Annual Report

DOE Grant FG07-96ER45618

For the period 15 September 2000 to 15 June 2001

Research Objective:

The two, multifaceted objectives of this research project are to

- (1) investigate the feasibility of vitrifying 2 or 3 high priority wastes, as identified by the Tank Focus Area group, using iron phosphate glasses (i.e., determine chemical durability as a function of waste loading, establish maximum usable waste loading, evaluate melt characteristics and wastefrom properties), and
- (2) acquire the technical data for the types of raw materials and optimized melting and processing parameters that can be used to produce practical-size (prototype) quantities of iron phosphate glassy wastefroms.

This research is intended to provide the scientific and engineering knowledge that is needed to utilize iron phosphate glasses for vitrifying selected nuclear wastes on a production scale.

Research Progress and Implications:

General

During the nine months covered by this progress report, personnel have been assembled, general planning of the research has been completed, two high priority nuclear wastes were identified in cooperation with TFA personnel, experimental work was started using these two wastes, and several (12) papers describing this and earlier research on iron phosphate glasses were written and published.

In addition to the PI and Co-PI, one post-doctoral fellow, one graduate student (MS candidate) and two undergraduate research aides are currently working on this project. Another graduate student is being sought.

Wastes selected for Study

Based on input from TFA and other sources, a Soda Bearing Waste (SBW) at INEEL and a High Soda/Sulfate Waste (HSSW) at Hanford were selected for study. The composition of these two wastes were simplified by ignoring components present in small amounts, typically below 0.5 %. The "simplified" composition of each waste is given below. These wastes were chosen primarily because their high soda and sulfate content could limit the maximum waste loading in borosilicate glasses and because of the need to identify "alternative" glasses that could be used to vitrify such wastes.

Weight Percent Composition of the Soda Bearing Waste (SBW) at INEEL and the High Soda/Sulfate Waste (HSSW) at Hanford.

Oxide	Wt %	
	SBW	HSSW
Al ₂ O ₃	27.5%	4.4%
B ₂ O ₃	0.7%	0.0%
CaO	2.2%	0.0%
Cl	1.0%	0.6%
Cr ₂ O ₃	0.5%	0.4%
Fe ₂ O ₃	1.6%	0.0%
F	1.0%	1.6%
K ₂ O	8.0%	0.0%
MnO	0.8%	0.0%
Na ₂ O	50.3%	75.3%
NiO	0.6%	0.0%
P ₂ O ₅	1.2%	7.7%
SiO ₂	0.0%	0.5%
SO ₃	3.7%	9.5%
ZrO ₂	1.0%	0.0%
Total	100.0%	100.0%

To date, more than 20 iron phosphate wasteforms containing the SBW waste and 12 iron phosphate wasteforms containing the HSSW waste have been prepared and are being evaluated. The preliminary results are encouraging for both wastes in terms of the chemical durability and waste loading. Iron phosphate glasses have been obtained from trial melts containing up to 60 wt % SBW. Based upon dissolution rates measured in distilled water at 90⁰ C, which vary from 1×10^{-10} gm cm⁻² min⁻¹ at lower (30%) waste loadings to 5×10^{-8} gm cm⁻² min⁻¹ at 50 wt % loading, the maximum waste loading is estimated at 45 to 55 %. These melts are fluid and easily melted at only 1000⁰ C.

Fewer melts have been made with the HSSW waste (that contains 75 % soda and 9.5% SO₃), but a maximum waste loading between 35 to 50 wt % appears likely, based on preliminary dissolution rate (chemical durability) measurements. An attractive feature of these fluid iron phosphate-HSSW melts is that they can be melted and poured as low as 900⁰ C. This low melting temperature can reduce the cost and energy for melting as well as improving the sulfate solubility in the glass. In silicate glasses, the sulfate solubility rapidly decreases with increasing temperature.

Planned Activities:

During the forthcoming year, the investigation of the chemical, physical, and thermal properties of iron phosphate wasteforms containing SBW and HSSW will continue. This work should near completion by June 2002.

Starting in the second half of 2001, the investigation of methods and materials for melting iron phosphate glasses will commence and is expected to continue through 2002.

The main purpose of this work is to determine practical methods for melting iron phosphate glasses on a scale that is needed for vitrifying nuclear wastes. It is intended to investigate joule heating, cold wall crucible induction melting (hopefully in collaboration with Russian scientists), and ordinary crucible melting. This work will include corrosion tests on candidate refractories in iron phosphate melts in order to identify commercial refractories suitable for long term use.

Publications :

1. G. K. Marasinghe, M. Karabulut, X. Fang, C. S. Ray, D. E. Day, "Vitrified Iron Phosphate Nuclear Wasteforms Containing Multiple Waste Components", *Ceramic Transactions*, **107**, 115-22 (2000).
2. G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, D. K. Shuh, P. G. Allen, "Properties and Structure of Vitrified Iron Phosphate Nuclear Wasteforms", *J. Non-Cryst. Solids*, **263 & 264**, 146-54 (2000).
3. X. Fang, C. S. Ray, G. K. Marasinghe, D. E. Day, "Properties of Mixed Na₂O & K₂O Iron Phosphate Glasses", *J. Non-Cryst. Solids*, **263 & 264**, 293-98 (2000).
4. A. Mogus-Milankovic, B. Santic, C. S. Ray, D. E. Day, "Electrical Relaxation in Mixed Alkali Iron Phosphate Glasses", *J. Non-Cryst. Solids*, **263 & 264**, 299-304 (2000).
5. X. Fang, C. S. Ray, G. K. Marasinghe, D. E. Day, "Properties of Mixed Na-K Iron Phosphate Glasses", *Ceramic Transactions*, **107**, 207-14 (2000).
6. M. Karabulut, G. K. Marasinghe, C. S. Ray, D. E. Day, "Local Environment of Iron and Uranium Ions in Vitrified Iron Phosphate Glasses Studied by FeK and U_{LIII}-edge X-ray Absorption Fine Structure Spectroscopy", *J. Mater. Res.*, **15**, 1972-84 (2000).
7. A. Mogus-Milankovic, B. Santic, D. E. Day, C. S. Ray, "Electrical Conductivity in Mixed Alkali Iron Phosphate Glasses", *J. Non-Cryst. Solids*, **283**, 119-28 (2001).
8. X. Fang, C. S. Ray, A. Mogus-Milankovic, D. E. Day, "Iron Redox Equilibrium, Structure, and Properties of Iron Phosphate Glasses", *J. Non-Cryst. Solids*, **283**, 162-72 (2001).
9. G. K. Marasinghe, M. Karabulut, X. Fang, C. S. Ray, D. E. Day, "Iron Phosphate Glasses: An Alternative to Borosilicate Glasses for Utilizing Certain Nuclear Wastes", *Ceramic Transactions* (in press).
10. B. Santic, A. Mogus-Milankovic, D. E. Day, "The dc Electrical Conductivity of Iron Phosphate Glasses", *J. Non-Cryst. Solids* (in press).
11. M. Karabulut, E. Melnik, R. Stefan, G. K. Marasinghe, C. S. Ray, C. R. Kurkjian, D. E. Day, "Mechanical & Structural Properties of Phosphate Glasses", *J. Non-Cryst. Solids* (in press).
12. C. Fuyi, J. Wanqi, D. E. Day, "Electrical Resistivity of Iron Phosphate Melts", *J. Non-Cryst. Solids* (in press).

DOE-GRT/RPT/6-15-01--

Delbert E. Day
Materials Research Center
University of Missouri-Rolla
Rolla, MO 65409-1170

Tel: 573-341-4354, Fax: 573-341-2071, e-mail: day@umr.edu