Environmental Management Science Program

Project ID Number 55110

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

Dr. Delbert E. Day
University of Missouri-Rolla
101 Graduate Center for Materials Research
Rolla, Missouri 65409
Phone: 573-341-4873
E-mail: day@umr.edu

Chandra S. Ray
University of Missouri-Rolla
110 Straumanis Hall
Rolla, Missouri 65409
Phone: 573-341-6432
E-mail: csray@umr.edu

G. K. Marasinghe
University of Missouri-Rolla
101 Graduate Center for Materials Research
Rolla, Missouri 65049
Phone: 573-341-4873
E-mail: gkmars@umr.edu

M. Karabulut
University of Missouri-Rolla
101 Graduate Center for Materials Research
Rolla, Missouri 65049
Phone: 573-341-4873
E-mail: mevlutk@umr.edu

X. Fang
University of Missouri-Rolla
101 Graduate Center for Materials Research
Rolla, Missouri 65049
Phone: 573-341-4873
E-mail: fxiang@umr.edu

June 1, 1998

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

Dr. Delbert E. Day, University of Missouri-Rolla

Chandra S. Ray, University of Missouri-Rolla
G. K. Marasinghe, University of Missouri-Rolla
M. Karabulut, University of Missouri-Rolla
X. Fang, University of Missouri-Rolla

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 20 months of a three year (9/15/96 - 9/14/99) project (DOE Contract # DOE96ER45617). Approximately 250 samples, binary iron phosphate glasses and iron phosphate glasses containing one or two common nuclear waste components such as UO_2, Na_2O, Bi_2O_3, Cs_2O, SrO, and MoO_3, have been prepared. Weight loss has been used to measure the chemical durability and the redox equilibria between Fe(II) and Fe(III) has been 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*. The effect of radiation on iron phosphate glasses is being studied at the *Pacific Northwest National Laboratory* while the electrical conductivity is being measured at the *Ruder Boscovic Institute*, Croatia.

1. Chemical durability

In contrast to conventional phosphate glasses, the chemical durability of iron phosphate glasses is comparable to or better than that of borosilicate glasses. Considerable amounts, up to 35 wt% in certain cases, of waste components mentioned above can be present in iron phosphate glasses with no deterioration in the chemical durability. In addition, iron phosphate glasses can contain large amounts of selected simulated sludges. For example, iron phosphate wasteforms containing up to 60 wt% of a phosphate rich waste from tank C-112 at Hanford have been prepared.

2. Redox Equilibria

Irrespective of the valence state of iron ions in the starting batch, a redox equilibria corresponding to a Fe(II)/[Fe(III)+ Fe(III)] ratio of 0.2 to 0.3 is reached when melted under normal conditions, i.e. in air at 1100 -1200°C for 1-2 h. The process by which the redox equilibria is reached appears to be independent of the oxygen content in the melting atmosphere. However, the Fe(II) content in the glass can be increased beyond the equilibrium value by increasing the partial pressure of a reducing gas in the melting atmosphere or by increasing the melting temperature. The glass forming ability of iron phosphate melts is reduced considerably when the Fe(II) fraction exceeds 0.5. Additions of UO_2 or MoO_3 reduce the Fe(II) fraction in the glass, as compared to the base glass, whereas, Na_2O, Cs_2O, SrO, or Bi_2O_3 causes an increase in the Fe(II) content. Under normal melting conditions, none of the waste components cause the Fe(II) fraction to exceed 0.5, the value above which the glass forming ability decreases.

3. Atomic Structure

a.) Mössbauer Spectroscopy: Mössbauer hyperfine parameters measured for the binary iron phosphate glasses and their simulated wasteforms indicate that both species of iron ions are six-fold coordinated with near neighbor oxygens. Neither the isomer shifts nor the quadrupole splittings depend appreciably on the type or the concentration of the waste elements indicating that the addition of waste elements do not alter the local environment of the iron ions. It is reasonable to assume that the waste elements are situated outside the second coordination shell of iron ions.

b.) X-ray Absorption Spectroscopy (EXAFS/XANES): Fe-K edge EXAFS data suggest that the majority of oxygen ions in iron phosphate glasses are bonded via -Fe-O-P- links instead of via -P-O-P- links. This difference in the structural role of oxygen is believed to be the reason for the superior chemical durability of iron phosphate glasses. EXAFS data for the iron phosphate waste forms supports an atomic structure where the near neighborhood of the iron ions is unaffected by the addition of waste elements.

c.) X-ray Photoelectron Spectroscopy (XPS): O1s XPS spectra show that two types of oxygen ions are present, namely bridging (-P-O-P-) and non-bridging (-Fe-O-P- etc.) oxygens. In agreement with EXAFS measurements, only a minority of the oxygens appear to be bonded via -P-O-P- links. The addition of waste elements does not appreciably affect the bridging to non-bridging oxygen ratio.

d.) Raman Spectroscopy: Raman spectra of iron phosphate glasses studied herein are consistent with a P-O network dominated by $P_2O_7^{-4}$ dimer units instead of by PO_4^{-3} monomer units, in good agreement with EXAFS and XPS measurements. Major features in the Raman spectra do not change with the addition of waste components indicating that the P-O network is not disturbed by the waste elements.

e.) Neutron and High Energy X-Ray Scattering: Radial distribution functions obtained from neutron and high energy X-ray scattering suggest that the waste elements probably occupy Avoids@ in the glass structure without appreciably disturbing the -Fe-O-P- network.

4. Crystallization and Glass Forming Characteristics

Binary iron phosphate glasses possess a glass transition temperature of approximately 500°C and display two crystallization peaks in the DTA thermogram at approximately 580 and 775°C. Adding UO_2, SrO, or MoO_3 suppresses the crystallization tendency, but, at concentrations > 15 mol% Na_2O and Cs_2O promotes crystallization. None of the waste components lowers the glass transition temperature below 400°C, the acceptable lower limit for a vitrified wasteform.

5. Glass Manufacturing

a.) Refractories: Even though most phosphate glasses are highly corrosive to common commercial refractories, commercial alumina, zircon, or chrome refractories can be used to melt iron phosphate glasses and their waste forms. Under practical melting conditions, i.e in air at

1100°C, the corrosion rate of alumina, zircon, or chrome refractories was below 0.33 mm/day when tested in three different iron phosphate wasteform melts.

b.) Joule Heating: The AC conductivity of iron phosphate melts is suitable for Joule heating. The addition of waste elements, especially simulated sludges, further increases the conductivity.

Planned Activities

The analysis of the data obtained by the techniques mentioned above will be completed within the next 4-6 months. During the remaining time of this project, the main focus will be on iron phosphate glasses containing simulated HLWs. During this time, iron phosphate glasses containing simulated waste will be prepared and their atomic structure, redox equilibria, structure-property relationships, crystallization products and characteristics, and glass manufacturing processes will be investigated. We intend to acquire the compositional, property, and melting process information that is needed to evaluate the potential usefulness of iron phosphate wasteforms.

Other Access To Information

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. "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance and Evolved Gas Mass Spectroscopy", J. Non-Cryst. Solids (In Press).
5. "Chemical Durability, Crystallization, and Iron Redox Equilibria of Iron Phosphate Glasses", J. Non-Cryst. Solids (In Press).
6. "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses", Ceramic Transactions, 93 (1999) (In Press).
7. "Iron Redox Equilibria and Crystallization of Iron Phosphate Glasses", Ceramic Transactions, 93 (1999) (In Press).
8. "Corrosion of Selected Refractories by Iron Phosphate Melts", Ceramic Transactions, 93 (1999) (In Press).
9. "Electrical Conductivity in Iron Phosphate Glasses", Phys. Chem. Glasses (In Press).

Web Access

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