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DEVELOPMENT OF GLASS COMPOSITIONS FOR
IMMOBILIZATION OF SAVANNAH RIVER PLANT WASTE

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ABSTRACT

Two fundamental problems related to processing Savannah River Plant wastes are the formation of ferrite-spinel crystals during melting, and the high viscosity and ready devitrification of high aluminum sludge-melts. The effects of several glass composition variables on these processing problems have been investigated. The most important variables are the TiO_2 content, the molar alkali-to-silica ratio, and the molar ratio of Li_2O to total alkali. As the TiO_2 content decreases, the amount of crystalline material (either ferrite-spinel or aluminosilicate) also decreases; however, the viscosity of the melt increases. Increasing the alkali to silica ratio and the Li_2O to total alkali ratio decreases the viscosity greatly, but also increases the tendency to devitrify. Other variables investigated were MO content ($M = \text{Mg}, \text{Ca}, \text{or Ba}$), R_2O_3 content ($R = \text{Al or B}$), and the addition of other viscosity-reducing metal oxides. None of these are of major importance.

INTRODUCTION

Two processes for immobilizing high-level radioactive waste from the Savannah River Plant (SRP) into glass are currently being studied: in-can melting and joule-heated melting. For in-can melting, glass frit and calcined waste are vitrified in a canister that also serves as the primary storage container. To produce an acceptable product by this method, a viscosity of ≤ 200 poise at the melting temperature is necessary. Joule-heated melting places stricter

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requirements on the viscosity of the melt. Glass frit and calcine are fed continuously to a ceramic-melter, vitrified, and poured into the primary storage container. To produce an acceptable product by this method, a viscosity of ≤ 50 poise at the melting temperature is necessary. In addition, a viscosity of ≤ 500 poise is necessary for smooth pouring.

SRP sludges contain large amounts of iron and aluminum as hydrous oxides and appreciable quantities of uranium, manganese, nickel, and calcium (1,2). Although all of these affect the processability and the product quality of SRP waste glasses, iron and aluminum have the largest effects on waste processing. Compositions high in either can cause problems (3,4,5).

Sludges containing large amounts of iron produce crystals of a ferrite-spinel type when vitrified. At high concentrations, these crystals cause the melts to become non-Newtonian (apparent viscosity depends on shear rate) pseudoplastic fluids (6). However, even at low concentrations, an extremely viscous layer gradually forms at the bottom of a joule-heated melter. This layer disrupts smooth operation of the melter and plugs narrow channels. Thus, eliminating this phase is desirable.

Sludges containing large amounts of Al_2O_3 make extremely viscous melts (6), which readily devitrify to alkali aluminosilicates (5). Sludge-melts of this type are very sensitive to processing mistakes.

Four methods have been identified to improve the processing behavior of SRP waste glasses.

- Increase the melt temperature. This also increases the amount of volatiles to be collected and decreases melter life.
- Reduce the amount of sludge. This increases the number of glass forms which must be manufactured, shipped, and stored.
- Blend sludges to eliminate the extremes. This will be done, but the amount of homogenization achievable is unknown.
- Change the glass composition.

The effects of several glass composition variables on process parameters have been determined.

VARIATIONS IN ALKALI METAL OXIDE COMPOSITION

Melts were prepared in which the alkali metal oxide composition was changed in several ways. Some melts substituted potassium for some of the sodium to try to reduce separation of the ferrite phase, and devitrification due to a high aluminum phase. These efforts did

not succeed, and greatly increased the melt viscosity. Other melts substituted more Li_2O for Na_2O (while maintaining the alkali metal oxide content at 22.5 wt % of the frit) to reduce the viscosity. This was very successful. For any sludge, the viscosity of the waste glass is mainly determined by:

- Moles of alkali metal per mole of silica.
- Moles of Li_2O per mole total alkali metal oxide.

Figure 1 shows the viscosity of several melts at 1150°C as a function of the moles of alkali metal oxide/mole SiO_2 . In general, melts containing potassium were much more viscous and much less homogeneous than potassium free melts. No further work was done with melts containing K_2O .

The variation of log viscosity at 1150°C with alkali metal oxide/silica ratio (R) is almost linear (Figure 1). Melts were prepared with the same value of R (0.494) but different values of the Li_2O /total alkali ratio (R_a). For constant R, R_a controls the viscosity.

Two other important observations were made during this series of tests. For values of R_a greater than about 0.6, the glasses readily devitrified to form a LiAlSiO_4 -type phase, similar but not always identical to β -eucryptite. As R_a increased, this phase appeared at increasing temperatures. Thus, a value of $R_a < 0.6$ should be maintained.

VARIATION IN TiO_2 CONTENT

Melts were prepared containing 0-11 wt % TiO_2 . In general, TiO_2 slightly decreased the viscosity in the melting range ($\sim 1150^\circ\text{C}$). The amount of ferrite observed was reduced by lower TiO_2 content, as was the extent of devitrification to the LiAlSiO_4 phase. Eliminating TiO_2 from the frit allows frits with higher values of R_a to be used.

VARIATIONS IN ALKALINE EARTH OXIDE COMPOSITION

Melts that substituted 5 wt % MgO or BaO for the 5 wt % CaO in Frit 21 were prepared. A melt that contained 2.5 wt % MgO and 2.5 wt % CaO was also prepared. At any temperature above $\sim 925^\circ\text{C}$, the viscosity decreased in the order, $\text{MgO} + \text{CaO}$ melt $>$ CaO melt $\sim$ $\text{MgO} >$ BaO . Below 925°C , the BaO melt became non-Newtonian. Subsequent microscopic examination suggested devitrification as the probable cause.

VARIATIONS IN BORIC ACID CONTENT

Melts in which the B_2O_3 content was varied, and some in which Al_2O_3 was substituted for B_2O_3 , were prepared. Variations in the B_2O_3 content of the glass did not seriously affect the viscosity. However, substituting Al_2O_3 for B_2O_3 increased viscosity by up to a factor of 4 at $1150^\circ C$. Also, the glasses containing Al_2O_3 were of poorer quality due to extensive devitrification.

INCLUSION OF OTHER OXIDES

Melts in which 4 wt % Cu_xO , PbO_x , or V_2O_5 were included (instead of Li_2O) were prepared. None was as effective as Li_2O in reducing viscosity. PbO_x -high aluminum sludge-melts were very inhomogeneous. V_2O_5 melts had the lowest viscosity and were adequately homogeneous.

FIGURE 1. Effect of Alkali/Silica Ratio on Viscosity at 1150° . All glasses contain 25 wt % composite sludge.

REFERENCES*

1. J. A. Stone, J. A. Kelley, and T. S. McMillan, *Sampling and Analyses of SRP High-Level Waste Sludges*. USERDA Report DP-1399, Du Pont Company, 50 pp, August 1976.
2. J. A. Stone, *Separation of SRP Waste Sludge and Supernate*. USERDA Report DP-1441, Du Pont Company, 31 pp, November 1976.
3. J. A. Kelley, *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste - Nonradioactive and Tracer Studies*. USERDA Report DP-1382, Du Pont Company, 28 pp, May 1975.
4. J. A. Kelley, *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste - Radioactive Studies*. USERDA Report DP-1397, Du Pont Company, 21 pp, October 1975.
5. M. J. Plodinec and J. R. Wiley, *Evaluation of Glass as a Matrix for Solidifying Savannah River Plant Waste: Properties of Glasses Containing Li_2O* . USDOE Report DP-1498, Du Pont Company (to be issued).
6. M. J. Plodinec, *Viscosity of Glasses Containing Simulated Savannah River Plant Waste*. USDOE Report DP-1507, Du Pont Company, 23 pp, September 1978.

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