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EVALUATIONS OF GLASS VITRIFICATION TECHNIQUES ON IRON RATIO DETERMINATIONS (U)

by

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EVALUATIONS OF GLASS VITRIFICATION TECHNIQUES ON IRON RATIO DETERMINATIONS

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ABSTRACT

High-level liquid waste at the Savannah River Site (SRS) will be processed into borosilicate glass at the Defense Waste Processing Facility (DWPF). Waste glass will be transported to a geologic repository for permanent disposal. Control of the redox properties of the melter feed is necessary for smooth operation of the melter. The Fe(II)/total Fe ratio in glass is a measure of the redox conditions in the melter. To simulate final glass product conditions, melter feed samples will be vitrified at the DWPF laboratory. A colorimetric method was used to determine the Fe(II)/total Fe ratio on vitrified melter feed samples. Because the crucible vitrification technique can have a large effect on the Fe(II)/total Fe ratio, crucible sealing during vitrification of the waste feed sample, and the type of heating applied during vitrification, were the variables investigated for Fe(II)/total Fe ratio measurement effects. Various lid sealants were used for determining crucible sealing effects. Microwave and conventional heating were tested for glass vitrifications. Microwave heating and a nepheline gel sealant, to exclude oxygen from the alumina crucibles during vitrification, was adopted for use at the DWPF laboratory. This paper discusses microwave vitrification and crucible sealing techniques.

INTRODUCTION

The high-level liquid waste at the Savannah River Site is stored in large underground carbon steel tanks. The waste consists of a supernate layer and a sludge layer. Cs-137 will be removed from the supernate by precipitation with sodium tetraphenyl borate. Decontaminated supernate is further processed and fixed as a grout for disposal in concrete vaults. The precipitate

remaining is processed at the DWPF with treated waste tank sludge and glass-making chemicals into borosilicate glass.

During processing, slurry samples will be taken for chemical analyses and then vitrified to predict the required glass properties. The Fe(II)/total Fe ratio will be measured on a sample of vitrified feed. The oxidation/reduction (redox) equilibrium is critical to the processing of high-level nuclear waste.¹ The Fe(II)/total Fe ratio must be maintained in the range of 0.09 to 0.33 to meet the DWPF glass property specifications.^{2,3,4} If the sample feed is too reducing, metallic species may form a conductive layer that short-circuits the electrodes in the Joule-heated melter. The analytical method for measuring the Fe(II)/total Fe ratio requires vitrification of the feed at 1150 degrees C for 1 hour in a closed crucible, followed by a colorimetric analysis for Fe(II) concentration and total Fe concentration of the vitrified feed.^{2,5,6} The vitrification effects must be minimized and controlled so that the Fe(II)/total Fe ratio indicates as closely as possible the true melter feed redox properties.

The techniques used for vitrifying the melter feed in crucibles can have a significant effect on the Fe(II)/total Fe ratio. This paper discusses the effects that various sample crucible heating and sealing techniques have on the Fe(II)/total Fe determinations. The use of microwave or conventional furnace heating of the sample feeds may lead to some differences in the measured oxidation state. Five different crucible sealants were tested for their respective effectiveness in minimizing air leakage to the sample crucible during vitrification. Significant air leakage can lead to sample oxidation and subsequent low or erratic Fe(II)/Fe total ratio measurements.

EXPERIMENTAL METHODS

Microwave and Conventional Vitrification

Microwave vitrifications were performed using a modified Floyd RMS 150 microwave system. A specially designed microwave insert with an Echofoam outer shell and a silica carbide inner shell was used to hold the sample crucible. The dimensions of the microwave insert were designed to be compatible with the microwave heating pattern of the Floyd RMS 150 microwave system. An incompatible insert design would result in cracking or melting of the echofoam shell of the microwave insert at 1150 degrees C. Also, the insert was designed to enable remote handling with a master slave manipulator in the analytical shielded cells.

A CM 1200B bottom loader furnace with controller was used for all conventional furnace vitrifications.

Crucible Sealing Techniques

All sample slurries (30mL) were predried for 2.5 hours in an oven to a paste at 115 degrees C. After predrying, the samples were treated by the varying crucible sealing techniques described below:

- No Seal – The slurry–paste (sample) was placed in an open crucible.
- Paste Seal – The slurry–paste (sample) was placed on the crucible lid with a transfer bulb and placed on the crucible to create a seal.
- S–Prime (NaAlSiO₄) and Z–Prime (ZrO₂) gel sealants, manufacturer:

Z Y P Coatings, Inc.
P. O. Box 208
Oak Ridge, TN 37831

The S–Prime and Z–prime gel sealants are available from the manufacturer as a viscous liquid. Either sealant is placed on the perimeter of the crucible lid using a transfer bulb.

- Argon Purge – The dried sample paste was purged for 5 minutes with argon. A crucible lid treated with S–prime gel was then quickly placed on the crucible under the argon purge.
- Slurry seal – The slurry (sample) was directly applied to the crucible lid.

After applying the crucible sealant, the samples were vitrified for 1 hour at 1150 degrees C by either microwave or conventional heating. The slurries for these experiments were approximately 45 wt% total solids. Ramp times from room temperature to 1150 degrees C were approximately 40 minutes for the Floyd RMS 150 microwave system and the CM1200B conventional furnace.

Colorimetric Fe(II)/total Fe Ratio Method

The Fe(II)/total Fe measurement was performed on the vitrified sample. The method for measuring the Fe(II)/total Fe ratio was developed by E. W. Baumann.⁵ The method consists of:

- Dissolution of the glass in an HF/H₂SO₄ mixture containing NH₄VO₃
- Addition of H₃BO₃, pH 5 buffer, and ferrozine reagent, to the sample mixture. The ferrous ion forms a redox couple with vanadium:



The fluoride ion in the sample complexes with H₃BO₃.

- Measurement of Fe(II) concentration at 562nm
- Addition of ascorbic acid to reduce the Fe(III) to Fe (II) in the sample mixture
- Measurement of the total Fe(II) concentration in the sample mixture at 562nm. The ratio of Fe(II)/total Fe is calculated from the absorbances measured

During the current study, sample feeds were vitrified for each type of crucible sealant technique used and the resulting glasses were analyzed for the Fe(II)/total Fe ratio. Each glass sample was analyzed five times. The overall Fe(II)/total Fe ratio precision between sample preparations was checked on specific melter feed samples. The Fe(II)/total Fe ratio measurements were then taken to estimate the effect that the sample preparation technique had on the resulting redox values. The colorimetric measurements on the feed vitrifications by microwave or furnace heating were performed in random order for the evaluations described below.

Graphical Representation of Data

Box–and–whisker (BW) plot was the graphical method used for displaying data and making comparisons among different data sets. The BW plots, produced by

Statgraphics (an IBM-PC product) for the furnace vs. microwave and paste vs. slurry comparisons are shown in Figures 1 through 4. The box displays the minimum and maximum values, the 25th, 50th (median), and 75th percentiles. The box is aligned vertically and encloses the interquartile range. The upper part of the box represents the 75th percentile while the lower part represents the 25th percentile. The extreme points are shown extending from the box.

RESULTS AND DISCUSSION

Microwave vs. Conventional Furnace Heating

The Fe(II)/total Fe measurements on glass produced in microwave ovens were slightly lower than those produced in a conventional furnace. Median Fe(II)/total Fe ratios were 0.30 for microwave produced glasses, and 0.35 for furnace produced glasses. As indicated by the composite multiple box-and-whisker plot, the microwave variance was greater between vitrifications, and the median value was lower (Figure 1).

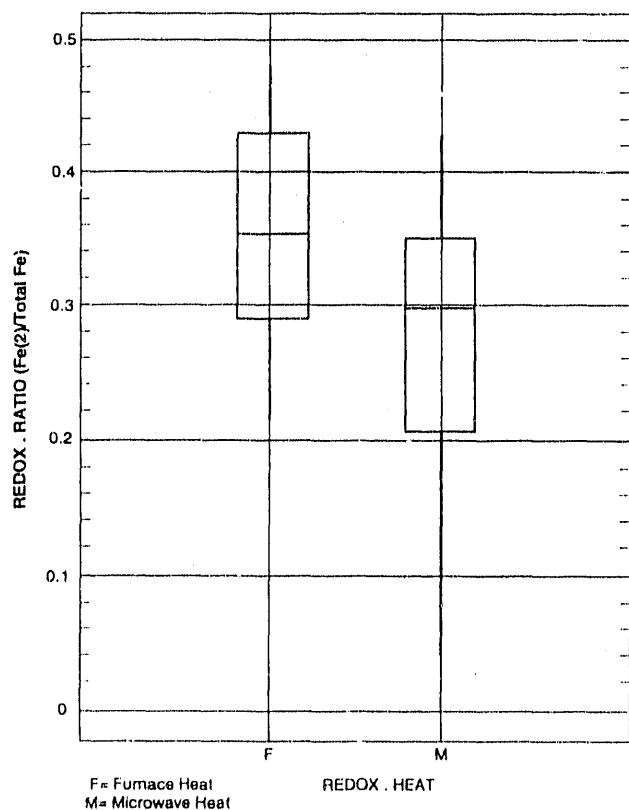


Figure 1. Furnace vs. Microwave (Multiple Box-and-Whisker Plot)

To check for possible differences, thirteen separate vitrifications on different melter feed samples from the same process batch and different seal techniques were grouped according to the type of heating applied; furnace or microwave heating.

Because of distinct differences between microwave and conventional heating, it was not known what effect the different heating modes would have on the Fe(II)/total Fe measurement. Also, since the power output for most microwaves is known to fluctuate with the in-line voltage drop for the line power, it was unknown whether normal line power fluctuations would cause a significant variation in the Fe(II)/total Fe ratio measurement using undedicated line power.

Visual inspections of the vitrified sample feed revealed that microwave glass had a smoother, more polished appearance when compared to furnace glasses from the same sample lots. This finding suggests that possible structural differences are evident in the resulting glass.⁷ Also, a lower median value for microwave glasses may suggest that more intense heating of the sample is occurring, to produce a more oxidized Fe(II)/total Fe ratio measurement. Possibly, the continuous operation of air exhaust fans for the microwave heating cavity during heating may be contributing to the increased oxidation noted for the Fe(II)/total Fe ratios measured. The conventional furnace does not have exhaust fans, and the heat dissipates from the cavity by convection. However, the differences noted for the Fe(II)/total Fe ratio precision are not considered to be significant enough to offset the important safety advantages of localized microwave heating in the analytical shielded cells.

The microwave furnace insert consists of two shells. The outer shell is Echofoam, which is transparent to microwave energy. The inner shell is lined with silicon carbide. The sample crucible is placed in the inner cavity for heating. As microwave energy is absorbed by the silicon carbide the resulting heat is transferred to the sample by convection. This results in localized heating of the sample. The outer surface of the insert remains cool during heating, and does not create an additional ignition source at vitrification temperatures. The insert has a vent to release gasses and some heat from the inner cavity. An external fan/hose assembly is used to exhaust the heating cavity of the microwave unit. Heat from the microwave unit can be diverted away from flammables within the analytical shielded cells for safer operation. Sample temperatures are monitored at the point of placement of the

sample crucible in the furnace insert via a thermocouple for the Floyd RMS 150 microwave system. This thermocouple is in contact with the silicon carbide and reads the surface temperature of the silicon carbide.

When using the CM 1200B resistance heated furnace, the temperature of the cavity is monitored via a thermocouple. However, the area within the CM furnace is an 8-in. cube, and the placement of a 100-mL sample crucible will not be at the exact location of the thermocouple. This thermocouple reads the temperature of the air space within the heated cavity. However, this is a more accurate measure than that in the microwave. In addition, heat is dissipated by convection, and a larger area of the analytical cells is subjected to excessive heating.

Variance

Most of the variability for the redox measurement comes from the variance between vitrifications. The within-group variance that results from dissolution of the glass gave a mean square value of 0.0086 for 133 degrees of freedom at 95% C.I. The between-group variance, for 27 separate vitrifications between microwave and furnace-heated sample feeds gave a mean square value of 0.243 for 1 degree of freedom at 95% C.I.

Open Crucible Vitrification

The open crucible vitrification was done as a test case to assess the worse-seal scenario that could apply for a crucible seal preparation. As expected, the colorimetric measurements for the sample indicated complete oxidation during vitrification. The Fe(II) measurable by the spectrophotometer in the vitrified sample was at the detection limit for the method (<0.006 absorbance units).

If the sample is nearly or completely oxidized, then there should be little or no ferrous ion to measure for the initial reading. The absorbance measurements will be at or below the blank measured. This test also suggests that the crucible seal is critical for obtaining redox values on melter feed samples.¹

Paste vs. Slurry Seal

Variance for the slurry (sample) seal was significantly greater, and median value (0.21) was much lower (Figure 2) as compared to the paste (sample) seal. The precision of the Fe(II)/total Fe ratio measurement was significantly improved using the paste (sample) seal technique relative to the slurry (sample) seal (Figure 2). The paste (sample)

seal technique gives a redox value (0.32) that approximates the referenced sample value.

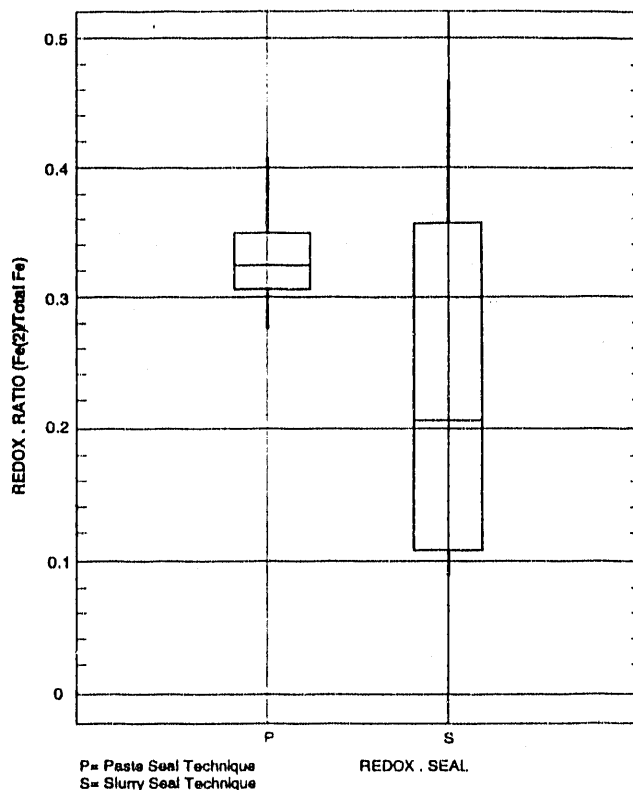


Figure 2. Paste vs. Slurry Seal Technique (Multiple Box-and-Whisker Plot)

Groupings of five sets each of paste(sample) and slurry(sample) seal type preparations for vitrifications indicates that more variance is evident for the slurry (sample) seal technique. These data set include furnace and microwave heating.

The slurry (sample) seal may allow in more air during the vitrification heating due to contained particulates; consequently, the resulting precision is greater and relative Fe(II)/total Fe ratio values are lower than from the paste (sample) seal technique.

Sample preparation methods used for vitrifications at the Savannah River Laboratory (SRL) prior to the addition of organics to the simulated DWPF feed streams allowed the high-wt%-solids sample to heat in the crucible and form a self-seal upon heating. After organic addition was started at SRL on simulated DWPF feed streams, the presence of volatile organics and a lower wt% solids content altered the repeatability of the crucible lid seal formed due to the offgas generated upon heating. The solids composition changed, and the consistency of the

simulated feed varied due to the organics present. These developments warranted further investigation.

For this evaluation, the slurry (sample) technique was developed to approximate the technique of forming a self-seal on the crucible. The paste (sample) seal technique was developed to help seal the crucible prior to vitrification, so that the oxygen fugacity of the vapor space inside the crucible was more representative of the redox effects in the DWPF melter. Because the (sample) paste is more homogeneous it forms a better seal than the particulate-containing (sample) slurry.

Argon Purge Technique

The S-prime sealant - argon purge technique resulted in increased values for both microwave (>0.35) and furnace (>0.38) heated samples (Figure 3). Figure 3 is based on six separate vitrifications each. The relative standard deviations for microwave and furnace heated samples were 14 and 8 percent respectively for this data set.

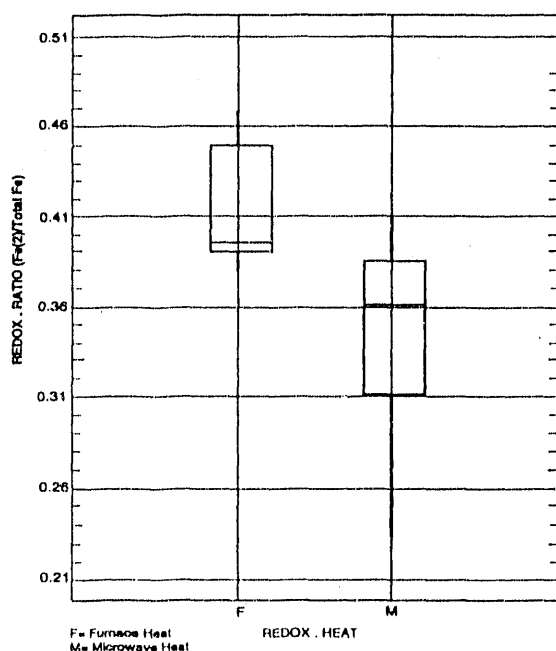


Figure 3. Argon Purge Technique (Multiple Box-and-Whisker Plot)

Additional improvements to vitrification techniques were obtained by using argon to purge the crucible before vitrifying the sample. By inerting the vitrification environment, the effects from air leakage could be eliminated. An argon purge of the crucible followed with

the S-prime sealant produced a more inert environment upon heating, and the resulting Fe(II)/total Fe ratios measured were higher (more reduced). The melt temperature of nepheline sealant is less than the glass melt temperature; therefore, the crucible seals before the glass melts. Nepheline sealant is also somewhat viscous and will not run down the crucible once applied. By applying a homogeneous paste (nepheline) to the crucible, inconsistencies in sealing are minimized due to the homogeneity of the sealant.

As indicated earlier, improved precision for the Fe(II)/total Fe measurement was noted using the paste (sample) seal technique. Visual inspections of the paste (sample) seal after vitrifications indicated little or no air gap visible in the seal. The precision of the data also reflected an improvement. However, the paste (sample) seal of the crucible could still vary due to the solids consistency of the feed material applied. To improve the technique, a way to inert the sample environment and to repeat the seal with the same solids consistency was developed. A nepheline sealant was selected for use.

S-Prime - Furnace and Microwave

The S-prime technique gave the best crucible seal. Inspection of the seal after a vitrification revealed little or no air gaps visible (Figure 4). Figure 4 is based on six separate vitrifications each.

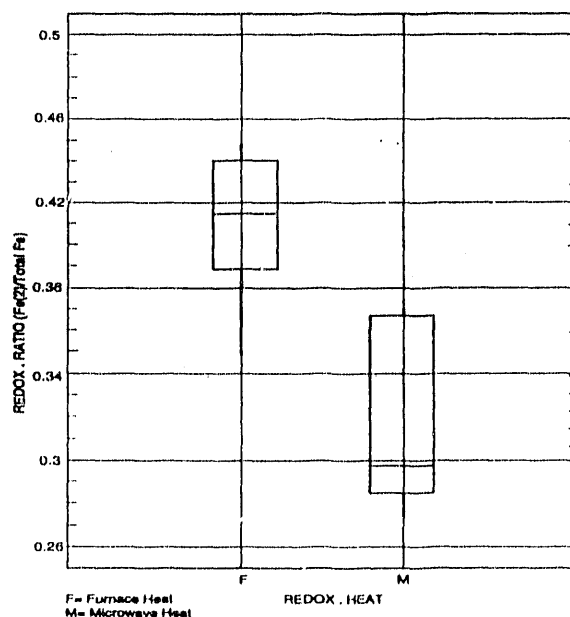


Figure 4. S-Prime Technique (Multiple Box-and-Whisker Plot)

The S-prime technique (of the methods tested) appears to be the method most amenable to remote applications for the shielded cells. The S-prime sealant is viscous and it adheres to the alumina crucible lid surface. Current plans are to apply the S-prime sealant to crucible lids outside of the analytical shielded cells and place the lids inside the analytical shielded cells as required. The remote handling time using master slave manipulators and the resulting personnel radiation exposure would be reduced by using this technique, relative to the other crucible sealing techniques described.

Additional Sealants and Techniques

Other tests were also performed using a Z-prime sealant (zirconium based), and utilizing a nitrogen-purged furnace for vitrification. The Z-prime did not seal as well as the paste or S-prime on the alumina crucibles, and subsequent testing was curtailed. The Z-prime sealant does not melt at as low a temperature as the S-prime sealant to generate the seal prior to vitrification. The nitrogen purged furnace technique did not give vitrified glass on initial attempts, but further testing with better nitrogen flow regulation may result in vitrification of the sample.

In addition, x-ray diffraction (XRD) analysis for microwave and furnace-vitrified sample feed slurries revealed no indications of inhomogeneity in the glass as a result of different types of heating (Figure 5). Further evaluations of microwave and furnace-produced glasses are planned.

CONCLUSIONS

Microwave heating will be implemented for samples requiring Fe(II)/total Fe ratio measurements at the DWPF analytical shielded cells. While furnace values are typically higher than those obtained with microwave heating, during DWPF cold runs the microwave heating time will be finalized so that the sample tests duplicate melter behavior. However, microwave heating is a safer application for shielded cell use, due to localized heating of the sample. Dissipation of heat in the analytical shielded cells is better controlled using microwave technology. Also, the Fe(II)/total Fe ratio precision resulting from furnace and microwave heated sample feeds is small enough so as not to eliminate a heating mode based on the relative method precision.

Testing of crucible sealants indicates that a seal is necessary for precise Fe(II)/total Fe ratio measurements.

Because of its adaptability for shielded cell use, and the improved precision of the Fe(II)/total Fe ratio measurement, the S-prime sample crucible sealing technique will be adopted at the DWPF analytical shielded cells.

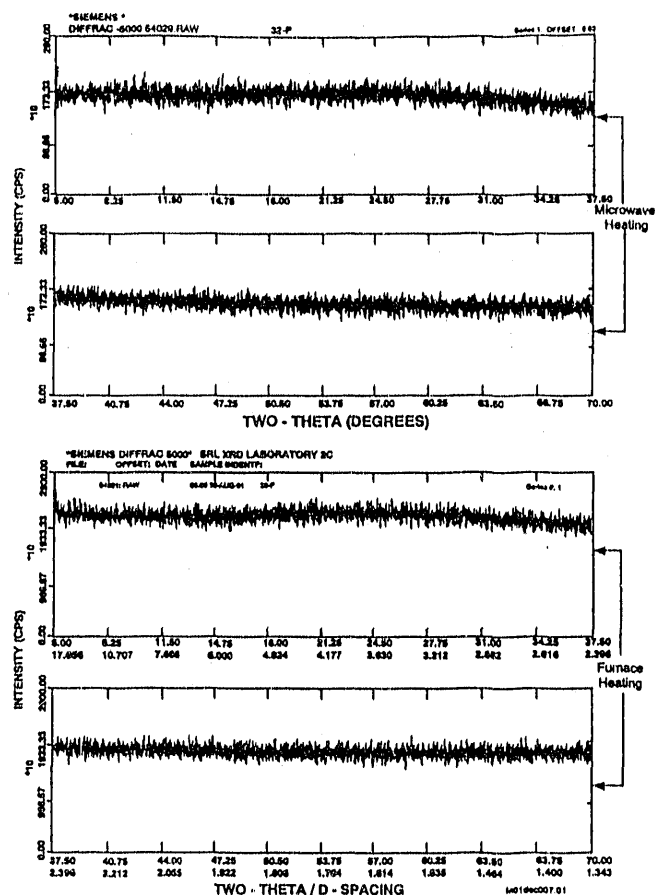


Figure 5. X-ray Diffraction Patterns (Microwave and Furnace Heating)

ATTACHMENT

Instruments:

- Floyd RMS 150 Remote Microwave Digestion System, manufacturer:
Floyd Inc.
5440 Hwy 55E
Lake Wylie, SC 29710
- CM 1200B Furnace, manufacturer:
CM Furnaces Inc.
103 Dewey Street
Bloomfield, NJ 07003

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