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REDOX CONTROL OF ELECTRIC MELTERS WITH COMPLEX FEED COMPOSITIONS
PART I: ANALYTICAL METHODS AND MODELS

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ABSTRACT

The redox state of glass from electric melters with complex feed compositions is determined by balance between gases above the melt, and transition metals and organic compounds in the feed. Part I discusses experimental and computational methods of relating flowrates and other melter operating conditions to the redox state of glass, and composition of the melter offgas. Computerized thermodynamic computational methods are useful in predicting the sequence and products of redox reactions and in assessing individual process variations. Melter redox state can be predicted by combining monitoring of melter operating conditions, redox measurement of fused melter feed samples, and periodic redox measurement of product. Mossbauer spectroscopy, and other methods which measure Fe(II)/Fe(III) in glass, can be used to measure melter redox state.

Part II develops preliminary operating limits for the vitrification of High-Level Radioactive Waste. Limits on reducing potential to preclude the accumulation of combustible gases, accumulation of sulfides and selenides, and degradation of melter components are the most critical. Problems associated with excessively oxidizing conditions, such as glass foaming and potential ruthenium volatility, are controlled when sufficient formic acid is added to adjust melter feed rheology.

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INTRODUCTION

Slurry Fed Melters (SFM) are being developed in the U.S., Europe and Japan for the conversion of high level radioactive waste to borosilicate glass for permanent disposal. Pilot scale operations with various melter feed compositions have indicated that redox control of melters is necessary to meet the operating goals of the various sites. Controlled burning of organic materials in the melter feeds is necessary to prevent the accumulation of combustible gases, or soot which could lead to premature melter component failure. Excessively high oxygen fugacity can result in glass foaming, which lowers the glass production rate. Excessively low oxygen fugacities favor the accumulation of dense, electrically-conducting selenides and sulfides, shortening melter operating life.

The methods discussed below are applicable to slurry-fed electric glass melters as a class. Specific calculations are based upon the requirements of the Defense Waste Processing Facility (DWPF), which is being constructed at the

U.S. Department of Energy's Savannah River Plant.

SUMMARY AND CONCLUSIONS

Melter oxidizing power is balanced between the oxidizing power of purged or inleaking air, and transition metals in the feed, and the reducing power of organic compounds in the melter feed.

Several series of crucible and melter tests have been conducted to quantify the dependence of glass redox state on the melter feed and operating conditions. A priori predictions of the glass redox state have been partially sucessful. General trends, sequences of reaction, and sensitivities to normal process variations can be assessed. Computerized models of melter redox require calibration with pilot-scale tests coverring the anticipated ranges of melter feed compositions and melter opeating conditions. Combination of computerized models with routine feed analyses, off-gas analyses, melter temperature measurements, and periodic glass sampling is expected to provide a reliable indication of melter redox state.

EXPERIMENTAL METHODS

Batch glass reactions were conducted in high-purity alumina crucibles, with tight-fitting lids. Continuous melt reactions were conducted in electrically-heated slurry-fed melters varying in melt surface area from 0.5 to 9 square feet. Nominal reaction temperature was 1150 °C. Crucible fusion times were standardized at 3 hours.

Feed simulations are given in another paper in this volume [1]. Most tests

used simplified average composition slurries containing the major components of SRP defense waste. Formic acid contents are reported in the convenient engineering unit gram moles per pound of dried sludge solids (gM/#SS) or percentage of the stoichiometric (%ST) amount required for complete acid/base reaction with the sludge, plus decomposition of carbonates and nitrites, plus the reduction of mercury and silver hydroxides. Tests have indicated that precious metal content in the sludge causes additional formic acid decomposition through catalysis.

EFFECTS OF MELTER OPERATING CONDITIONS ON GLASS REDOX STATE

Glass melter designs combine many of the characteristics of 1) flash boilers, 2) calciners, 3) incinerators and 4) electrically heated glass melters. The flash boiler aspect is a result of the feed's 50 - 60 weight percent water impinging upon the 500 - 900 °C surface of the glass pool. Light, nonionized organic compounds contained in the feed, such as benzene, can be considered to boil off at the same temperature as the water. Calcination occurs as the batch settles into the melt pool and is further heated. The formates and hydroxides of aluminum, sodium, calcium, iron, manganese, nickel and others are converted to oxides. Organic compounds in the melter feed must be incinerated. Organics include coal from spent radioiodine scrubber beds, formates from formic acid used to reduce the viscosity of radioactive sludge, benzene produced as a byproduct of removal of radio-cesium from waste supernate, and organic reducing agents such as sugar. The melters are electrically heated, requiring the continued operation of submerged electrodes, and booster heaters in the melter plenum above the melt.

The overall gas flow through the melter is minimized to limit the power

requirements, and to minimize the cost of providing and operating the Melter Offgas Scrubber System. This places additional constraints on the system, since it precludes the use of large volumes of air.

Reducing agent effects have been assessed with both crucible and SFM tests. Table I shows the non-linear response of even simple glass systems. Fe_2O_3 and Fe_3O_4 were mixed with a glass frit and reducing and oxidizing agents under different conditions. The iron oxide species served as both redox buffer and redox indicator. The extreme cases of closed crucibles versus those open to air indicate a strong response to the atmosphere above the melt. The addition of minor amounts of water and other compounds which tend to purge the reducing gasses cause major shifts in the glass redox state.

Hydroxide sludges similar to the average SRP defense waste composition were heated under total reflux conditions with various amounts of formic acid. The resulting sludges were mixed with frit and fused. At low formic acid levels, the redox response was relatively constant for closed crucibles, with no effect on open crucibles. In the closed crucible tests, once most of the Fe(III) had been reduced the buffering effect of the iron was lost, and small increases in formic acid content caused large shifts in oxygen fugacity. See Table I. Large quantities of formic acid were required to overcome combustion during open crucible tests. (Data not shown). Once this threshold was overcome, the redox reaction of the glass was similar to the low formic acid response in closed crucibles. This marked difference between open and closed crucible results demonstrates sensitivity to the atmosphere above the melt.

In joint SRL/PNL melter tests, the effects of normal processing variations on glass redox were investigated, by varying the formic acid content, air

inleakage rate and melter plenum temperature. Results are shown in Table II, which indicates that glass redox is not strongly, affected by moderate changes in feed formic acid content, and melter air inleakage rate. Closed crucible batch tests yield glass with an oxygen fugacity similar to glass from melter operations with minimal air inleakage.

Formic acid is also a reducing agent when in solution. For example, before treatment with formic acid, Mn exists as Mn(IV) in alkaline waste. Treatment with formic acid converts 40 - 48% of the Mn(IV) to Mn(II), as evidenced by an increase in solubility. Thus, this amount of reduction precedes carbothermic reduction in the melter. The strength of this effect can be seen by comparing the valence state of glass fused from formate salt mixtures to a virtually identical mix fused from hydroxides reacted with formic acid. The formic salt derived batches are orders of magnitude more reduced, showing the effects of complete prereaction and prereduction. Table II.

GRAPHICAL REPRESENTATION OF GLASS REDOX STATE

Gibbs Free Energies of formation for single reactions of interest in the standard states were calculated using the normal methods and published data [2]. They have been plotted using the format developed by Richardson & Jeffres [3] as modified by Darken and Gurry [4]. This is a particularly useable way to present standard state calculations, since it indicates the sequence of reductions at various temperatures. In addition, use of H_2/H_2O, CO/CO_2, and O_2 scales permits the immediate determination of standard state gas mixtures in equilibrium with the reactions at temperature.

Evaluations utilizing reduced chemical activities are based upon scales

developed by Schreiber using SRL131 frit with individual redox elements [5,6]. This permits the estimation of the valence of minor glass components when the average valence of the major redox couple (Fe(II)/Fe(III)) is known. Schreiber has also developed scales for oxygen fugacity as a function of Fe(II)/Fe(III) at different melt temperatures [7]. While Fe(II)/Fe(III) can be measured by a num ber of methods, all the following discussions are based upon Mossbauer spectroscopy, which has been demonstrated on glass containing actual high level radioactive waste [8].

COMPUTER REACTION MODEL

A model of melter chemistry was developed to improve upon the graphical representation techniques. In this method, the melter was first divided into zones corresponding to steps in the melting process. As shown in Figure 1, the melter feed slurry flash boils at about 100°C, and the volatile compounds (H_2O, free aromatic hydrocarbons) enter the plenum vapor space where the temperature is 550-800°C. The residual metal salts form the "cold cap" which floats on the melt pool. The upper layer of the cold cap consists of porous, partially calcined sludge sintered to the powdered frit. Further down in the cold cap, the temperature exceeds the glass transition temperature for the frit, and dense partially-reacted glass is filled with interconnected tubular porosity. The lowest section of the cold cap is a foam layer comprised of almost fully reacted glass, with closed porosity. Bubbles coalesce in the foam layer, and vent through numerous vent holes. The foam layer acts as a thermal insulator, slowing the melt rate of the glass batch above it. At the nominal melt temperature of 1150°C, equilibration of oxygen states can take place, and depending upon the residual species, additional gases can be released.

The various zones were modeled using the most appropriate simplifying criteria. Flash boiling was assumed to occur without chemical change. The cold cap and melt were modeled based upon equilibrium thermodynamics and standard states. The vapor space was modeled using a gaseous reaction network, with appropriate reaction kinetics.

In the model, equilibrium computations are made using a computer package similar to one developed by NASA [9]. In this program, the feed stream is decomposed into its constituent elements, and recombined to that chemical state which results in the minimum Gibbs Free Energy. All condensed phases are treated as distinct pure phases of unit activity in computing product free energy. Up to 10 chemical elements can be included per calculation. Normally the elements chosen are O, H, C, N, S, Fe, Mn, Ni, Ti, and U. In order to study the chemistry of the other elements, it is possible to subtitute one element at a time into the calculation set (e.g. Ru for Ti). The model data base contains 1400 separate species from references [1,9]. The program algorithm is based on linear programming techniques, with free energy as the function to be minimized under constraints of constituent atom and enthalpy balances. Stages can be run adiabatically or isothermally.

For the computations, an effective cold cap temperature was chosen by matching computed sulfur volatility to observed values. For five different experimental cases, the values ranged from 520-645°C, and averaged 620°C. This average value has been used in all predictive calculations.

The solid residues from the cold cap calculation are used as the source for a second equilibrium calculation at 1150°C to check for reequilibration of the melt. If any gases are released, several iterations between the melt and cold

cap may be necessary to obtain consistant results. Usually, all of the gases are released in the cold cap, and this is not necessary.

The plenum vapor space model treats the vapor space as a plug flow reactor or, in some cases, several such reactors in parallel. The feed to this reactor includes the gases evolved from the cold cap, flash boiled volatiles, air purges and inleakages, and decomposition products of organic salts.

Free organic species such as biphenyl and phenol are assumed to oxidize by a mechanism involving a limiting step, the oxidatively assisted thermal breaking of a bond, followed by nearly instantaneous oxidation to CO and H2. Oxidation of CO and H2 follows. Oxidation of phenyl boric acid decomposition fragments is treated identically. Literature values [11-14] were utilized to obtain rate constants for the initial decomposition steps, which are first order in the decomposing species.

The scheme for CO and H2 oxidation consists of 12 elementary reaction steps from reference 14 with minor modifications for thermodynamic consistency. This scheme predicts complete oxidation of CO and H2 in the presence of even a small excess of O2 at temperatures above 535°C, but no oxidation below 535°C at typical residence times (5-25 sec) regardless of O2 excess.

Two melter experiments have monitored CO/CO2 ratios with the plenum temperature below 535°C. No aromatics were included, and it is assumed that no vapor space reactions took place, so results reflect the gas evolved from the cold cap. The melter runs were at different feed compositions, and the model correctly predicted the effects of the more reducing composition. The predominant cold cap gas phase chemistry is the water gas shift reaction, resulting from the

large relative amount of water in the melter feed.

If the assumption of gas phase equilibrium is retained, and the calculations redone to force agreement with the experimental off gas CO/CO_2 ratio, then the glass Fe(II)/Fe(III) ratio is also brought into better agreement. See Table III.

In both cases above, the model correctly predicts the direction, but not the magnitude, of the effect of changing the feed composition. Precipitated nickel sulfide was found in the melter after Run 1, but not Run 2. These results suggest that the gas/condensed phase reactions are slower than the gas phase reactions, and that perhaps their kinetics, or the fact that the condensed phases are not in their standard states needs to be considered explicitly in future cold cap models. Devitrification studies imply that the formation of spinels and alkali-iron-silicates competes with redox reactions, and may further decrease the chemical activity of these metals [1]. CO_2, and 10% H_2O are found in residual gas analyses of pores removed from a melter's foam layer. The ratio of carbon to hydrogen in the formate salts is inconsistent with this analysis, suggesting that in the absence of external oxygen, at least some of the carbon pyrolyzes and later reacts to form CO_2.

In most experiments, the melter plenum temperature was in the 700°C range. Under these conditions thermodynamics predicts negligable CO in the offgas. However, oxidation of aromatics was not always complete. The agreement of experimental results with the kinetic model is satisfactory, and conservative, i.e. it tends to slightly overpredict the remaining combustibles. Table IV.

In summary, thermodynamic calculations can be used to compute the valence of

other redox species if the glass Fe(II)/Fe(III) ratio is known. A computer model has been developed which relates melter feed composition, and melter offgas composition to the glass Fe(II)/Fe(III) ratio. The computer model is not capable of independently predicting both glass and offgas composition. However, combination of the computerized model with routine melter monitoring, and periodic glass product sampling is expected to provide a reliable indication of melter redox state.

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TABLE I: EFFECT OF VARIOUS REDOX COMPOUNDS IN CLOSED CRUCIBLE TESTS

SAMPLE	Fe(II)/Fe(III)	log(pO2) AT 1150°C
90 SRL165 FRIT + 10 Fe_2O_3 +		
4 NaCOOH + 1 $Ni(NO_3)_2.6H_2O$	0.06	-3.20
4 NaCOOH + 1 $NaNO_3$	0.09	-3.72
4 NaCOOH + 2 MnO_2	0.18	-5.02
0.2 C	0.28	-5.79
1.0 Phenyl Boric Acid (PBA)	0.37	-6.29
4 NaCOOH + 1 $Mn(COOH)_2$ + 1 MnO_2 + 1 $Ni(NO_3)_2.6H_2O$	0.42	-6.50
4 $Mn(COOH)_2$	0.51	-6.83
2 NaCOOH	0.54	-6.93
5 $Fe(COOH)_3$	0.70	-7.38
6 $Mn(COOH)_2$	0.71	-7.41
2 PBA	1.11	-8.18
5 NaCOOH	1.40	-8.58
1 C	1.45	-8.65
5 PBA + 1 $CaCO_3$	2.00	-9.20
5 PBA (soot in crucible after test)	100	-16
90 SRL165 + 10 $Fe(COOH)_3$	100	-16
90 SRL165 FRIT + 10 Fe_3O_4 +		
2 $Ni(NO_3)_2.6H_2O$	0.01	0.00
1 MnO_2	0.13	-4.46
NO ADDITIONS	0.23	-5.42
1 Na_2SO_4 + 1 $CaSO_4$	0.25	-5.59
1 C	0.53	-6.88
1 NaCOOH	0.54	-6.93
1 $Mn(COOH)_2$	0.57	-7.02
1 PBA	1.29	-8.44

SIMULATED MELTER FEED WITH VARYING FORMIC ACID CONTENT

gM/#sludge	% stoichiometric		
1.5	48	0.01	0.00
1.7	60	0.26	-5.66
2.0	70	0.12	-4.32
2.5	85	0.62	-7.17
3.1	110	1.00	-8.00

Batches in parts by weight. All fusions 3 hr at 1150°C.
gM/#SS is gram moles of formic acid per pound dry sludge solids.
% ST is the % of stoichiometric formic acid needed to complete reactions with hydroxide sludge.

TABLE II: MELTER TESTS TO DETERMINE THE EFFECT OF MELTER OPERATIONS ON GLASS REDOX STATE

SAMPLE	Fe(II)/Fe(III)	log(pO2) AT 1150°C
MELTER FEED PREPARED BY REACTING FORMIC ACID WITH HYDROXIDES		
LSFM#10	0.19	-5.15
LSFM#11	0.14	-4.60
COLD CAP SAMPLE	0.21	-5.27
COLD CAP SAMPLE	0.45	-6.59
MELTER FEED PREPARED BY SLURRYING FORMATE SALTS AND FRIT		
PSCM#6	1.39	-8.57
PSCM#7	1.08	-8.46
PSCM#8 SAMPLE 100	1.30	-8.46
SAMPLE 114	20.00	-13.20
MELTER FEED WITH NO AROMATICS		
ESCMIII 110%ST, OPEN CRUCIBLE FUSION	0.01	0.00
ESCMIIA 86%ST, 6.2 g AIR / g GLASS	0.15	-4.70
ESCMIIB 86%ST, 0.51 g AIR / g GLASS	0.20	-5.24
ESCMIIIA 110%ST, 0.39 g AIR / g GLASS	0.33	-6.06
ESCMI 90%ST, 0.29 g AIR / g GLASS	0.37	-6.29
ESCMIIIB 110%ST, 0.51 g AIR / g GLASS	0.43	-6.53
ESCMIII 110%ST, CLOSED CRUCIBLE FUSION	0.62	-7.15
MELTER FEED WITH AROMATICS		
SCM2 80% AROMATIC REMOVAL, 7.8 g AIR / g GLASS	0.22	-5.35
SCM2 90% AROMATIC REMOVAL, 11 g AIR / g GLASS, HIGH HALIDE	0.49	-6.77
SCM2 90% AROMATIC REMOVAL 9 g AIR / g GLASS, HIGH HALIDE	0.59	-7.20

TABLE III: COMPARISON OF EXPERIMENTAL AND CALCULATED Fe(II)/Fe(III) IN GLASS

MELTER RUN	OBSERVED	CALCULATED (FORCED CO/CO2)	CALCULATED (GAS-SOLID EQUILIBRIUM)
1	1.39	6.02	INFINITE
2	0.24	0.22	5.91

TABLE IV:
COMPARISON OF EXPERIMENTAL AND PREDICTED AROMATIC CONTENT OF MELTER OFF GAS
(MOLE % OF DRIED OFFGAS)

MELTER RUN	OBSERVED	CALCULATED
3	0.000	0.000
4	0.030	0.030
5	0.066	0.096

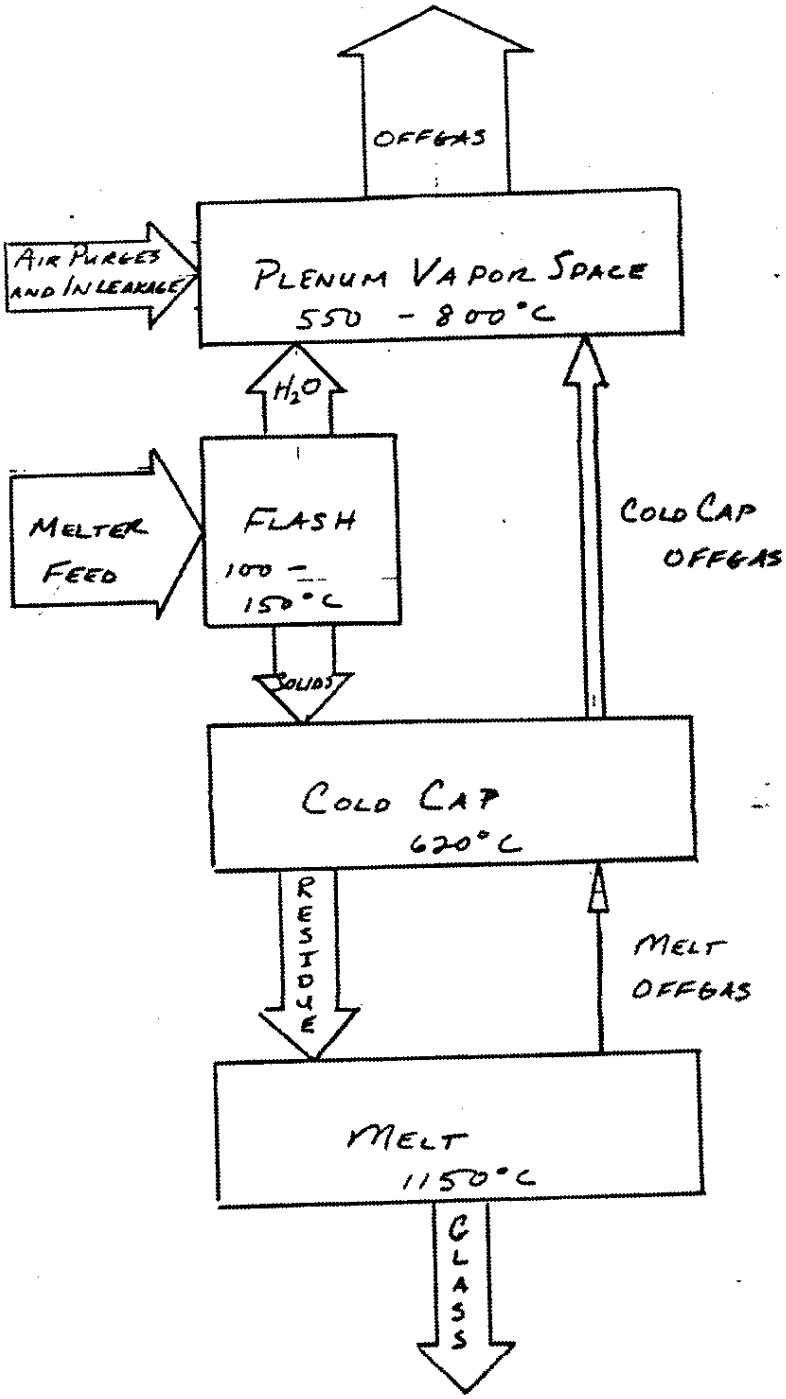

FIGURE I: SCHEMATIC OF MELTER CHEMISTRY MODEL

(WIDTH OF ARROWS INDICATES RELATIVE MASS FLOW RATES)