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Vitrification Of Waste Containing Salts (U)

by
J. C. Marra
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808
M K Andrews

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VITRIFICATION OF WASTES CONTAINING SALTS

James C. Marra and Mary K. Andrews
Westinghouse Savannah River Company
P. O. Box 616
Aiken, SC 29802

Glass is attractive for immobilization of radioactive and hazardous wastes due to its ability to accept a wide variety of components into its network structure. The resulting glass product is very stable and highly durable. Vitrification was designated as the Best Demonstrated Available Technology (BDAT) by the Environmental Protection Agency (EPA) for the treatment of radioactive liquid high level wastes [1]. Technologies are currently being developed by the U. S. Department of Energy's (DOE) nuclear sites to immobilize low-level radioactive and hazardous wastes (low-level mixed wastes) for permanent or long term disposal. Vitrification is an attractive alternative for treatment of these compositionally varied wastes. Vitrification is cost-effective and produces an extremely durable waste form. Significant volume reductions (up to 97 volume percent) for radioactive wastes have been realized utilizing vitrification [1]. These volume reductions greatly reduce waste disposal costs and more than offset the waste glass processing costs. Durability tests show that glass can be 10,000 times more durable than other waste forms, such as cement [2]. Waste glass has been found to be so stable that some vitrified wastes, such as municipal incinerator ash, can be made into consumer products like ceramic tile, building materials or insulation [2].

Although many wastes are readily vitrified, wastes containing high salt contents can offer several processing challenges. Many common salts found in low-level mixed wastes such as sulfates, chlorides, phosphates and chromates have limited solubility in glass. Processing and product problems may arise if the solubility of these salts is exceeded. The presence of segregated salt phases in the glass melt may hinder pouring of the glass melt and affect the durability of the resulting waste form. The presence of salt species in the melt combined with the relatively high temperatures required for waste glass processing can lead to extensive corrosion of melter and superstructure components. Several recent efforts at the Savannah River Site have examined the effects of the presence of salts on vitrification. Statistically designed screening experiments were performed to examine the solubility of several salt species in glass. The corrosion behavior of typical glass melter materials in glass melts containing high salt concentrations was also studied.

The statistically designed screening experiments utilized a Plackett-Burman design. This allowed efficient estimation of effects of variables such as the composition of the glass, the temperature of the melt, the duration of melting, and the cooling rate of the glass on the relative solubility of salt species in the glass. Twelve typical low-level mixed waste glass compositions were tested in the screening experiments. For each glass composition, nine crucibles, each with varying salt concentrations (Table I) were vitrified. Following vitrification, the glasses and any salt layers which may have formed were analyzed. The composition of the glass and salt layers were determined analytically and the crystallinity of the glass was assessed. The durability of the glasses was determined using the Product Consistency Test (PCT).

Table I. Salt Concentrations for Screening Experiments

	wt % of species in glass composition			
Sample Code	SO_4	NaCl	PO_4	Cr_2O_3
Baseline	0.0	0.0	0.0	0.0
S1	0.3	0.0	0.0	0.0
S2	0.5	0.0	0.0	0.0
S3	0.7	0.0	0.0	0.0
C1	0.0	0.5	0.0	0.0
C2	0.0	1.0	0.0	0.0
C3	0.0	1.5	0.0	0.0
AN	0.4	1.0	3.0	0.3
AH	0.7	1.5	4.5	0.6

The composition of the glass was the factor which most greatly affected salt solubility. Of the chemical constituents examined, boron and calcium contents in the glass appeared to have the most pronounced influence. A higher boron content and lower calcium content allowed for greater incorporation of the salts into the glass. The results of the effect of salt concentration on glass durability were often mixed, however, in many cases the presence of all salt species in the glass yielded lower durability results. The durability tests also showed that a higher level of boron and lower alkali content in the glass enhanced durability. The relationships of boron and alkali content with durability are consistent with observations in other waste glass compositions.

Laboratory scoping tests were performed to examine the performance of several candidate melter materials when exposed to glass melts containing varying salt concentrations. In these tests, two nickel based alloys (Joule heated melter electrode materials) and a high chromium content refractory (glass contact melter wall material) were exposed to glasses containing salt concentrations S3, C1, C3 and AH. Sample coupons were exposed at 1100 and 1300° C for 72 hours. Corrosion rates were estimated by dimensional measurements of the coupons before and after exposure. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) was utilized to gain insight into corrosion mechanisms.

Essentially no attack was evident in coupons exposed to the sulfate only glass composition. In the three other compositions studied, attack was evident on all coupons following exposure. The chloride containing melts typically caused the most significant degradation. In these cases, it was hypothesized that the chloride breaks down the protective oxide film on the surface of the material leading to subsequent oxidation of the base material. The greatest amount of corrosion occurred at the melt line (the interface between the melt and vapor space). Corrosion rates were also observed to dramatically increase with increasing melt temperature. The corrosion rates at 1300° C were typically at least two times faster than the rates at 1100° C. In some cases the increase was almost an order of magnitude different.

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