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ADVANCED METHOD FOR MAKING VITREOUS WASTE FORMS*

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ABSTRACT

A process is described for making waste glass that circumvents the problems of dissolving nuclear waste in molten glass at high temperatures. Because the reactive mixing process is independent of the inherent viscosity of the melt, any glass composition can be prepared with equal facility. Separation of the mixing and melting operations permits novel glass fabrication methods to be employed.

INTRODUCTION

Glass is the most extensively studied solid waste form for the immobilization of high-level nuclear waste. Usual practice is to dissolve waste oxide in molten glass at temperatures in excess of 1000°C. In order to achieve homogenization of the melt in reasonable times, glass forming systems are selected that have low viscosities at these temperatures. This constraint is best met by borosilicate glass compositions. Conversely, highly durable glass compositions, such as natural obsidian and nepheline syenite, require such high forming temperatures (~1350°C) when made by conventional waste glass processing methods that they have been largely eliminated from consideration as a solid waste form.

*Prepared for the U.S. Department of Energy, Contract DE-AC-08-76NV00597.

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Westinghouse has developed a process for making nuclear waste glass that largely eliminates the problems of volatilization, foaming, slagging and dusting by chemically combining the waste sludge and glass additives at low temperatures prior to melting. Because the reactive mixing process is independent of the inherent viscosity of the melt, waste glass compositions that are high in alumina can be prepared with ease. Separation of the mixing and melting operations permits novel glass fabrication techniques to be employed

PROCEDURE

Reactive Mixing Process

Overall the reactive mixing process consists of four steps: (1) hydrolysis of the individual metal-alkoxide glass additives; (2) blending of the alkoxide glass additives; (3) mixing of the glass additives and waste sludge to develop the required glass composition; and (4) heating of this blend to promote chemical reaction by removal of alcohol and water. In order to avoid gross precipitation during blending of the alkoxides, the individual alkoxides must be hydrolyzed to the correct degree. Once this is accomplished the alkoxides and waste sludge will readily blend into a homogeneous mixture that is insensitive to variations in composition, temperature and time.

Two variations of the reactive mixing process have been developed. One is named the reference alkoxide process which employs all metal alkoxide glass additives. The other, called the simplified process, uses only silicon and boron alkoxide, the other additives being in the form of hydroxides.

Glass Fabrication

After the water and alcohol are removed, the reactively mixed waste material may be transformed into a glass by melting at temperatures between 1000 and 1200°C. Typically, glasses were formed by melting 50 cc batches of either wet or dry reactively mixed material in Al₂O₃-998 crucibles. A few 1 kg glass ingots were prepared by intermediate feeding of a larger alumina crucible. The nominal firing schedule involved heating at 5°C/min, holding at temperature for 1 hour (for convenience) and furnace cooling at about 20°C/min. Furnace cooling could be programmed to be as low as 2°C/min.

RESULTS

Reactive Mixing Evaluation

X-ray diffraction and IR absorption spectra of reactively mixed glass additives alone and with waste additions were used to assess the degree of homogeneity achieved by means of the alkoxide process. The diffraction patterns of the glass additives after drying and

after melting are amorphous. Likewise, the diffraction patterns of the dried waste glass mixture are generally amorphous except for small peaks which are due to $Al(OH)_3$ and U_3O_8 . After melting the waste glass can be completely amorphous or, depending on composition, it can contain crystals of an iron-manganese-nickel spinel phase.

Surprisingly, calcined ($500^\circ C$) glass additives alone and those containing 30% waste have nearly identical IR spectra between 6 and 40 μm . An apparent difference between 2 and 6 μm is undoubtedly largely due to the difference in refractive index between the transparent glass additives and the highly colored waste glass.

Waste Glass Compositions

Table 1 lists the calculated low-, medium- and high-alumina glass additive compositions normalized at the 30 wt % waste level. Table 2 gives selected compositions of the "average", "high-ferric oxide" and "high-alumina" simulated waste sludge (supplied by Southwestern Analytical Chemicals, Inc.) normalized to the 70 % glass additive level. Thus, the complete waste glass composition is determined by the sum. For example, the total alumina content of the high-alumina glass added to a high-alumina waste is 27.7 wt %.

Confirmation of the calculated waste glass compositions by chemical analysis gives general agreement except for consistently higher values for the Al_2O_3 and lower values for the Fe_2O_3 . Melting in alumina crucibles may account for some of this discrepancy.

Compositions containing less than 15 wt % Al_2O_3 melt satisfactorily at $1100^\circ C$. Compositions containing 28 wt % Al_2O_3 and 11 wt % B_2O_3 melt nicely at $1200^\circ C$, but if they contain 11% CaO rather

Table 1. Calculated Melted Compositions (wt %) of Alkoxide Derived Glasses Compared to that of a Typical SRL Glass

Glass Designation	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	Total Waste, Oxides
Low-alumina	45.5	3.5	10.5	10.5		30.0
Medium-alumina	38.5	10.5	10.5	10.5		30.0
High-alumina (nepheline syenite)	35.5	14.0	10.9 ^a	9.0		30.6
Reduced Viscosity #1	40.8	3.5	10.5	10.5	4.7	30.0
Reduced Viscosity #2	40.8	3.5	10.5	15.2		30.0
Reduced Viscosity #3	40.8	3.5	7.8	14.4 ^b		30.0
Ref. SRL 211	40.8	c	7.8	14.4		30.0

^aCaO instead of B₂O₃ also studied.

^bIn addition, 3.9% CaO.

^c3.1% Li₂O + 3.9% CaO.

Table 2. Waste Compositions (wt %)

Waste Designation	Fe ₂ O ₃	Al ₂ O ₃	MnO ₂	U ₃ O ₈	CaO	NiO	SiO ₂	Na ₂ O	Na ₂ SO ₄	Ion-Siv
avg + Na ₂ CO ₃	13.4	2.7	3.8	1.2	1.0	1.7	1.2	1.8	0.4	2.8
avg	14.4	2.9	4.1	1.3	1.1	1.8	1.3	0.1	-	3.0
hi Fe + Na ₂ CO ₃	16.6	0.3	1.2	3.9	1.0	2.8	-	1.4	0.1	2.7
hi Fe	17.5	0.3	1.2	4.1	1.0	3.0	-	-	-	2.9
hi Al + Na ₂ CO ₃	5.5	12.9	3.2	2.4	0.4	0.6	0.4	1.6	0.1	2.9
hi Al	5.8	13.7	3.4	2.5	0.4	0.7	0.4	-	-	3.1

than B₂O₃ the temperature required to form a good glass increases to 1300°C. The high-alumina glasses were much too viscous to be poured from a crucible, yet they formed a smooth meniscus. Even the low-alumina waste glasses had higher viscosities than Savannah River Reference Glass 211. Consequently, the reduced viscosity glasses listed in Table 1 were prepared by increasing the alkali content.

Observation of one kilogram ingots being made by successive feeding of the melt through a tube clearly show that the feed is readily assimilated by the melt within a few minutes without foaming or any other difficulty. Air quenching or furnace cooling always gives a bubble-free glass monolith of either reference or simplified process material.

Volatilization

TGA and chromatographic determination of the volatile species at temperatures up to 600°C show them to be the alcohols and water expected from the condensation reactions of the various alkoxides.

Thermobalance results indicate the weight loss between 600 and 1300°C for the reference alkoxide process waste glasses is small for the low-alumina composition and negligible for higher-alumina glasses:

<u>aluminosilicate glass</u>	<u>% wt loss from 600 to 1300°C</u>
low-alumina	0.68
medium-alumina	0
high-alumina	0

These results are essentially the same for all of the waste types given in Table 2, including those with Na₂CO₃. Although the weight loss for the waste glasses produced by the simplified alkoxide route is slightly higher, it is still less than 1 wt % absolute.

Leaching Measurements

Leach tests were performed in a Pyrex soxhlet apparatus operating at 100°C with "circulating" water for 24 days. Emission spectroscopy was used to determine the amount of the species leached. Leach rates were calculated using the method of Kelley and Wallace¹

$$L = f \left(\frac{M}{A} \right) \frac{1}{t}$$

where f is the fraction of ions leached during the leaching period, t , and M/A is the ratio of mass to surface area of the sample. The ratio M/A was estimated to be 0.00583 g/cm² by assuming all particles to be spheres with a diameter of 250 μm (the smallest particle that will not pass through a 60-mesh sieve), a density of 2.8 g/cm³, and a roughness factor of 2. The upper sieve was 40-mesh through which all of the sample passed.

The leach rates were corrected for impurities in the deionized water and for species leached from the Pyrex apparatus during "blank" tests of the same duration. These initial leach results show similar leach rates of $\sim 4 \times 10^{-9}$ gm all species/cm²/day, for the low- and medium-aluminosilicate glass made by the reference alkoxide process and the low-alumina glass produced by the simplified route. All glass tested contained "average" waste plus Na₂CO₃.

Waste Glass Microstructure. At the 30 wt % loading level, average waste and especially high-iron waste compositions yield glasses that exhibit cubic or occasionally tetrahedral shaped crystals of an iron-nickel-manganese spinel as determined by EDAX and x-ray diffraction. Increasing the proportion of either soda or alumina in the glass composition decreases the number of spinel crystallites. High-alumina sludges, on the other hand, result in glasses that are free of crystalline phases that can be detected by either petrographic, electron optic, or x-ray techniques.

DISCUSSION

Reactive Mixing

The melting behavior of material made by the reactive mixing process indicates that the glass additives and nuclear waste sludge are combined on essentially a molecular level by the time the alcohol and water are evaporated. Whether this is the result of a chemical polymerization reaction between the alkoxides and waste sludge or a high degree of reactivity that promotes homogenization at modest temperatures is not clear. The best indicators of a chemical reaction are gelation and the unique role of boron alkoxide. If the alkoxide-waste mixture is allowed to remain quiescent, a weak gel will form. Since stable gel formation signifies chemical polymerization, even a weak gel which is destroyed on mixing is suggestive of localized

polymerization. This supposition is supported by the markedly different behavior of boric acid and boron alkoxide. Glass additives plus waste sludge made using boric acid exhibit upon heating the bubbling and copious vapors that are typical of compositions containing boric acid. However, when trimethylborate is used instead, these characteristics disappear, again signifying that the boron is chemically combined. Other evidence supporting a chemical polymerization reaction is the effect of a slight change in pH. A few drops of nitric acid will cause the calcined mixture to form a cake rather than a fine powder, which suggests an electrolyte effect.

That chemical polymerization may only partially explain the results is indicated by the tolerance of the process to variations in temperature, time and composition. The glass additives alumina and soda may be added as either alkoxides or hydroxides, and a wide range of waste compositions can be treated with equal facility. This insensitivity to process and compositional variables contrasts with the close control required when stable gels are produced using metal alkoxides exclusively in the conventional manner. A high reactivity resulting from the use of alkoxides may also contribute to the homogenization of the mixture at the modest temperatures needed to drive off the alcohol and water.

Diagnostic examination of the reactive mixing process has thus far revealed little. X-ray analysis shows the dried waste-glass precursor mixture to be generally amorphous with minor amounts of a few discrete phases such as $Al(OH)_3$, U_3O_8 and occasionally $CaCO_3$. More surprising is the absence of any major shifts in the IR spectra of the glass additives when 30 weight percent waste is incorporated.

Melting Characteristics

Furnace Melting. The most notable characteristic of the reactively mixed material is the ease with which it melts. Melting progresses rapidly without foaming or slagging and little bubbling. Withdrawing a melt as soon as it reaches furnace temperature always gives a uniform, bubble-free glass.

Since no thermal driving force is required for homogenization, the apparent melting temperature of the waste glass is decreased. For example, a nepheline syenite waste glass composition containing 28% Al_2O_3 and 11% B_2O_3 will melt into bubble-free glass at 1200°C, which is about 150°C lower than the temperature required by conventional waste glass processes. This melting behavior suggests that the waste glass composition is mixed on a "molecular scale." Waste glass compositions prepared by the reactive mixing process have the characteristics of high melting rates, short residence times, and low volatility. They exhibit neither foaming, reboil nor slagging, and they may be tailored to the desired waste glass composition. In contrast, the conventional process of using glass as a high temperature solvent gives low melting rates, long residence times for melt

homogenization, high volatility, persistent foaming, reboil, slagging, and permits minimal compositional control of the melt.

Compositions high in Fe_2O_3 and low in either Al_2O_3 or alkali exhibit cubic or tetrahedral crystals of an iron-nickel-manganese spinel. These crystals will disappear as either the alumina or alkali content is increased. Because these two components strongly affect the viscosity in opposite directions, the indication is that the spinel crystals developed under equilibrium conditions rather than as a result of devitrification during cooling.

Remote Heat Source Melting. The feasibility of glass making by localized melting was explored using a continuous 18 kW/cm^2 CO_2 laser, a pulsed 150 watt/cm^2 YAG-Nd laser, and a 200 watt/cm^2 xenon lamp source. The localized melting produced by either the CO_2 , YAG or xenon lamp sources appears to depend mainly on the magnitude of the lattice absorption and the low thermal diffusivity of the oxide material. As would be expected from the absorption spectra of the waste glass material, a $10.2 \mu\text{m}$ CO_2 laser coupled extremely well and gave rise to high surface temperatures and copious volatilization (smoke). In contrast, a $1.0 \mu\text{m}$ YAG-Nd laser gave excellent melting characteristics with negligible smoke formation, and it required less than one percent of the energy density. This behavior indicates that the radiant energy is being absorbed in a larger volume of material while generating lower surface temperatures. The melting characteristics of the xenon lamp are surprising in that it behaved more like a CO_2 laser in terms of the amount of smoke produced while most of its emission is at wavelengths below one micron. The reasons for this phenomenon and the significantly lower melting rates at comparable power densities may be revealed in the details of the emission spectra.

Waste Glass Composition

A wide variety of waste glass compositions can be prepared by the reactive mixing process because it is independent of the inherent viscosity of the melt. Compositions ranging from the Savannah River 211 Glass, which contains less than 3% alumina, to nepheline syenite, which contains over 25% alumina, have been produced. Each of these waste glass compositions contains 30 weight percent simulated waste, and they span the range from high Fe_2O_3 to high Al_2O_3 waste sludges (see Table 2). All of these compositions form bubble-free glasses, over the range of compositions from the viscous, high-alumina to the fluid "reduced viscosity" glasses. Of the four glass additives (silica, alumina, boron oxide and soda), the soda and alumina can be added as either alkoxides or hydroxides. Aluminum and sodium hydroxides contained in the waste sludge appear to contribute to the final glass composition in the same way as when they are added supplementarily. This property permits tailoring of the final waste glass composition, and it negates any need to remove sodium from the waste sludge. Experience has shown that zeolite added to the sludge is readily

incorporated in the waste glass during melting. This capability provides a means for disposing of cesium contaminated zeolite ion-exchange resins.

The reactive mixing process necessarily results in the production of alcohol due to condensation reactions involving partially hydrolyzed metallic alkoxides. Since the reactive mixing of radioactive materials must be performed remotely, the alcohol could be either burned (perhaps in a waste heat boiler) inside of the canyon, or recycled to make the required alkoxides outside of the canyon. Fortunately, the steam/alcohol mixture is not explosive, only flammable, which should create no formidable safety problems. By using the same alcohol to control the rate of hydrolysis as is used to make the alkoxides, recycling is simplified and the economics of the process are improved.

Waste Glass Durability

As would be expected, compositions high in alumina have excellent chemical durability. Soxhlet leach tests conducted at 100°C typically show release rates of $\sim 10^{-9}$ total g/cm²/day for our low- and medium-alumina glasses. These leach results show that the reference and simplified alkoxide processes give comparable results. Furthermore, over the range of glass compositions and cooling rates investigated the waste glasses made by the reactive mixing method are resistant to devitrification.

Waste Glass Fabrication

After the alcohol and water are removed at temperatures below 600°C, very little weight change occurs. Separation of the mixing and melting operations at this stage permits innovation in waste glass fabrication. The high melting rates and short residence times characteristic of the reactive mixing process will permit the design of smaller volume, higher throughput joule heated melters. On the other hand, the more viscous melts of the more chemically durable compositions can be prepared using either hot or cold wall in-can melting techniques. Cold wall techniques utilizing a remote heat source such as a laser would permit a variety of canister materials to be used, including low carbon steel, maleable cast iron, polycrystalline ceramics, glass and graphite.

REFERENCE

1. J. A. Kelley and R. M. Wallace, "Procedure for Determining Leachabilities of Radioactive Waste Forms," Nucl. Tech. 30: 47-51 (1976).