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ELECTRON EQUIVALENTS REDOX MODEL FOR HIGH LEVEL WASTE VITRIFICATION (U)

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Westinghouse Savannah River Company
Aiken, SC 29808

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Savannah River Technology Center
Westinghouse Savannah River Co.
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ABSTRACT

Control of the REDuction/OXidation (REDOX) equilibrium in High Level waste (HLW) glass melters is critical in order to eliminate the formation of metallic species from overly reduced melts while minimizing foaming from overly oxidized melts. To date, formates, nitrates, and manganic (Mn^{+4} and Mn^{+3}) species in the melter feeds going to the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) have been the major parameters influencing melt REDOX. The sludge being processed for inclusion in the next DWPF Sludge Batch (SB-3) contains several organic components that are considered non-typical of DWPF sludge to date, e.g. oxalates and coal. A mechanistic REDOX model was developed to balance any reductants (e.g. oxalate, coal, sugar, formates) and any oxidants (e.g. nitrates, nitrites, and manganic species) for any HLW melter feed. The model is represented by the number of electrons gained during reduction of an oxidant or lost during oxidation of a reductant. The overall relationship between the REDOX ratio of the final glass and the melter feed is given in terms of the transfer of molar Electron Equivalents, ξ.

INTRODUCTION

High-level nuclear waste (HLW) is being immobilized at the Savannah River Site (SRS) by vitrification into borosilicate glass at the Defense Waste Processing Facility (DWPF). A similar HLW vitrification program has just been completed at West Valley Nuclear Services (WVNS) and another facility is being built to process HLW at the Hanford Waste Vitrification Project (HWVP). The REDOX equilibrium in a HLW melter must be controlled to prevent the following:

- liberation of oxygen which can cause foaming from decomposition of Mn^{+4} or Mn^{+3} because the $MnO_2 \rightarrow MnO + \frac{1}{2} O_2$ reaction liberates oxygen at the melt temperature
- liberation of NOx and oxygen caused by decomposition of nitrate species via reactions such as $NO_3 \rightarrow NO_x + O_2$
- retardation of melt rate due to foaming from nitrates and manganic species
- reduction of metallic species such as $NiO \rightarrow Ni^\circ$ and $RuO_2 \rightarrow Ru^\circ$ which can fall to the melter floor and cause shorting of electrical pathways in the melt and accumulations which may hinder glass pouring
- reduction of sulfate ($SO_4^=$) to sulfide ($S^=$) which can complex with Ni° and/or Fe° to form metal sulfides which can fall to the melter floor and cause shorting of electrical pathways and/or hinder glass pouring
- overly reduced glasses which can be less durable than their oxidized equivalents [1].

Controlling the HLW melters at a REDuction/OXidation (REDOX) equilibrium of $Fe^{+2}/\Sigma Fe \leq 0.33$ [2, 3] prevents the potential for conversion of $NiO \rightarrow Ni^\circ$, $RuO_2 \rightarrow Ru^\circ$, and $2SO_4^= \rightarrow S_2 + 4O_2$ during vitrification. Control of foaming due to deoxygenation of manganic species is achieved by having 66-100% of the MnO_2 or Mn_2O_3 species converted to MnO [4] during pretreatment in the Sludge Receipt Adjustment Tank (SRAT). At the lower redox limit of $Fe^{+2}/\Sigma Fe \sim 0.09$ about 99% of the Mn^{+3} is converted to Mn^{+2} [2, 3]. Therefore, the lower REDOX limit eliminates melter foaming from deoxygenation.

BACKGROUND

During melting of HLW glass, the REDOX of the melt pool cannot be measured. Therefore, the $Fe^{+2}/\Sigma Fe$ ratio in the glass poured from the melter must be related to melter feed organic and oxidant concentrations to ensure production of a high quality glass without impacting production rate (e.g. foaming) or melter life (e.g. metal formation and accumulation).

Most REDOX models developed to date only include one oxidant and one reductant. For example, at SRS the first REDOX model developed balanced formic acid [F] and nitric acid [N] with a 1:1 stoichiometry, e.g. $Fe^{2+}/\Sigma Fe = -0.8 + 0.87\{[F]-[N]\}$, $R^2 = 0.80$ [5, 6, 7, 8]. The data used to develop the $\{[F]-[N]\}$ relationship was revisited in 1997, and glass quality and REDOX measurement criteria were developed to screen the experimental data used for modeling [9]. This redefined the population of glasses used for modeling by excluding those below the $Fe^{+2}/\Sigma Fe$ measurement detection limit of 0.03 and those that precipitated metallic and/or sulfide species.

Regression of the redefined data demonstrated that the $\{[F]-[N]\}$ parameter was a less accurate predictor ($R^2=0.68$) of waste glass REDOX than had previously been calculated ($R^2=0.80$). The regression of the redefined data showed that there was an $\{[F]-3[N]\}$ relationship between the feed reductants,

oxidants, and the glass REDOX ratio, e.g. $Fe^{2+}/\Sigma Fe = 0.217 + 0.253[F]-0.739[N]\}$, $R^2=0.89$ where the F and N concentrations are normalized to a feed that is 45 wt% solids. Both the $\{[F]-[N]\}$ and the $\{[F]-3[N]\}$ REDOX models assumed that the melter feeds were properly formated and refluxed to ensure that 66-100% of the Mn^{3+} and Mn^{4+} were converted to Mn^{+2} as $Mn(COOH)_2$ during preprocessing, e.g. before the melter feed entered the melter.

Investigations were also performed at West Valley Nuclear Services (WVNS) to determine the effect of total solids and the concentrations of oxidants and reductants on the REDOX state of iron in glass. The major difference between the WVNS and SRS feeds is that the reductant in WVNS feed is sugar instead of formate. Preliminary investigations by WVNS indicated that the logarithm of the REDOX state, e.g. $\log(Fe^{2+}/Fe^{3+}$, in a glass can be predicted from the feed using the Index of Feed Oxidation (IFO) which is defined as [10]:

$$IFO \equiv \frac{(1-\phi)[NO_3]_{ppm}}{[TC]_{ppm}}$$

where ϕ is the fraction of solids and TC is Total Carbon. While the IFO parameter predicted the REDOX of WVNS glasses it did not predict the REDOX of SRS glasses very well [9]. Conversely, it was shown that the WVNS data fit the $\{[F]-3[N]\}$ model when the formate coefficient was multiplied by a factor of two in order to account for the differences in the oxidation state of carbon in formic acid and sugar[*] [9].

PNNL had also developed an iron REDOX model which was similar to that developed by WVNS. The iron REDOX index (ri) suggested by PNNL models two feed oxidants and two feed reductants. The $\log(Fe^{2+}/Fe^{3+})$ is related to ri computed from the concentrations in M/L and normalized to 130g waste oxides/L using either of the following stoichiometrically based relationships depending on whether or not the feed was formated [11].

$$ri = \begin{cases} \dfrac{[COOH^-]-[NO_2^-]+[TC]}{[NO_3^-]} & \textit{formated} \text{ samples} \\ \dfrac{[TC]}{[NO_2^-]+[NO_3^-]} & \textit{unformated} \text{ samples} \end{cases}$$

The effects of manganic species as oxidizers was noted during this study but not incorporated into the model. A separate REDOX model was developed by PNNL for oxalated feeds at WVNS. In this study the $Fe^{+3}/\Sigma Fe \propto g\ NO_3^- / g\ TOC$ [12] where TOC is Total Organic Carbon. While the PNNL models were each fit to the

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[*] the ratio of the number of electrons transferred during oxidation of C in sugar divided by number of electrons transferred during oxidation of C in formic acid

data generated in the respective studies, these models did not predict the REDOX of SRS glasses very well [9].

Thus there was a need for a mechanistic REDOX model that could account for all oxidizers (nitrates, nitrites, soluble and insoluble manganic species) and reductants (formates, sugar, coal, oxalate). In addition the model needed to be able to account for the relative oxidizing and reducing power of each species.

EXPERIMENTAL

Twenty-nine simulated SB3 melter feeds were tested in sealed crucibles at four different waste loadings with two different frits, e.g. a high sodium frit (F320) and a low sodium frit (F202). Detailed preparation and analyses of the refluxed feeds used and the sealed crucible studies are given elsewhere [13]. The feeds varied in formic, nitrate, nitrite, oxalate, coal, and manganese. The noble metals were varied from 10 wt% to 100 wt% of the amount calculated to be present, e.g. 0.0511 wt% Rh, 0.183 wt% Ru, 0.0275 wt% Pd and 0.0005 wt% Ag. Manganese varied from 2.92 wt% to 3.87 wt%. The feeds contained Sm (as a Pu surrogate) and Gd. The Sm was present at 0.024 wt% while Gd varied from 0.037-0.061 wt%. Mercury was added at a constant 0.076 wt%.

Over 200 sealed crucible melts were performed. Sealed crucible vitrification was achieved by sealing Al_2O_3 crucibles with a nepheline ($NaAlSiO_4$) gel that melts at a temperature lower than that at which the slurry vitrifies. This causes the crucible to seal before the slurry vitrifies so that air inleakage does not occur during vitrification. This is extremely important as air inleakage will alter the glass REDOX ratio, $Fe^{2+}/\Sigma Fe$, and allow oxidizers and reductants to escape, rather than reacting with the transition elements in the glass. The $Fe^{+2}/\Sigma Fe$ analyses were performed by the Baumann colormetric method [14].

Fifty three glasses for modeling were selected out of the 200 glasses melted by applying the following criteria used in previous modeling studies [9]:

- Vitrified material must be visibly black and homogeneous; that is, it must contain no brown discoloration due to metallic copper and/or no crystalline or other metallic material as these species make both reliable REDOX ratio and cation measurements difficult
- The iron REDOX ratio must be greater than or equal to the measurement detection limit of $Fe^{2+}/\Sigma Fe = 0.03$
- Both REDOX and feed chemistry measurements must be available for the same sample
- Measured or as-made total solids information must be available: measured total solids are preferred to minimize modeling error.

REDOX REACTIONS IN THE MELTER COLD CAP

During melter feed-to-glass conversion, multiple types of reactions occur in the cold cap and in the melt pool. The REDOX reactions occur in the cold cap along with feed decomposition and calcination. In the melt pool, further degassing and homogenization occur primarily by additional REDOX reactions. The gaseous products from the cold cap and the volatile feed components further react with air in the vapor space. In order to represent the gradual nature of the feed-to-glass conversion, a 4-stage cold cap model was developed by Choi [15] which approximates the melting of feed solids as a continuous, 4-stage counter-current process [16]. In Stage 1 formated salts such as NaCOOH, are decomposed to CO, CO_2 and H_2. The CO subsequently gets oxidized by the air diffusing into the cold cap from the top and by the oxygen being liberated during the Stage 2 denitration reactions (at further depth in the cold cap). Multiple oxides begin to form during Stage 3. These oxides are assumed to form solid solutions such as spinels which coexist with the REDOX species in the same phase. Stage 4 represents the final fusion where the oxides formed in Stage 3 dissolve in a silica-rich matrix to form silicate groups in the melt, e.g. Fe_2SiO_4 and Na_2SiO_3. In order to represent all four stages of cold cap reaction simultaneously and include terms for reduced and oxidized iron and silica one can assume a generalized form of the reactions as follows:

$$Fe_2O_3 + 5SiO_2 + 6NaCOOH + 2NaNO_3 \rightarrow Fe_2SiO_4 + 6CO_2 + N_2 + 4Na_2SiO_3 + 3H_2O \quad (1)$$

Equation 1 assumes that Fe^{3+} enters the melter as Fe_2O_3 and that reductants such as $COOH^-$ and oxidizers such as NO_3^- both enter as properly formated and nitrated sodium compounds. The formated and nitrated salts react with glass formers such as SiO_2 to form Fe^{+2} and Na_2SiO_3 components in the glass and liberate CO_2, N_2 and H_2O vapors to the melter plenum.

ELECTRON EQUIVALENTS MODEL

For simplicity, the generalized REDOX cold cap reaction (Equation 1) can be rewritten in terms of Fe^{2+} and Fe^{3+} instead of the iron oxides and the SiO_2 term can be omitted. This generates Equation 2 below as one of the controlling REDOX reactions, the one between reducing formate salts and oxidizing nitrated salts, in the cold cap:

$$2Fe^{+3} + 6Na\overset{+2}{C}OOH + 2Na\overset{+5}{N}O_3 \rightarrow 2Fe^{2+} + 6\overset{+4}{C}O_2 + \overset{0}{N_2} + 3Na_2O + 3H_2O + 2Na^+$$

with annotations: $-2e^-/C$ or $-12e^-/6$ formate; $+2e^-$; $+5e^-/NO_3$ or $1x(+10e^-/2NaNO_3)$

$$(2)$$

The oxidation/reduction equilibrium shown in the Equation 2 between nitrate and formate indicates that one mole of nitrate gains 5 electrons when it is reduced to N_2 while one mole of carbon in formate loses 2 electrons during oxidation to CO_2. This is an oxidant:reductant ratio of 5:2 which indicates that nitrate is approximately 2½ times as effective an oxidizing agent as formate is a reducing agent (when nitrogen gas is the reaction product).

The oxidation/reduction equilibrium shown in Equation 3 between coal and the oxidized nitrated salts indicates that one mole of nitrate gains 5 electrons when it is reduced to N_2 while one mole of carbon in coal loses 4 electrons during oxidation to CO_2. This is an oxidant:reductant ratio of 5:4 which indicates that nitrate is only 1¼ times as effective an oxidizing agent as coal is a reducing agent (when nitrogen gas is the reaction product).

$$-4e^-/C \text{ or } -12e^-/3 \text{ coal}$$

$$2Fe^{+3} + 3C^{0} + 2NaN^{+5}O_3 \rightarrow 2Fe^{+2} + N^{0}_2 + 3C^{+4}O_2 + 2\ Na^+$$

$$2x(+1e^-/Fe)$$

$$+5e^-/NO_3 \text{ or } +10e^-/2NaNO_3 \tag{3}$$
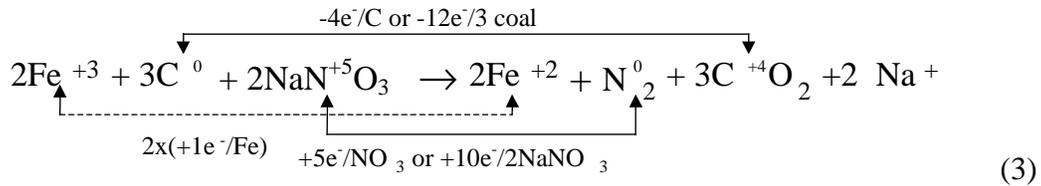
The oxidation/reduction equilibrium between the oxalate and nitrate salts is given in Equation 4. This reaction, written in the format of the preceding cold cap reactions (Equations 2 and 3), indicates that one mole of nitrate should gain 5 electrons when it is reduced to N_2 while one mole of carbon in oxalate should lose 1 electron during oxidation to CO_2. This is an oxidant:reductant ratio of 5:1 which indicates that nitrate is 5 times as effective an oxidizing agent as the carbon in oxalate is a reducing agent (when nitrogen gas is the reaction product).

$$-1e^-/C \text{ or } -2e^-/\text{oxalate or } -12e^-/6 \text{ oxalates}$$

$$2Fe^{+3} + 6Na_2C^{+3}_2O_4 + 2NaN^{+5}O_3 \rightarrow 2\ Fe^{+2} + N^{0}_2 + 12C^{+4}O_2 + 2\ Na^+ + 6Na_2O$$

$$2x(+1e^-/Fe)$$

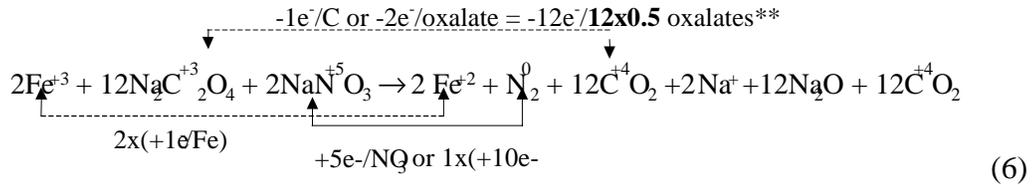$$+5e-/NO_3 \text{ or } 1x(+10e-/2NaNO3) \tag{4}$$
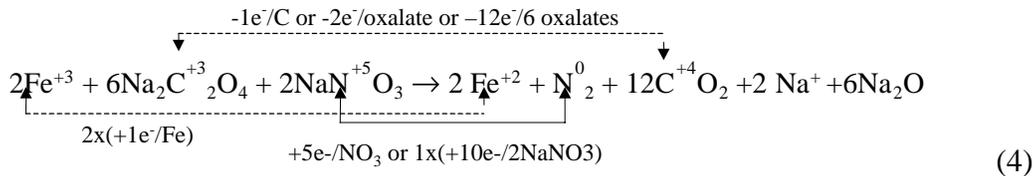
During REDOX modeling the data indicated that oxalate appeared to be twice as strong a reductant as indicated by Equation 4. During further investigation of the apparent increase in the reducing power of oxalate, data became available that demonstrated that oxalate salts convert to oxalic acid and then disproportionate to formic acid and CO_2 during SRAT processing [17] via the following equation:

$$HC^{+3}_2O^-_4 \rightarrow HC^{+2}O^-_2 + CO_2 \uparrow \tag{5}$$

Experimentally, it was found that between 8-37% of the oxalate present in the SRAT was determined to disproportionate during processing into HCOOH and CO_2 gas [17].

Therefore, it was assumed that additional disproportionation occurs in the cold cap when the liquid slurry impacts the melt pool surface. The pertinent oxidation/reduction equilibrium for oxalate, including the disproportionation, would then be as expressed in Equation 6. Note that this equation includes the decomposition of the oxalate into formic acid and CO_2. Only half the oxalate is acting as a reductant (the half that disproportionates does not affect the REDOX equilibrium). Hence, the reduction potential of oxalate is doubled.

$$-1e^-/C \text{ or } -2e^-/oxalate = -12e^-/\mathbf{12x0.5} \text{ oxalates**}$$

$$2Fe^{+3} + 12Na_2C^{+3}{}_2O_4 + 2NaN^{+5}O_3 \rightarrow 2\,Fe^{+2} + N^0{}_2 + 12C^{+4}O_2 + 2Na^+ + 12Na_2O + 12C^{+4}O_2$$

$$2x(+1e^-/Fe)$$

$$+5e^-/NO_3 \text{ or } 1x(+10e-$$

(6)

A similar equation can be written for the reduction of manganese by any carbon containing species, for example:

$$-4e^-/C$$

$$2Mn^{+4}O_2 + C^0 \rightarrow 2Mn^{+2}O + C^{+4}O_2$$

$$2x+2e^-/Mn$$

(7)
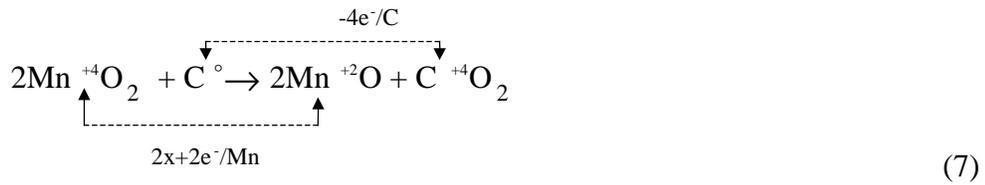
Equations 2, 3, 4 and 7 demonstrate that the relative factors for the electrons exchanged upon oxidation and reduction are the following:

- 4 for the number of moles of coal
- 2 for the number of moles of formate
- 4 for the number of moles of oxalate
- 5 for the number of moles of nitrate
- 2 for the number of moles of manganese.

The signs for the oxidation of the reductants are positive while the signs for reduction of the oxidants is negative indicating gain and loss of electrons.

The effectiveness of the oxidants and reductants depends on their concentrations relative to the other slurry components. Therefore, the molar Electron Equivalents term must be multiplied by the factor 45/T, where T is the total solids (wt%) content of the slurry. This factor puts all concentrations on a consistent basis of 45 wt% total solids. The normalized molar Electron Equivalents, ξ, are then:

$$\xi\left(\frac{mol / kg\ feed}{@\ 45\ wt\%\ solids}\right) = \left(2[F] + 4[C] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T} \qquad (8)$$

Therefore, the basis for the relation of REDOX to electron equivalent transfers, ξ, is

$$\frac{Fe^{2+}}{\Sigma Fe} = f\left[\left(2[F] + 4[C] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T}\right] = f[\xi] \qquad (9)$$

where f = indicates a function
       [F] = formate (mol/kg feed)
       [C] = coal (carbon) (mol/kg feed)
      [O_T] = oxalate$_{Total}$ (soluble and insoluble) (mol/kg feed)
      [N] = nitrate + nitrite (mol/kg feed)
    [Mn] = manganese (mol/kg feed)
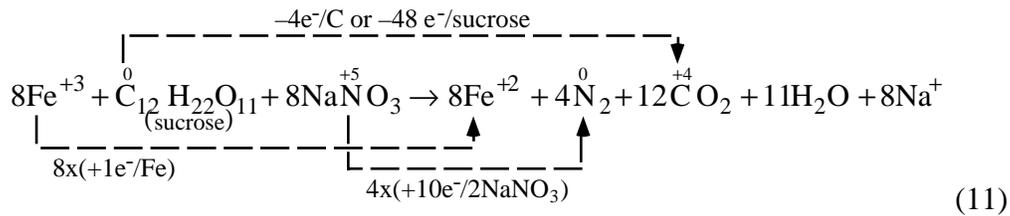   T = total solids (wt%)

$$\xi = \left(2[F] + 4[C] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T}$$

When the REDOX data generated in this study and the data from the 1997 study [9] are then fit as a linear function of ξ:

$$\frac{Fe^{2+}}{\Sigma Fe} = 0.1942 + 0.1910\xi \qquad (10)$$

which is the DWPF Electron Equivalents REDOX model (see Figure 1) with an adjusted R^2 of 0.8037 and a Root Mean Square Error of 0.0690 for 120 data observations (53 from the current study and 67 from the 1997 study.

If sugar were used in HLW processing then the form of the model would be changed to include Equation 11:

$$8Fe^{+3} + \overset{0}{C}_{12}H_{22}O_{11} + 8Na\overset{+5}{N}O_3 \rightarrow 8Fe^{+2} + 4\overset{0}{N}_2 + 12\overset{+4}{C}O_2 + 11H_2O + 8Na^+$$

–4e⁻/C or –48 e⁻/sucrose
8x(+1e⁻/Fe)
4x(+10e⁻/2NaNO₃)

$$(11)$$

The Electron Equivalents term becomes:

$$\xi = \left(2[F] + 4[C] + 4[S] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T}$$
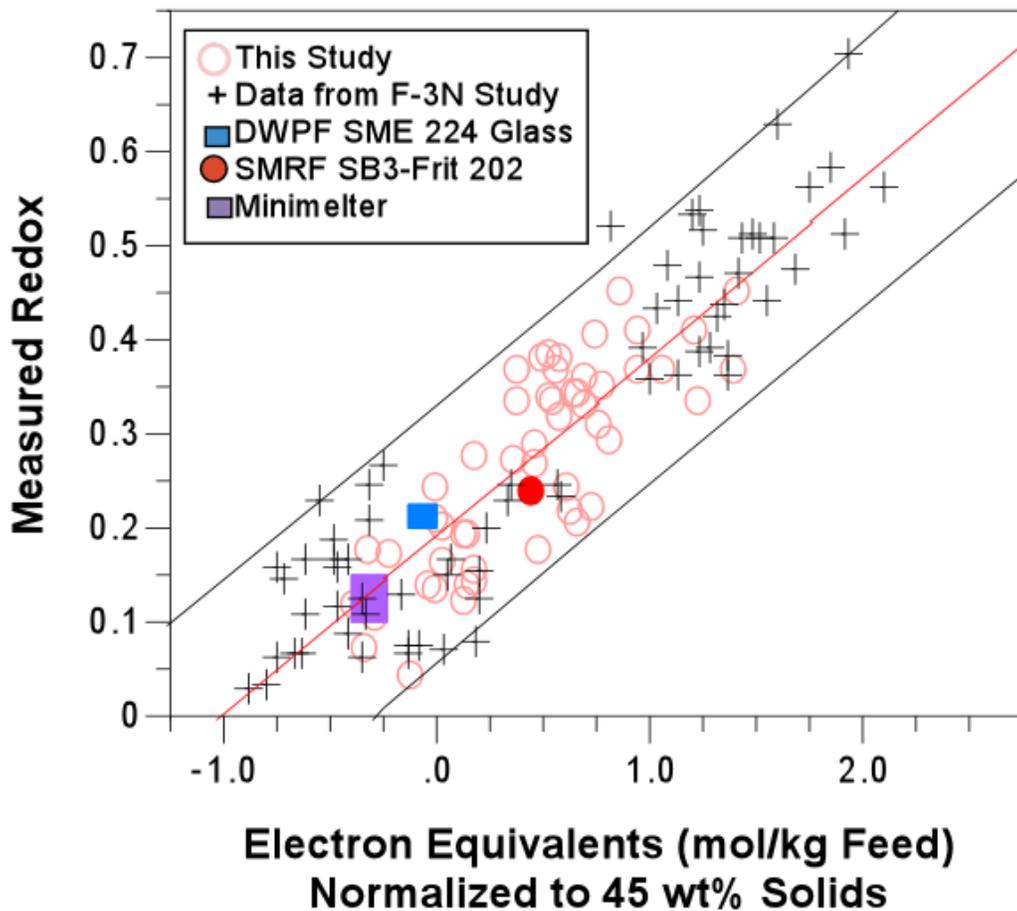
where [S] = sugar (carbon) (mol/kg feed).

Figure 1.   REDOX model with formate, oxalate, coal, nitrate, and manganese normalized for 45 wt% solids, where $\dfrac{Fe^{2+}}{\varSigma Fe} = 0.1942 + 0.1910\xi$.

VALIDATION OF ELECTRON EQUIVALENTS MODEL

Data for three glasses produced in various SRS melters, including the DWPF, were analyzed for REDOX.   The validation data are shown in Figure 1 (see solid symbols).

- The DWPF sample REDOX was from a sample pulled from the pour spout of the DWPF during radioactive operation and analyzed at SRTC in the Shielded Cell Facility (SCF). The feed to the melter was comprised mostly of melter feed from SME Batch 224. The target REDOX based on the Electron Equivalents model was ~0.2.
- Samples of minimelter feeds were vitrified in closed crucibles and preliminary analysis of the redox indicated that the target REDOX using the Electron Equivalents model was achieved in the closed crucible tests.

A REDOX of 0.12 was achieved after continuous feeding in the minimelter due to air inleakage.

- Lastly, Slurry-fed Melt Rate Furnace (SMRF) tests were performed at a target REDOX of 0.22 based on the Electron Equivalents model. The resulting measured REDOX values shown in Figure 1 indicate an average REDOX of 0.239 (ten REDOX values measured after the SMRF had achieved steady state conditions).

The data from these validation melter tests are shown in Figure 1 (see solid symbols) along with the "Model Data" and the fitted model. The Electron Equivalents term is fitted using the SME analyses. All three data points from actual melters fall well within the 95% confidence interval of the Electron Equivalents model.

The Electron Equivalents REDOX model was also validated against REDOX and feed data from the SRS Integrated DWPF Melter System (IDMS), which was a one-ninth scale (of DWPF) facility used to test various aspects of DWPF operation [13]. Agreement between the Electron Equivalents model and data generated in quartz crucible and pilot-scale melter runs at Pacific Northwest National Laboratory (PNNL) [18,19,20] was also excellent (see reference 13). The PNNL quartz crucible tests used both formate and sugar as reductants, while nitrate and nitrite provided the oxidant.

Crucible studies of the effect of formate and nitrate on glass REDOX adjustment were performed by PNNL in 1996 [21]. These studies were performed on feeds that were very similar to the DWPF, since at that time the Hanford Waste Vitrification Project (HWVP) process was similar to the DWPF process. Nineteen crucible melts were made with varying amounts of nitrate and formate. This data was also used to validate the Electron Equivalents model. Detailed discussions are given elsewhere [13].

Lastly, REDOX and feed data from WVNS was assessed against the Electron Equivalents model. The data included crucible melts [22] and data from the operation of a 1/10th scale test melter [10]. This melter was a 1/10th scale prototype of the joule-heated, ceramic-lined melter used to vitrify wastes stored at the West Valley Demonstration Project (WVDP). Tests were run by doping simulated waste slurries with varying amounts of nitric acid to simulate WVDP flowsheet levels of nitrate, and sucrose was used as a reductant. All data were then normalized to 45 wt% solids. The WVNS data show that the Electron Equivalents model handles sugar as a reductant quite well [13].

CONCLUSIONS

Glasses used in REDOX modeling must be produced from refluxed melter feed material to ensure conversion to nitrate and formate species. Vitrified material must be visibly (10X magnification) black and homogeneous for reliable REDOX ratio and cation measurements. The iron REDOX ratio (i.e., $Fe^{2+}/\Sigma Fe$) should be measured using a highly reproducible and accurate method such as the

Baumann colorimetric technique, which was recommended, for use in DWPF in 1989 [23]. Use of other REDOX measurement techniques has been shown to give less reliable measurements [23]. REDOX values must be greater than or equal to the method detection limit of $Fe^{2+}/\Sigma Fe \leq 0.03$. Both REDOX and feed chemistry measurements must be available for the same sample to decrease modeling error. Measured or as-made total solids information must available.

Reduction makes an atom or molecule less positive by electron transfer. Oxidation makes an atom or molecule more positive by electron transfer. The number of moles of electrons transferred for each REDuction/OXidation reaction are weighted by the number of electrons transferred providing an Electron Equivalents term for each reductant and oxidant species defined. The weighted Electron Equivalents are then summed (oxidation reactions have a positive sign and reduction reactions have a negative sign:

$$\frac{Fe^{2+}}{\Sigma Fe} = f\left[\left(2[F] + 4[C] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T}\right] = f[\xi]$$

where f =   indicates a function
     $[F]$ =   formate (mol/kg feed)
     $[C]$ =   coal (carbon) (mol/kg feed)
     $[O_T]$ =   oxalate$_{total}$ (soluble and insoluble) (mol/kg feed)
     $[N]$ =   nitrate + nitrite (mol/kg feed)
     $[Mn]$ =   manganese (mol/kg feed)
     T   =   total solids (wt%)
and ξ(mol/kg feed) = Electron Equivalents

In the presence of sugar the Electron Equivalents term becomes

$$\xi \text{ (mol/kg feed)} = \left(2[F] + 4[C] + 4[S] + 4[O_T] - 5[N] - 2[Mn]\right)\frac{45}{T}$$

The REDOX data generated in this study were fit along with previous model data as a linear function of ξ:

$$\frac{Fe^{2+}}{\Sigma Fe} = 0.1942 + 0.1910\xi$$

with an $R^2 = 0.80$ and a RMSE = 0.0690.

The $\frac{Fe^{2+}}{\Sigma Fe}$ predictions from the Electron Equivalents model were validated against (1) REDOX data generated from the DWPF melter from SME Batch 224, (2) data generated by the SRTC mini-melter and (3) data from the SRTC Slurry-fed Melt Rate Furnace (SMRF). All the data from these melters fell within the 95% confidence bands of the Electron Equivalents REDOX model developed in this study. Validation data from SRS pilot scale melters, Pacific Northwest Laboratory testing, and West Valley Nuclear Fuel Services testing agreed with the Electron Equivalents model better than all previous REDOX models.

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