle Pacific Northwest Laboratory (PNL) with reducing melter feeds produced by digesting simulated DWPF waste hydroxides with formic acid [8,3]. Results of the tests were analyzed using a standard state thermodynamic equilibrium program, which indicated the correct direction of variations, but could not predict actual glass redox state as measured by Fe(II)/Fe(III) [3].

The improved computer model is built on STGSOL 2.5, a software program which was developed at the University of Missouri - Rolla with support from the U. S. Bureau of Mines, and the Savannah River Laboratory [9]. STGSOL is an extension of the SOLGASMIX algorithm for minimizing the total free energy of a system in order to calculate the equilibrium compositions. STGSOL models steady state, multistage countercurrent reactor systems, and is run on personal computers.

The validity of this STGSOL application is determined entirely by how close the actual process is to thermodynamic equilibrium and by the accuracy of the free energy database. Moreover, perhaps the most important requirement of the free energy database is a reasonable treatment of nonideality of solution phases. For systems higher than ternary, both experimental and theoretical treatment of the activity coefficients becomes exceedingly complex. For this reason, the Gibbs free energy database for complex liquids by the National Institute of Standards and Technology (NIST) is used in place of activity coefficients to partially handle the solution nonideality problem [10]. The NIST database currently has free energy data for only a limited number of species which are of interest to us, and especially needs data on borosilicate melts.

Melting of the feed solids is envisioned as a 4-stage process, outlined in Figure 3; Stage 1 is at the top of the cold cap, and the final melt is formed in Stage 4. The goal of a multistage approach is to approximate the complicated melting process by a series of simple, recognizable physical and chemical events, similar to those seen by differential scanning calorimetry and X-ray diffraction experiments [1]. The major assumption of the model is that gas and solids are at local equilibrium in each stage.

Once the equilibrium gas and solids compositions are calculated in each stage, the gas stream is fed to the next stage above, while the solids are fed to the next stage below, thus establishing gas - solids countercurrent flows between stages. The gas stream from Stage 1 enters the plenum and further reacts with the feed volatiles and air before exiting the melter. These plenum reactions are considered in another model for plenum combustion.

The nonvolatile feed solids are split into two groups. The first group includes salts with low melting points such as formates, nitrates, and hydroxides. These salts are first predecomposed to oxides and gases, and the decomposition products are then fed to Stage 1 at 973 K. Other inorganic salts with higher melting points such as sulfates and carbonates constitute the second group, and are fed to Stage 2 at 1,123 K along with frit. Carbonates are predecomposed to oxides and CO_2 before being fed, whereas the degree of sulfate decomposition is determined by the equilibrium between sulfates, sulfides, oxides and SO_3 in Stage 2 or higher.

Stage 1 represents the initial stage of melting before a melt appears. All oxides remain as solids, and each forms an invariant condensed phase. From Stage 2, all oxides are assumed to be in a liquid state and, therefore, form a solution. Silica and other non-redox species form one melt phase, and all redox species such as Fe_2O_3 and MnO form the other. The model assumes that these two melt phases are in equilibrium with each other and with the gas and the invariant condensed phases.

Multiple oxides begin to form from Stage 3 at 1,323 K. Each multiple oxide is of the spinel type, $\text{M(II)R(III)}_2\text{O}_4$, such as FeFe_2O_4 , NiFe_2O_4 , etc. These oxides are assumed to form a solid solution and coexist with the redox species in the same phase. The gas phase includes O_2 and SO_3 only at these high temperatures in Stage 3 and 4.

Stage 4 represents the final fusion at 1,423 K. All oxides are allowed to dissolve in silica to form silicates. Furthermore, the cation pairs of Al(III) and alkali are allowed to replace Si(IV) by chance substitution to form MAIO_2 . Unstable multiple oxides such as NiFe_2O_4 and MnFe_2O_4 are excluded from consideration at 1,423 K.

The equilibrium temperatures given for Stage 1 and 2 have been set so as to ensure complete decomposition of all salts in each stage. The validity of the equilibrium temperature chosen for Stage 1 is checked by comparing the calculated off-gas compositions from Stage 1 with the off-gas data obtained without the lid heat.

The oxidizing effect of plenum air is accounted for simply by adding O_2 into the two feed stages along with the feed solids. This is based on a physical picture of plenum air sweeping across the top surface of the cold cap and some of it diffusing into the inner reactive zones. The absolute quantity of O_2 to be fed to the model is a complicated function of all operating variables involved, and it seems practically impossible to measure it experimentally. Until a suitable model for oxygen transfer

is developed, the O₂ feed rate is used for now as an invariant fraction in order to match calculated redox ratios with experimental values.

In order to add some validity to this concept of air addition, the total air flow fed to Stage 1 and 2 has been checked to see how it correlates with the experimental air-to-glass mass ratios. Distribution of plenum O₂ between the two feed stages is assumed to be equimolar.

The base case for the simulation was the Engineering Scale Ceramic Melter (ESCM) runs made at PNL [3]. Four variables considered include:

1. Plenum air flow rate.
2. Amount of formic acid addition.
3. Use and nonuse of lid heater.
4. Amount of Na₂SO₄ and NaCl addition.

The first two variables have opposite effects on the glass redox state, and are accounted for by the model. Calculations showed that more than 50% of the total heat supply to the cold cap comes from the lid heaters for joule-heated melters. This means that turning off the lid heater power will definitely slow down the overall cold cap kinetics, resulting in a lower melt rate. The equilibrium model is not intended to explain melt rate effects and, lid heat was assumed to have no effect on the redox. This effect should be reinvestigated if appropriate melter data become available. Similarly, increased melt rates induced by the addition of Na₂SO₄ and NaCl are not accounted for by the model, but might be expected to shift the effective temperature of the first stage.

Simulation Results

Table 1 summarizes the key experimental conditions and simulation results. Case 2B was run with the lid heater off. The melter feed for all cases had the same level of halides and Na₂SO₄ except for Case 3B, where excess amounts of NaCl and Na₂SO₄ were added by 50 and 260 wt%, respectively.

No sulfides were formed in the simulation. This is in agreement with the experiments.

The experiment showed that 0.5 to 4 wt% of the feed sulfur was detected in the off-gas analysis as SO_x. The simulation showed 0% volatilization, and that all Na₂SO₄ was converted to CaSO₄. This is in qualitative agreement with the experimental data in that sulfur was less volatile from CaSO₄ than from Na₂SO₄.

Table 1. Summary of 4-Stage Model Simulation Results
(per 1000 lb. Feed Solids)

Case	% Stoich	g air		O ₂ Feed (Model) (lb mole)	% Stoich (Model)			Fe(II)/Fe(III)	
		HCOOH	g glass		CO ₂	CO	H ₂	Exp	Model
1	90	0.26	0.22	192	11	46	0.36	0.37	
2A	85.7	6.20	0.29	195	8	36	0.15	0.15	
2B	85.7	0.51	0.27	195	9	37	0.2	0.2	
3A	110	0.39	0.26	186	17	59	0.32	0.33	
3B	110	0.51	0.23	186	17	60	0.43	0.43	

The oxidizing effect of plenum air and the reducing effect of HCOOH addition are clearly shown in all cases except Case 3B. When Cases 3A and 3B are compared, an increased plenum O₂ supply in case 3B resulted in more reducing glass. Many factors may have contributed to this seemingly contradictory result. One possible explanation may be that the excess Na₂SO₄ fed during Case 3B resulted in formation of a thin molten salt layer on the top surface which may have limited oxygen transfer into the inner region.

A fair proportionality relationship can be seen between the air to glass mass ratio and the calculated O₂ feed in lbmoles/1,000 lb feed solids, again except for Case 3B.

The % stoichiometric conversion given in Table 1 is based on the following formate decomposition, and it represents the cold cap off-gas composition assuming no reaction in the plenum with the lid heater off:



The calculated values compare fairly well with the ESCM data except for H₂ ;
CO₂ : CO : H₂ = 180 : 18 : < 20

The observed plenum temperature measured in the thermowell without lid heat was 500 - 550 °C. According to SRL data, this is equivalent to a true gas temperature of about 380 °C, which is still high enough to oxidize some of CO and H₂. This may explain much lower observed H₂ conversion than the calculated ones, whereas conversion of CO to CO₂ may be strongly kinetic controlled.

When the simulation was calculated with no plenum O₂ feed to the cold cap, the glass became reducing enough to form Cu₂S. For Case 1 and 3A, the ferrous/ferric ratios were increased to 1.95 and 2.31, respectively.

Based upon these thermodynamic calculations, the dominant forms of Fe(II) and Fe(III) in glass are Fe_2SiO_4 (I) and Fe_2O_3 , respectively. The only form of Al in glass is calculated to be LiAlO_2 .

CONCLUSIONS

Crucible and melter tests have been examined to determine the amount of organic which can be tolerated in feed to the DWPF melter. Preliminary Operating Goals have been established to preclude nickel sulfide accumulation: $p_{\text{O}_2} > 10^{-6}$ atm at 1150°C , which is equivalent to: $\text{Fe(II)} / \text{Fe}_{\text{total}} < 0.25$ or $\text{Fe(II)} / \text{Fe(III)} < 0.33$ for a melter feed sample fused at 1150°C in a closed crucible. Maximum short term increases in melter feed organics are, on a wt% glass basis: 0.2 wt% Carbon, or 1.2 wt % HCOOH , or 1.0 wt% NaCOOH , 1.2 wt% KCOOH , or 0.7 wt% phenyl boric acid or other aromatic, or 2.8 wt% Cs Resin to preclude the formation of sulfides.

Further pilot-scale melter testing under varying feed composition and purge gas rates is necessary to qualify staged reaction models of waste-glass melting.

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REFERENCES

- [1] D.F. Bickford, et al, "Control Requirements for Radioactive Waste Glass Melters-Parts 1 & 2", *J. Am. Ceram. Soc.* 73 [10] 2896-2915.
- [2] D.S. Goldman, "Melt Foaming, Foam Stability and Redox in Nuclear Waste Vitrification", *J. Non-Cryst. Solids* 84 (1986) 292-298.
- [3] D.F. Bickford, R.B. Diemer, and D.C. Iverson, "Redox Control of Electric Melters with Complex Feed Compositions, Parts I & II", *J. Non-Crystalline Solids*, 84(1986) 276-291.
- [4] H.D. Schreiber, et al, "Oxidation-Reduction Chemistry of Nonmetals in a Reference Borosilicate Melt", *Advances in the Fusion of Glass*, *Am. Cer. Soc.* (1988) 29.1-29.14
- [5] D.S. Goldman, "Investigation of Potential Analytical Methods for Redox Control of the Vitrification Process", PNL -5581, November 1985.
- [6] D.F. Bickford, R.C. Propst, and M.J. Plodinec, "Control of Radioactive Waste-Glass Melters: Part 3- Glass Electrical Stability", *Advances in the Fusion of Glass*, *Am. Cer. Soc.* (1988) 19.1-29.17
- [7] H.D. Schreiber, et al, "Redox Equilibria and Kinetics of Iron in a Borosilicate Glass-Forming Melt", *J. Non-Crystalline Solids* 84 (1986) 186-195.
- [8] R.W. Goles and G.J. Sevigny, "Off Gas Characteristics of Defense Waste Vitrification,....", PNL-4819, September 1983.
- [9] H.E. Flynn, A.E. Morris, and D. Carter, "Staged Thermodynamic Model of Glass Fusion Based on Solgasmix-PV", *Advances in the Fusion of Glass*, *Am. Cer. Soc.* (1988) 28.1-28.14 .
- [10] E.R. Plante, D.W. Bonnell, and J.W. Hastie, "Experimental and Theoretical Determination of Oxide Glass Vapor Pressures and Activities", *Advances in the Fusion of Glass* *Am. Cer. Soc.* (1988) 26.1-26.18 .
- [11] O. Kubaschewski and C.B. Alcock, *Metallurgical Thermochemistry*, Pergamon (1979).
- [12] L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill (1953).
- [13] H.D. Schreiber, et al, "Ruthenium in Glass Forming Borosilicate Melts", *J. Less Common Metals*, 115 (1986) 145-154.
- [14] J. Conkling, *Chemistry of Pyrotechnics*.
- [15] B. W. Bowman, WVDP Report EK: 89:0021, January 25, 1989.
- [16] J.L. Barton and M.-H. Chopinet, "The Problem of Predicting the Redox State of a Glass", *Advances in the Fusion of Glass*, *Am. Cer. Soc.* (1988) 30.1-30.8 .
- [17] P.M. DiBello, "Controlling the Oxidation State of a Glass as a Means of Optimizing Sulfate Usage in Melting and Refining", *Glass Tech.* [30] 5 (1989) 160-165.

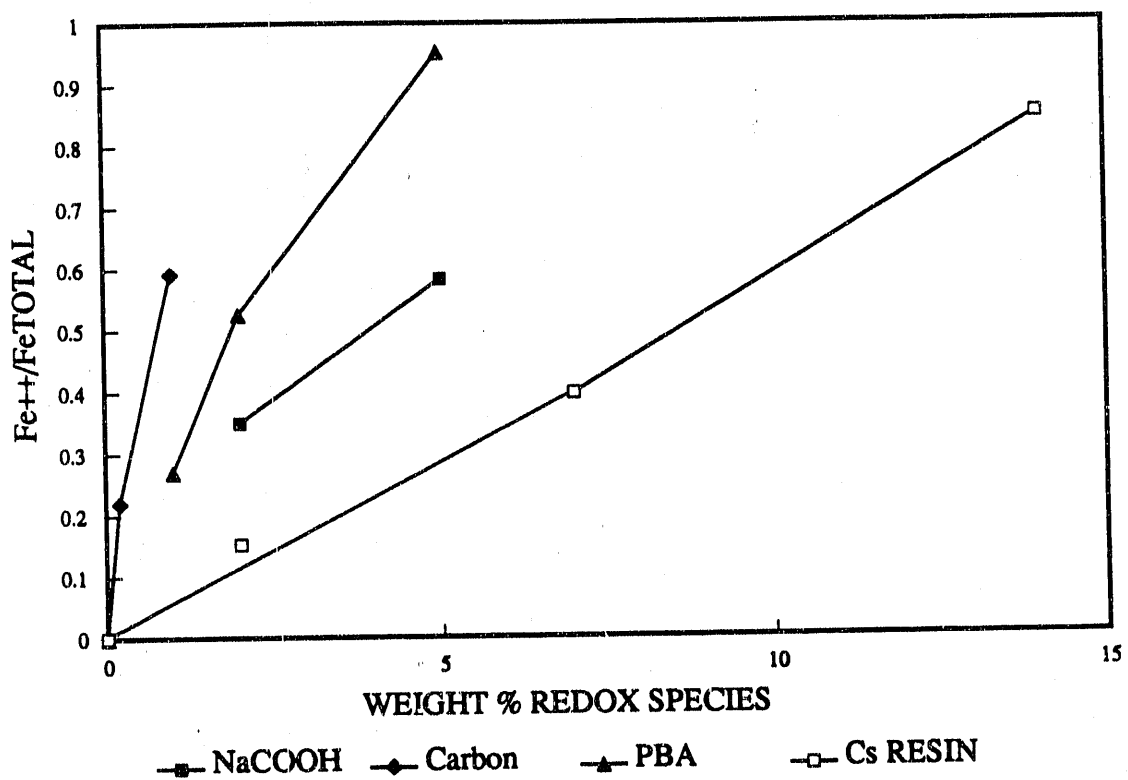


Figure 1. Stoichiometry of Glass Redox Reactions. When redox species are added to dried batch, the efficiency of their reduction decreases slightly with increasing amounts of the reducing agent. Redox species are wt% on glass basis. Data reanalyzed from [3].

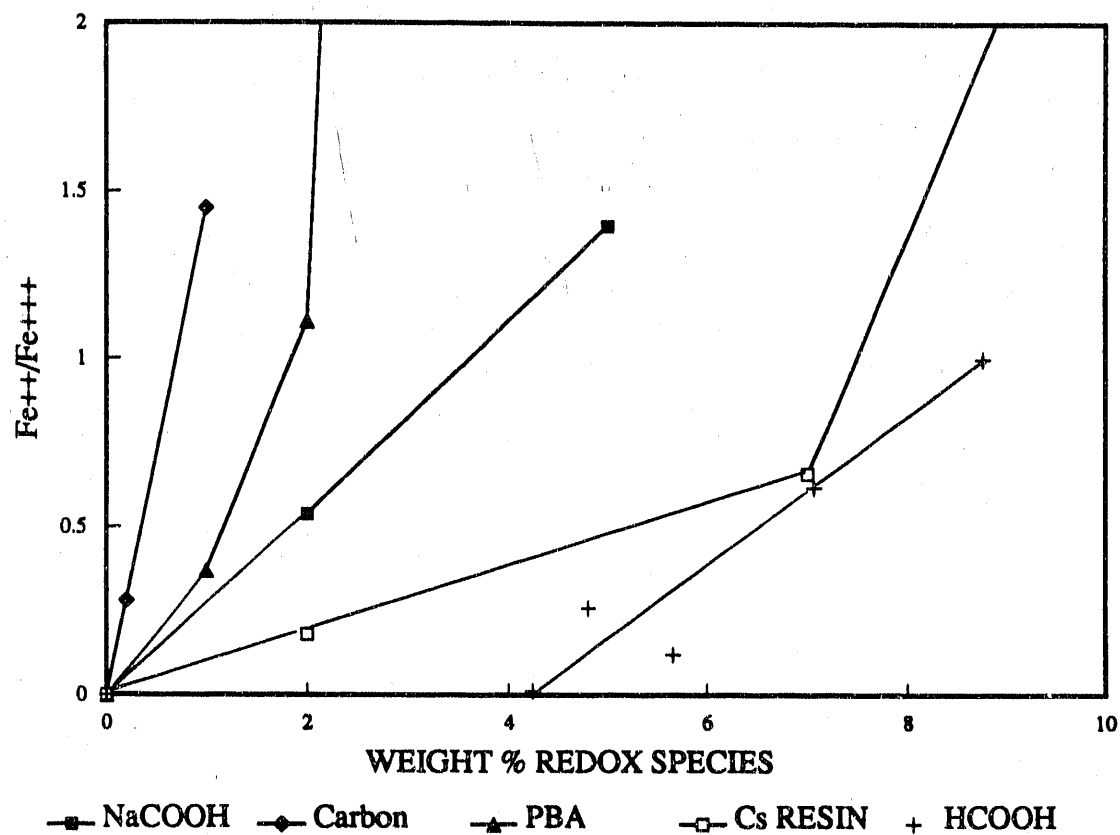


Figure 2. When redox species are added to dried batch, the efficiency of their reduction decreases with increasing amounts of the reducing agent. For the NaCOOH and Carbon, this nonlinearity can be compensated for by the nonlinearity of the Fe(II)/Fe(III) ratio in the finished glass. Data reanalyzed from [3].

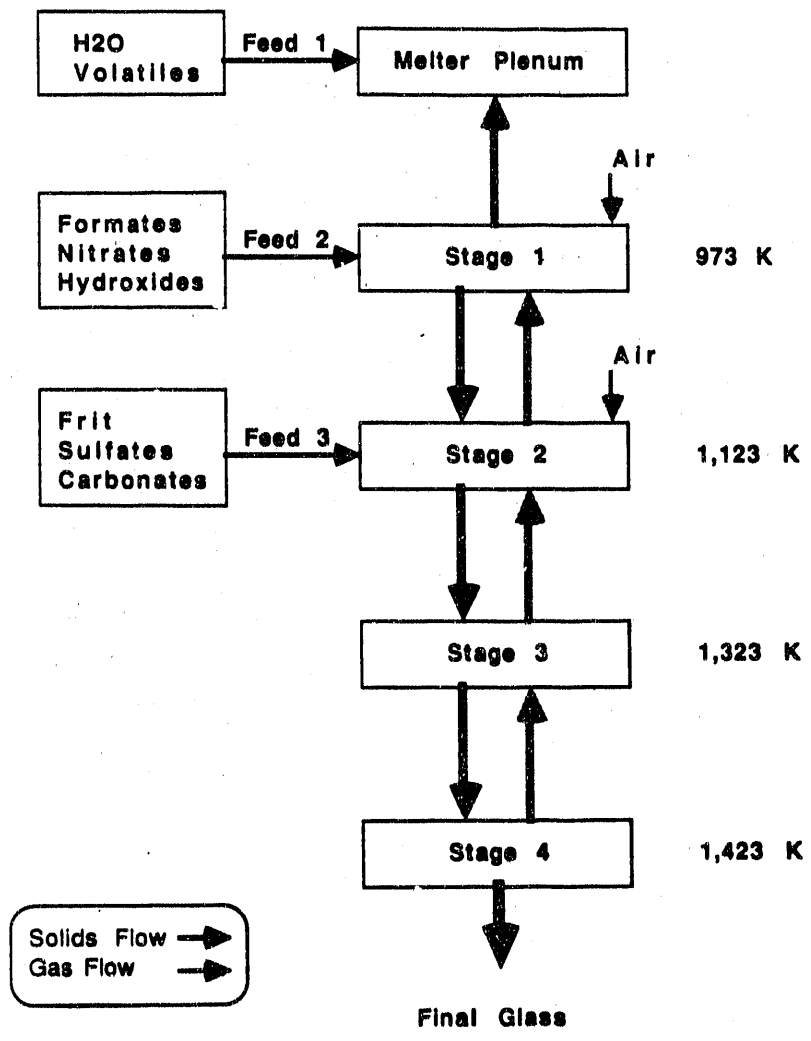


Figure 3. Schematic of Four-Stage Equilibrium Cold Cap Model.

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