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Project Title: **An Alternative Host Matrix Based on Iron Phosphate Glasses for the Vitrification of Specialized Nuclear Waste Forms**

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AN ALTERNATIVE HOST MATRIX BASED ON IRON PHOSPHATE GLASSES FOR THE VITRIFICATION OF SPECIALIZED NUCLEAR WASTE

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RESEARCH OBJECTIVE

Certain high level wastes (HLW) in the U.S. contain components such as phosphates, heavy metals, and halides which make them poorly suited for disposal in borosilicate glasses. Iron phosphate glasses appear to be a technically feasible alternative to borosilicate glasses for vitrifying these HLWs. The iron phosphate glasses mentioned above and their nuclear wasteforms are relatively new, so little is known about their atomic structure, redox equilibria, structure-property relationships, and crystallization products and characteristics. The objective of this research is to gain such information for the binary iron-phosphate glasses as well as iron phosphate wasteforms so that a comprehensive scientific assessment can be made of their usefulness in nuclear waste disposal.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the work undertaken and completed in the first 34 months of a three year (9/15/96 - 9/14/99) project (DOE Contract # DOE96ER45617). Approximately 350 samples, binary iron phosphate glasses, iron phosphate glasses containing one or more common nuclear waste components such as UO_2, Na_2O, Bi_2O_3, Cs_2O, SrO, and MoO_3, and those containing simulated wastes from the Hanford and Idaho Falls sites have been prepared. Product Consistency Test and weight loss methods have been used to measure the chemical durability. Redox equilibria between Fe(II) and Fe(III) was investigated using Mössbauer spectroscopy. The atomic structure has been investigated using a variety of techniques including Mossbauer, Raman, X-ray absorption(XAS), and X-ray photoelectron (XPS) spectroscopies and neutron/high energy X-ray scattering. Glass forming and crystallization characteristics have been investigated using differential thermal analysis (DTA). In addition, information necessary for glass manufacturing such as suitable refractories and Joule heating parameters also have been obtained.

Productive research collaborations have been successfully established with the *Stanford Synchrotron Radiation Laboratory*, *Lawrence Berkeley National Laboratory*, *Argonne National Laboratory*, and the *Naval Research Laboratory*.

1. Chemical durability

Considerable amounts, in excess of 35 wt% in certain cases, of waste components and simulated wastes which are not well suited for borosilicate glasses can be present in iron phosphate wasteforms with no deterioration in the chemical durability, see Figure 1. The elemental leach rates shown in Figure 1corresponds to total dissolution rates in the order of 10^{-10} g/cm^2.min. Such dissolution rates are well within the requirements specified by DOE for a vitrified wasteform.

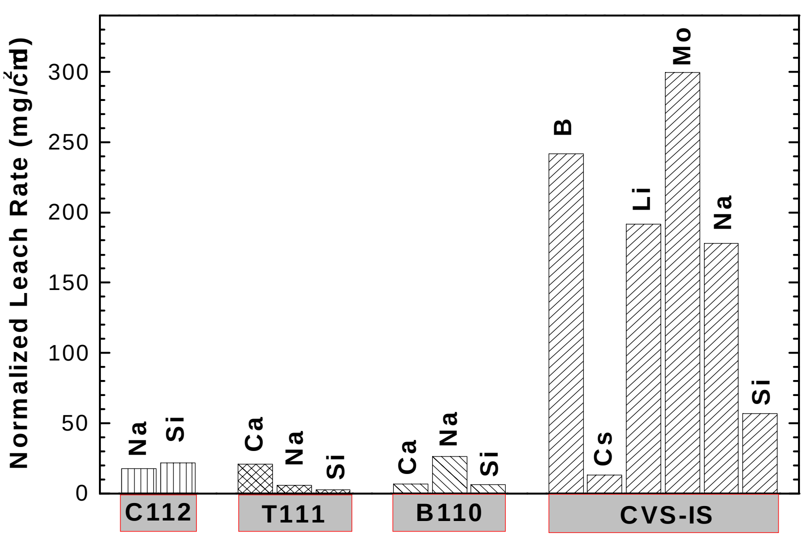

Figure 1. PCT determined normalized elemental mass release from three iron phosphate wasteforms containing 35 wt% simulated wastes from Hanford tanks C-112, T-111, and B-110.[1] CVS-IS is a borosilicate glass provided by Pacific Northwest National Laboratory.[2] Only those elements for which the mass release is greater than 2 mg/m^2.d are shown.

2. Redox Equilibria

When melted in air at their usual melting temperatures, i.e. 1000 - 1100°C, iron phosphate melts reach a redox equilibria that facilitates glass forming. In general, the addition of most waste components such as Na_2O, Cs_2O, SrO, and Bi_2O_3 cause the Fe(II) to increase as compared to the binary iron phosphate glasses. However, none of the waste components or simulated wastes investigated cause the Fe(II) fraction to exceed 0.4, the value above which the glass forming ability of iron phosphate melts is known to decrease. The addition of UO_2 results in glasses having smaller Fe(II) fractions. In the case of glasses containing UO_2 and a reducing oxide such as Na_2O or Bi_2O_3, the oxidizing nature of UO_2 appear to dominate.

3. Atomic Structure

Mössbauer and X-ray absorption spectroscopy show that both species of iron ions are coordinated with 5-5.5 near neighbor oxygen ions. Iron-oxygen coordination does not depend appreciably on the type or the concentration of the waste elements. X-ray photoelectron and Raman spectra of iron phosphate wasteforms suggest that the phosphorous-oxygen network is dominated by $(P_2O_7)^{-4}$ dimer units. With increasing waste content, the concentration of the dimer units increase slightly at the expense of the small number of remaining longer phosphate chains. These structural features and results of neutron and high energy X-ray scattering studies suggest that the waste ions are situated outside the second shell coordination environment of iron and phosphorus ions. Consequently, waste ions are unable to seriously influence the chemistry of the -Fe-O-P- network. Therefore, as observed, the addition of waste components does not cause major changes in properties such as the chemical durability of these iron phosphate wasteforms.

4. Crystallization and Glass Forming Characteristics.

The glass forming and crystallization characteristics of these glasses change in different ways with different waste components and simulated wastes. In general, the addition of alkali and alkaline earth oxides lead to sharper crystallization peaks which indicate less resistance to crystallization when heat treated at the appropriate temperatures. In contrast, the addition of UO_2 increases the crystallization temperature. However, none of the waste components investigated reduce glass transition and crystallization temperatures below 500 and 600°C, respectively. It must be noted that the measured glass forming and crystallization parameters are well within DOE specifications.

PLANNED ACTIVITIES

Comprehensive analysis of the large amount of data that was collected over the last 34 months will be the main focus of the project during remaining few months (a non-funded extension till December 1999 has been requested). In addition, we intend to research and develop melting techniques and laboratory scale melting apparatus that are best suited for processing iron phosphate wasteforms.

REFERENCES

[1] Compositions (wt%): C-112 - $30Fe_2O_3$,$45.2P_2O_5$, $10.7UO_2$, 5.6CaO, 3.3NiO, $2.5Na_2O$, $1.5Al_2O_3$, $1.0SiO_2$, and 0.4PbO, T-111 - $30Fe_2O_3$,$45.5P_2O_5$, $10.4Bi_2O_3$, $4.0SiO_2$, $3.6Mn_2O_3$, $2.0Na_2O$, $1.8La_2O_3$, 1.2UO2, 1.2CaO, and $0.4Al_2O_3$, B-110 - $30Fe_2O_3$, $46.3P_2O_5$, $9Bi_2O_3$, $8.2SiO_2$, $5Na_2O$, $0.9Al_2O_3$, and 0.5CaO.

[2] Composition (wt%) of CVS-IS is $53.3SiO_2$, $10.5B_2O_3$, $11.3Na_2O$, $3.7Li_2O$, $2.4Al_2O_3$, $7.0Fe_2O_3$, $3.9ZrO_2$, 1.3 Nd_2O_3, and 6.6 others.

INFORMATION ACCESS

1. Publications

1. "Structural Features of Iron-Phosphate glasses," J. Non-Cryst. Solids, **222** (1997) 144.
2. "Structural Study of Iron Phosphate Glasses", Phys. Chem. Glasses, **38** (1997) 74.
3. "Redox Characteristics and Structural Properties of Iron Phosphate Glasses:A Potential Host Matrix for Vitrifying High Level Nuclear Waste," Ceramic Transactions, **87** (1998) 261.
4. "Chemically Durable Iron Phophate Glass Wasteforms," J. Non-Cryst. Solids, **241** (1998) 1.
5. "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance and Evolved Gas Mass Spectroscopy," Nucl. Inst. Meth. Phys. Res. B, **141** (1998) 600.
6. "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses," Environment Issues and Waste Management Technologies IV:Ceramic Transactions, **93** (1999) 195.
7. "Iron Redox Equilibria and Crystallization of Iron Phosphate Glasses," Environment Issues and Waste Management Technologies IV:Ceramic Transactions, **93** (1999) 187.

2. Web Access

More information on this research is available at http://www.umr.edu/~gkmars/emsp.html.