248193

DP-MS-85-16B

REDOX CONTROL OF ELECTRIC MELTERS WITH COMPLEX FEED COMPOSITIONS PART II: PRELIMINARY LIMITS FOR RADIOACTIVE WASTE MELTERS

by

D. F. Bickford[1], R.B. Diemer, Jr.[2], and D. C. Iverson[1]

[1] E. I. du Pont de Nemours & Co.,
Savannah River Laboratory, Aiken SC 29808 USA

[2] E. I. du Pont de Nemours & Co.,
Engineering Department, Wilmington DE 19898 USA

A paper for presentation at the conference:
Physics and Chemistry of Glass and Glassmaking,
New York State College of Ceramics,
Alfred University,
Alfred, New York 14802
July 29 - August 2, 1985

and for publication in the proceedings.

This paper was prepared in connection with work done under Contract No. DE-AC09-7600001 with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or receipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

REDOX CONTROL OF ELECTRIC MELTERS WITH COMPLEX FEED COMPOSITIONS

PART II: PRELIMINARY LIMITS FOR RADIOACTIVE WASTE MELTERS

D. F. Bickford[1], R. B. Diemer, Jr.[2], and D. C. Iverson[1]

[1] E. I. du Pont de Nemours & Co.,
Savannah River Laboratory, Aiken SC 29808 USA

[2] E. I. du Pont de Nemours & Co.,
Engineering Department, Wilmington DE 19898 USA

INTRODUCTION

The Defense Waste Processing Facility (DWPF) is being constructed at the U.S. Department of Energy's Savannah River Plant to convert caustic-neutralized high-level radioactive waste into borosilicate glass for permanent disposal. Preliminary operating limits are required to assure safe operation of pilot scale nonradioactive melters, and to serve as a guide for operating limits for the DWPF production melter.

Thermodynamic, experimental and computational methods were discussed in Part I, in these proceedings. Methods used in the development of specific limits outlined below are applicable to slurry-fed radioactive waste melters as a class. Specific values used in calculations are based upon anticipated conditions in the DWPF.

SUMMARY AND CONCLUSIONS

Melter redox control is necessary for safe and continued melter operation. A combination of feed composition control, melter operational controls and monitors, and periodic determination of product glass redox state is sufficient to meet operating and safety requirements.

Mossbauer spectroscopy, or other methods which determine the Fe(II)/Fe(III) ratio of the glass product, can be used to determine the oxidation state of the glass and thereby assess operating conditions.

Slightly reducing conditions can eliminate radio-Ru volatility by suppressing the formation of RuO_4. Reducing conditions also limit foaming resulting from the release of oxygen as transition metal oxides are dissolved in the melt.

The calcination and partial combustion of organic compounds in the melter feed generates combustible mixtures of CO, H_2 and benzene. The organics must be essentially completely incinerated to avoid the accumulation of combustible offgas mixtures, and prevent fouling of the equipment by soot and tars. Operation of the melter plenum above the autoignition temperature, metering in of purge air in excess of that required for complete combustion, and dilution by water vapor from reacted feed all preclude this occurrence in the melter. Prevention of dangerous offgas compositions after water vapor removal is assured by combustion in the melter, the addition of dilution air, and by continuous monitoring by % Lower Explosive Limit meters.

Melter reducing power must be restricted to prevent formation of molten sulfides or selenides in the melter, and to prevent carburization and sulfidation attack of Inconel-690 melter components. Control of average oxygen partial pressure in the melter plenum is insufficient to assure prevention of localized attack of I-690. An additional requirement is therefore necessary, that no soot or tarry substances be deposited on the I-690.

LIMITS TO PREVENT COMBUSTIBLE GAS AND SOOT ACCUMULATION

One factor which places limitations on melter operation is the potential for accumulating combustible gas mixtures in the offgas system. Gas concentrations can shift because of changes in melter feed composition, air inleakage rates, purge gas rates, melt rates, effective melter temperatures, and surges which develop as a result of temporary cold cap instabilities. The major feed composition factor is the ratio of oxidizers to reductants. Oxidized transition metals, nitrites and nitrates are the principal oxidizing agents in the feed. Air inleakage to the melters, or deliberately added as purges, is the other major oxidizing agent. Reducing agents can either exist as deliberate additives, or as the residues from organic chemical operations. In slurry feed melters the effectiveness of reducing agents can be affected by boiling points, and average plenum temperatures: organics can volatilize (with no direct effect on the glass redox state), can react only during the last stages of glass melting (with quantitative effect on the glass), or can partially burn or pyrolyze in the initial stages of melting (with an intermediate effect). In the DWPF, the major organic species are formic acid (used to adjust feed rheology, and to reduce Hg to a strippable form) and aromatics remaining from the tetraphenyl borate (used to concentrate radioactive Cs in waste supernate solutions).

Flow rates are determined by nominal production rates, and the sizing of offgas equipment. Surges in combustible gas components up to 3X the normal rate have been observed in pilot scale melters.

A second, related concern with melter operation is the prevention of the formation and accumulation of soot. In addition to possible pluggage of equipment by soot or tarry substances, it is necessary to keep carbon deposits off of melter materials to prevent carburization or sulfidization of melter components. Details for the materials concerns are discussed below in a separate section.

The melter chemistry model described Part I was used to calculate offgas compositions. Based upon experiment, a glass Fe(II)/Fe(III) ratio of 0.24 was used. In addition, consideration was given to the distribution of air to the melter plenum. The results were evaluated against the criteria of explosivity and pyrolytic carbon formation. Based upon experiment, unburned aromatics were assumed to be phenol. This was conservative from an explosivity point of view since phenol's lower explosive limit (1.1%) is lower than , for instance, benzene's (1.4%). Mixture lower explosive limits (LELs) were calculated based upon standard methods [1]. Combustible gases were normalized to the LEL and evaluated against the criteria that the combustibles not exceed 70% of the LEL.

The results are shown in Figures 1 and 2. At high temperatures, combustible surges over 3X and aromatic removal rates less than 70% can be tolerated. At low temperatures, the tolerable surge factor is reduced to 1.4X, and the tolerable aromatic removal minimum becomes 80%.

To evaluate pyrolytic carbon formation, the thermal decomposition fragments of the aromatics were looked for in the offgas. The results are shown in Figure 3. At low temperatures, there will be no significant thermal decomposition. At the higher temperatures, the minimum acceptable upstream aromatic removal rate is 85%, and the maximum tolerable surge is 1.3X. Thus, pyrolysis prevention is a more restrictive criteria than explosivity.

UPPER OXYGEN PARTIAL PRESSURE LIMITS BASED UPON FOAMING

Uncontrolled glass foaming might result in the blockage of critical melter or melter offgas components. Glass foaming also reduces melt rates by decreasing the rate of heat transfer to the unreacted batch . No excessive foaming has been noted in any defense waste glass melter which contained sufficient formic acid to adjust the sludge viscosity.

Comparison of the melting characteristics of low vs. high temperature calcined sludge mixed with frit indicate that foaming is primarily a consequence of the dissolution of sludge in the glass rather than a calcination phenomena [2]. That is, while undergoing the change from transition metal oxides at standard state in equilibrium with air to dissolved ions in glass, the transition metals may liberate oxygen. Partially calcined carbonates, oxalates, formates, etc. can liberate CO, CO2, H2, H2O in addition to oxygen and would normally be expected to contribute to foaming. However, DTA/TGA , and evolved gas analysis, indicate that most of these compounds decompose at temperatures below the softening point of the glass frit, and the resulting gases are free to escape through open porosity.

Examination of the redox couples for a typical defense waste glass reveals that in a system dominated by the Fe(II)/Fe(III) content, MnO2 or Mn3O4 will release oxygen as they dissolve in the glass as Mn(II). Hrma has recently conducted a series of glass reaction studies which indicate that foaming will not be extensive if 2/3 of the Mn is reduced to Mn(II) [3]. This is close to the 40-48% level of conversion by aqueous formic acid during melter feed preparation at 90% of the stoichiometric amount for formic acid / alkaline sludge reactions.

In a time series of crucible melts containing formate salts and carbon, foaming developed in 1/4 hour and persisted for more than 24 hours at 700 °C. No Fe(II) was detected in any of these samples. This implies that other reactions, such as those associated with devitrification are more favored than reactions between the hypothesized pyrolyzed carbon and ferric iron. The foam at 700 °C is attributed to the expansion of gases trapped when the porosity closed at lower temperatures. The stability of the foam is attributed primarily to the high viscosity of the melt at 700 °C. Upon subsequent reheating to 950 °C, the foam collapsed within 1/4 hour, and did not reoccur. Mossbauer spectroscopy indicated no Fe(II) until about 950°C, indicating relatively slow iron reductions below this temperature, and that the major reducing agent for iron above this temperature is probably pyrolytic carbon from decomposed organics.

UPPER OXYGEN FUGACITY LIMIT BASED UPON RUTHENIUM VOLATILITY

Control of radioactive ruthenium was an early process concern because of expected difficulty in scrubbing out the volatile offgas species RuO4 [4,5]. Thermodynamic calculations have indicated that this species is unstable in the offgas system, decomposing to the scrubbable particulate form RuO2. Further calculations show that RuO4 formation is sensitive to oxygen fugacity at melter plenum temperatures, and is effectively suppressed by operating at the slightly reducing conditions typical for the melter plenum. In melting studies at SRL and in Germany [6], no ruthenium has ever been detected past the scrubber section, even in non-reducing atmospheres, indicating very rapid decomposition of any volatile Ru oxide formed.

LOWER OXYGEN FUGACITY LIMIT BASED UPON SULFIDE ACCUMULATION:

Excessively reducing melter conditions can result in the reduction of nickel sulfate to nickel sulfide (typically Ni_3S_2). Similar selenide formation is possible. The sulfide has limited solubility in the glass, is electrically conductive, melts at a temperature well below the nominal melter temperature, and is denser than the glass. Excessive sulfide is a concern, since electrically conductive globules would tend to build up on the bottom of the melter, possibly shorting out the melter electrodes. Nickel sulfides have only been found in one SFM run with very low oxygen fugacity. In this case, the melter feed was prepared by the dissolution of formic acid salts, rather than the actual production method of reacting formic acid with hydroxide sludge.

Nickel sulfide nuggets can be produced in crucible melts by the addition of excessive amounts of reducing agents to feed containing anticipated amounts of sulfates and nickel. Oxygen probes submerged in slowly heated closed crucibles containing formated sludge, indicate that even with low formic acid contents, the low temperature reducing potential is strong enough to convert nickel oxide in its standard state, in contact with dilute SO_2 gas, to nickel sulfide. Figure 4. Since Fe(II) is not seen at 700°C, and nickel sulfide is only seen in melts containing higher levels of reducing agents, slow kinetics and reduced chemical activities resulting from solution effects on the

Fe, Ni, and sulfate are the most likely causes of the general lack of sulfide formation.

OXYGEN FUGACITY LIMITS BASED UPON MELTER MATERIALS

Inconel-690 has good resistance to oxidation and sulfidation in high-temperature gaseous environments. Metal loss rates under melter operating conditions rarely exceed 50 mils per year, even in glass contact [7]. Nickel based alloys are, however susceptible to sulfidation attack, where sulfur and oxygen set up an autocatalytic reaction which can lead to rapid oxidation of the metal. Under weakly oxidizing conditions, I-690 is moderately attacked (91 mils/year in 1.5% H_2S / 3% O_2 / 36.5% H_2 / 59% Ar at 727°C [8]). Under strongly reducing conditions, sulfidation can be catastrophic (1366 mils/year in 1.5% H_2S/98.5% H_2 at 727°C [8]). Samples of alloys I-600, I-601 and I-690 subjected to melter operating conditions at PNL, have been examined at PNL and SRL for evidence of sulfidation. SEM and Electron Beam Microprobe analysis of the samples showed complete oxidation of the 1/4 inch thick I-600, and localized perforation of the I-601. Sulfur was present at the metal/oxide interfaces indicating sulfidation of these two alloys. The I-690 had only a thin oxide coating, with no evidence of sulfidation. Sulfidation has occurred in Germany, where I-690 was exposed to molten sulfate salts containing fluorides and molybdates at about 850°C.

No evidence of significant I-690 sulfidation attack has been seen in any defense waste glass melter test. However, definitive results require a melter scaled with respect to combustion characteristics, to assure that strongly reducing conditions do not occur locally. Based upon our experience with the feed composition, it is reasonable to assume that sulfidation will not occur, if sooty deposits are not developed during melter operation, and if operating time in the temperature range 600 - 900°C is minimized.

ACKNOWLEDGEMENTS

The authors wish to thank Profs. H. D. Schreiber of VMI , P. Hrma of C-WRU, and L. D. Pye of Alfred U. for their fundamental contributions to the understanding of these phenomena. SRL contributors include: P. D. Soper, D. G. Karraker, H. L. Hull, R. E. Eibling, R. E. Edwards, J. W. Fowler, C. T. Randall, S. E. Eissenberg, E. F. Sturcken, D. F. Steedly, P. E. O'Rourke, P. K. Smith, E. J. Weber, C. M. Jantzen, M. D. Boersma, and M. J. Plodinec.

This work was done under contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

References

[1] H.F. Coward, et al, Limits Flammability Gases & Vapors, NTIS AD-701-575 (1952).
[2] D.C.Iverson, M.S. Thesis, Alfred Univ. (1984).
[3] P. Hrma, Case-W.R. Univ. Contract Report (SRL Internal Report DPST-85-419, 1985).
[4] J. D. Christian, Control Air-Borne Eff. Fuel Cycle Plants,(ANS-AIChE,1976).
[5] C. Courtois, Ru Oxides & Trapping Volatile Ru Compounds, CEA-BIB-213, (1974) trans. M. Gerrard ORNL-TR-2922.
[6] M. Klein, C. Weyers, and W.R.A. Goosens, 17th DOE Nucl. Air Cleaning Conf.
[7] D.C. Iverson and D.F. Bickford, Mat. Res. Soc. Symp. Proc. 44(1985)839.
[8] Inconel Alloy 690, (Huntington Alloys, Inc., Huntington WV 1980).

FIGURES

Figure 1: Melter Offgas Surges Decrease the Safety Margin For Explosions.

Figure 2: Increases in the Efficiency of Aromatic Removal Increase the Safety Margin for Offgas Explosions.

Figure 3: Pyrolytic Carbon Deposition is Supressed by Low Offgas Surging, And High Aromatic Removal Rates.

Figure 4: Crucible Tests Indicate That Nickel Sulfide Formation During Glass Melting Is Suppressed By Kinetics Or Competing Processes, Rather Than By Thermodynamics. Experimental Lines are For Two Levels of Formic Acid, and For 90% Of the Stoichiometric Amount Of Formic Acid Plus 80% Removal Of Aromatics By Hydrolysis With Formic Acid. The Shaded Region Indicates the Thermodynamic Limits Of Oxygen Fugacity For Conversion of NiO (Standard State) To Nickel Sulfide.

FIGURE 1

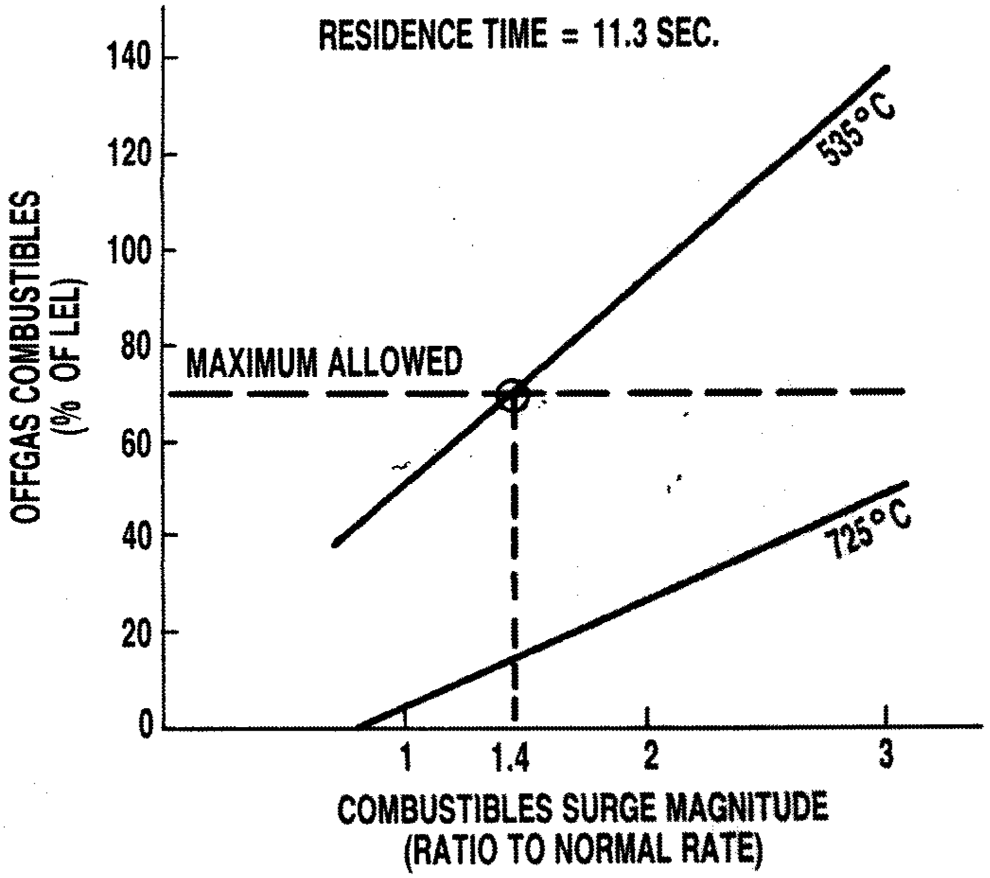

FIGURE 2

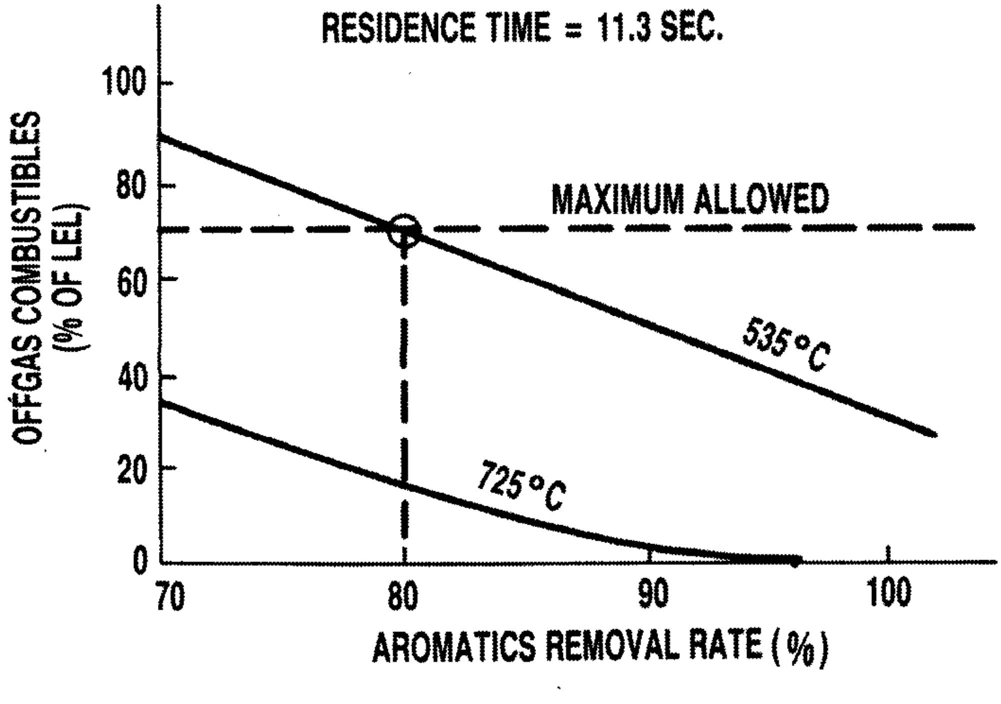

FIGURE 3

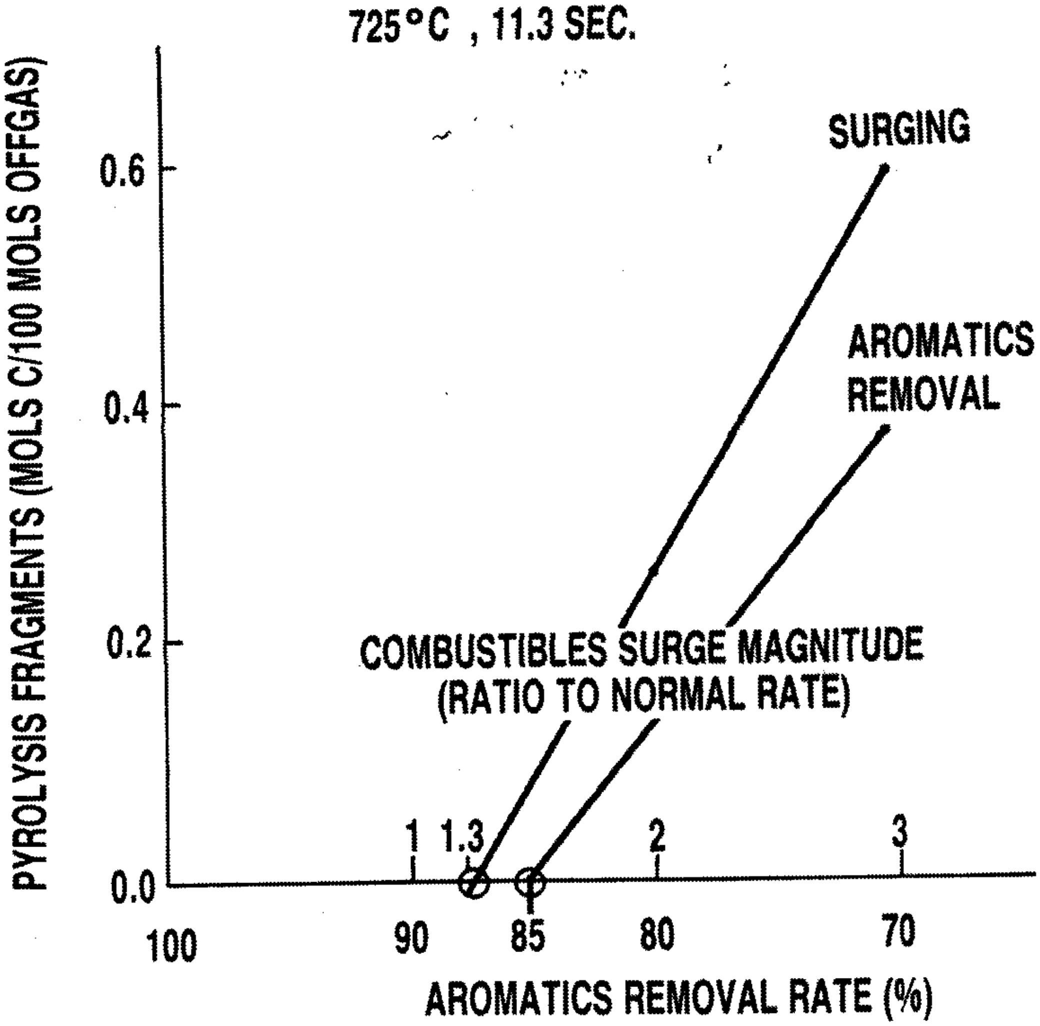
725°C , 11.3 SEC.
PYROLYSIS FRAGMENTS (MOLS C/100 MOLS OFFGAS)
0.6
0.4
0.2
0.0
SURGING
AROMATICS REMOVAL
COMBUSTIBLES SURGE MAGNITUDE (RATIO TO NORMAL RATE)
1
1.3
2
3
100
90
85
80
70
AROMATICS REMOVAL RATE (%)

FIGURE 4

OXYGEN PROBE OF MELTING GLASS