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USE OF DWPF REDOX MEASUREMENT TECHNIQUE ON GLASSES FROM WEST VALLEY NUCLEAR FUEL SERVICES DEMONSTRATION PROJECT (U)

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ABSTRACT

Liquid high-level nuclear waste will be immobilized at the Savannah River Site (SRS) by vitrification in borosilicate glass in the Defense Waste Processing Facility (DWPF). A similar vitrification facility exists at the West Valley Nuclear Fuel Services. In both of these facilities, control of the oxidation/reduction (redox) equilibrium in the glass melter is critical for processing of the nuclear waste.

Redox can be determined by measuring the ratio of ferrous to ferric ions in the glass melt. A colorimetric procedure has been developed for the DWPF which has been shown to give rapid and reliable analytical results. This colorimetric technique has been shown to measure the Fe^{2+} component of glasses more accurately than other existing redox measurement methods.

The DWPF redox technique was applied to a series of six glasses taken from the West Valley melter during a transient melter excursion. This excursion caused the glasses to become progressively more reducing with time. Application of the DWPF redox technique to these glasses correctly indicated the redox trends with a higher precision and with more accuracy than the West Valley wet chemical method and/or Alfred University's Mossbauer method.

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INTRODUCTION

Liquid high-level nuclear waste will be immobilized by vitrification in borosilicate glass at the Savannah River Site (SRS) and at the West Valley Nuclear Fuel Services Demonstration Project (WVNFS). In both facilities, control of the oxidation/reduction (redox) equilibrium in the glass melter is critical for processing of the nuclear waste. The glass needs to be somewhat reducing to minimize glass foaming[1,2] and devitrification.[3] However, overly reducing conditions may cause metallic species to form in the melt. The metallic species can agglomerate, settle to the floor of the melter, and potentially short the electrodes in the joule-heated melter.[4-7]

Redox can be determined by measuring the ratio of ferrous to ferric ions in the glass melt. A colorimetric procedure has been developed[8,9] for the DWPF which has been shown to give rapid and reliable analytical results.[10,11] This colorimetric technique has been shown to measure the Fe^{2+} component of glasses more accurately than other existing redox measurement methods.

The melter redox state can be measured from the Fe^{2+}/Fe^{3+} ratio of the final solidified glass. An Fe^{2+}/Fe^{3+} ratio between 0.1-0.5 has been recommended as an acceptable range for glasses produced in the DWPF.[12] This range appears to be optimum in terms of avoiding both (1) foaming, and (2) precipitation of metallic species during glass melting. This redox range agrees with the range determined at Pacific Northwest Laboratory in support of the West Valley project,[7,13] and redox determinations from Case Western University.[2]

A rapid and reliable method for predicting the melter redox conditions using the Fe^{2+}/Fe^{3+} ratio determined from a vitrified feed sample has been developed by Baumann.[8-9,14] In this procedure, glass is dissolved in HF/H_2SO_4 in the presence of NH_4VO_3. The ammonium vanadate stabilizes the Fe^{2+} to air oxidation so that the procedure can be performed routinely in air.[8-9] The dissolution procedure used at West Valley, the Goldman technique,[15] is performed in air but does not use the NH_4VO_3 to stabilize the Fe^{2+}. Hence, it is more likely to give redox ratios which are biased toward more oxidized values.

Mossbauer spectroscopy has been extensively examined[16-18] for measurement of the Fe^{2+}/Fe^{3+} ratio of vitrified melter feed samples. Mossbauer spectroscopy has the advantage that the glass does not need to be dissolved. However, Mossbauer spectroscopy may be subject to interferences from the radiation in actual waste.[15]

RESULTS

The six glass samples from West Valley were taken during a transient excursion in the melter during which unneeded reductant was added. Inaccurate nitrate analyses indicated that the melt was too oxidizing. Hence, excess reductant had been added in an attempt to balance the redox of the glass.

Continuous feeding of excess reductant should have provided a series of glasses with a trend of increasing Fe^{2+}/Fe^{3+} with time. Analyses at West Valley using the Goldman[15] wet chemical methodology did not indicate the correct redox sequence and neither did comparative analyses measured at Alfred University with Mossbauer spectroscopy (Table 1).

The DWPF redox methodology of Baumann[8-9] was used to analyze the West Valley glass series as a comparison. The DWPF methodology correctly indicated that the glass series became more reduced with time (Table 1).

The average values of the redox ratios given in Table 1 are shown in Figure 1. These plots show the changes in redox ratio as a function of cumulative time. The plots assume that the initial starting time, October 4, 1989 at 0303 hours, is time zero. Comparison of Figures 1a, b, and c shows that the DWPF redox methodology is more accurate in predicting the redox trends of the West Valley glasses than either the Goldman or Mossbauer techniques.

CONCLUSIONS

Six glasses had been sampled from the melter at West Valley Nuclear Fuel Services during a transient melter excursion. The redox methodology developed for DWPF by Baumann[8-9] was applied to determine the redox ratio of the six glasses. The redox ratio of the same samples had been measured at West Valley using Goldman's technique[15] and at Alfred University using Mossbauer spectroscopy. The results of these analyses demonstrated that the Baumann methodology was more accurate than either Goldman's wet chemical technique or Alfred's Mossbauer spectroscopy. This had previously been demonstrated at SRS on glasses made in laboratory scale studies.[10,11]

Table I. Comparison of Measured Redox Ratios from West Valley Airlift Sampler

Sample ID	SRS/DWPF Baumann Fe^{2+}/Fe^{3+}	West Valley Goldman Fe^{2+}/Fe^{3+}	Alfred University Mossbauer Fe^{2+}/Fe^{3+}
AIRL-12-002 (10/4/89 at 0303)	0.158 0.127	0.008 0.009 0.009	BDL*
AIRL-12-004 (10/4/89 at 0944)	0.242 0.256	0.21 0.20 0.19	0.15
AIRL-12-008 (10/5/89 at 0316)	0.512 0.507	0.47 0.43 0.43	0.44
AIRL-12-014 (10/6/89 at 0945)	0.847 1.093	0.84 0.76 0.83	0.95
AIRL-12-032 (10/9/89 at 0454)	1.322 1.349	1.34 1.28 1.13	1.38
AIRL-12-034 (10/9/89 at 1615)	2.450 3.220	0.80 0.70 0.70	0.71

*BDL = Below Detection Limit

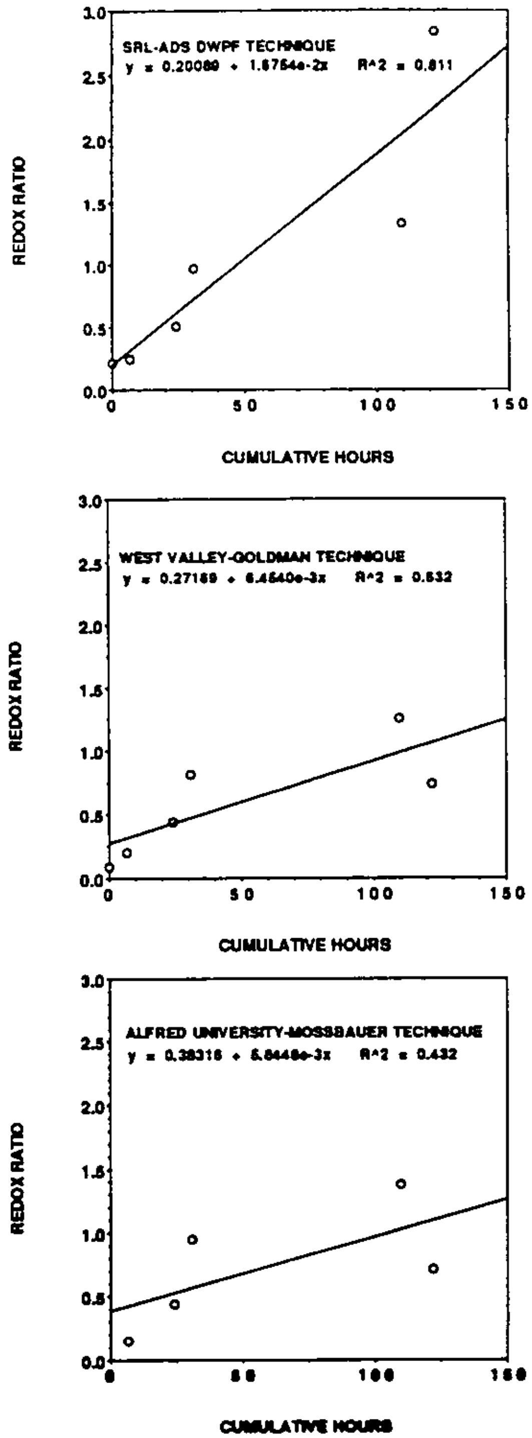

Figure 1. Comparison of the redox ratio of six West Valley glasses as a function of sampling time: (a) analyses performed by SRS with the DWPF spectrophotometric technique, (b) analyses performed by WVNFS with the Goldman technique, and (c) analyses performed by Alfred University with Mossbauer Spectroscopy.

REFERENCES

1. M. J. Plodinec, "**Factors Affecting the Iron Oxidation State and Foaming in SRP Waste Glass,**" Proceedings of the Symposium on High Temperature Materials Chemistry, D. D. Cubicciotti and D. L. Hildebrand (Eds.), The Electrochemical Society, Pennington, New Jersey, 201-209 (1982).

2. M. J. Plodinec, "**Foaming During Vitrification of SRP Waste,**" DPST-86-213 (January 10, 1986).

3. C. M. Jantzen, D. F. Bickford and D. G. Karraker, "**Time-Temperature-Transformation Kinetics in SRL Waste Glass**", Advances in Ceramics, V. 8, G. G. Wicks and W. A. Ross (Eds.), 30-38 (1984).

4. D. F. Bickford and R. B. Diemer, Jr., "**Redox Control of Electric Melters with Complex Feed Compositions, Part I. Analytical Methods and Models**", J. Non-Cryst. Solids, 84, 276-284 (1986).

5. D. F. Bickford and R. B. Diemer, Jr., D. C. Iverson "**Redox Control of Electric Melters with Complex Feed Compositions, Part II. Preliminary Limits for Radioactive Waste Melters**", J. Non-Cryst. Solids, 84, 285-291 (1986).

6. D. F. Bickford, R. C. Probst, and M. J. Plodinec, "**Control of Radioactive Waste Glass Melters: Part III. Glass Electrical Stability,**" Advances in the Fusion of Glass, D. F. Bickford, et. al. (Eds.), The American Ceramic Society, Westerville, OH, 19.1-19.17 (1988).

7. L. R. Bunnell, "**Laboratory Work in Support of West Valley Glass Development,**" USDOE Report PNL-6539, Battelle-Pacific Northwest Laboratory, Richland, WA, (May, 1988).

8. E. W. Baumann, "**Colorimetric Determination of Ferrous-Ferric Ratio in Glass,**" DPST-87-304 (February 20, 1987).

9. E. W. Baumann, "**Colorimetric Determination of Ferrous-Ferric Ratio in Glass,**" DP-MS-87-136 (1987).

10. C.M. Jantzen, "**Verification and Standardization of Redox Measurement for DWPF**", DPST-89-222 (January 11, 1989).

11. C.M. Jantzen, "**Incorporation of Cs-Specific Resorcinol Resin in SRP Waste Glass: Durability and Redox Considerations**," DPST-87-552 (February 2, 1989).

12. C. M. Jantzen and M. J. Plodinec, "**Composition and Redox Control of Waste Glasses: Recommendation for Process Control Limit**," DPST-86-773 (November 19, 1986).

13. D. S. Goldman, "**Investigation of Potential Analytical Methods for Redox Control of the Vitrification Process**," USDOE Report PNL-5581, Battelle-Pacific Northwest Laboratory, Richland, WA, (November 1985).

14. C. J. Coleman, "**Measurement of Fe^{2+}/Fe^{3+} Ratio in Melter Feed**," DPST-88-274 (April 14, 1988).

15. D. S. Goldman and D. E. Bewley, "**Ferrous/Ferric Mossbauer Analysis of Simulated Nuclear Waste Glass With and Without Computer Fitting**," J. Am. Ceram. Soc., 68[12],691-695 (1985).

16. C.M. Jantzen, "**DWPF Glass Redox Determination - Summary of Results from Clemson Subcontract**," DPST-86-745 (October 29, 1986).

17. D.G. Karraker, "**Ferrous/Ferric Ratio in DWPF Glass: Chemical and 57 Mossbauer Determinations**," Advanced Ceramic Materials, 3, 337-40 (1988).

18. R.T. Hunter, M. Edge, A. Kalivretenos, K. M. Brewer, N.A.Brock, A.E. Hawkes, and J.C. Fanning, "**The Determination of the Fe^{2+}/Fe^{3+} Ratio in Nuclear Waste Glass**," J. Am. Ceram. Soc., 72, 943-947 (1989).

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