FINAL REPORT

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

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A. EXECUTIVE SUMMARY

Borosilicate glass is the only material currently approved and being used to vitrify high level nuclear waste. However, some waste feeds in the U.S. contain components which are poorly soluble or chemically incompatible in borosilicate glasses. Current plans call for vitrifying even these problematic waste feeds in borosilicate glasses after the original waste feed has been pre-processed and/or diluted to compensate for the incompatibility. However, these pre-treatment processes, as well as the larger waste volumes resulting from dilution, will greatly increase the cost of cleaning up former DOE nuclear weapons production facilities. At least some, if not all of this additional cost can be avoided if a small number of alternative waste glasses are available and used to vitrify those nuclear wastes that are poorly suited for borosilicate glasses

With funds from the Environmental Management Science Program (EMSP), U.S. Department of Energy, we have investigated more than 350 compositions belonging to a new family of iron phosphate glasses. This work, done in collaboration with scientists from *Pacific Northwest*, *Lawrence Berkeley*, *Lawrence Livermore*, and *Argonne* national laboratories and the *Westinghouse Savannah River* and *Naval Research* laboratories and involving several simulated wastes from Hanford and Idaho Falls, indicates that iron phosphate glasses should be a lower cost and technically effective wasteform for vitrifying selected nuclear wastes.

Iron phosphate glass wasteforms either meet or exceed all DOE requirements for a vitrified wasteform. In terms of their properties, iron phosphate glasses are more like silica based glasses than other phosphate glasses. Up to 50 wt% of selected simulated wastes from the Hanford site have been vitrified in iron phosphate glasses compared to the roughly 28 wt% now being vitrified in borosilicate glasses at the Defense Waste Processing Facility (DWPF) at Savannah River. For certain wastes, the use of iron phosphate glasses may reduce the vitrified waste volume by as much as 50% over the volume of a borosilicate glass wasteform. The chemical durability of iron phosphate vitrified wasteforms is comparable to, and in many instances, better than that of most comparable borosilicate glass based wasteforms. Iron phosphate glasses are melted at 950-1100EC for 1-2 hrs. compared to the 1150EC for 24 hrs. for the borosilicate glasses now being melted at the DWPF. Lower melting temperatures and shorter melting times mean that smaller, less expensive furnaces can be used to melt iron phosphate wasteforms.

This research has resulted in more than 20 refereed technical publications and 15 presentations at national and international conferences.

B. INTRODUCTION

A major concern with high level radioactive waste disposal is the possibility of radioactive nuclides escaping from the storage site and contaminating the biosphere. To prevent such environmental contamination, the DOE has started to immobilize high level nuclear waste feeds by chemically dissolving them in host glass matrices by vitrification. Even though the chemical compositions of nuclear waste feeds found at sites like Hanford and Savannah River are complex and extremely diverse, see Table 1, only one glass material, namely borosilicate glasses, is currently approved as a host matrix for vitrifying high level nuclear waste.

Unfortunately, many of the high level waste feeds in the U.S. contain waste components which are either insoluble or incompatible with borosilicate glasses. For example, the solubility limit of phosphates, present in many radioactive waste materials at sites like Savannah River and Hanford, see Table 1, dramatically reduces the waste loading ability of borosilicate glasses in many cases. At Hanford alone, where 55 million gallons of high level waste must be immobilized, it is estimated that the low solubility of phosphates, ca. 1wt%, in borosilicate glasses will result in as much as 100,000 m^3 of waste glass at an additional cost of tens of billions of dollars [1-3].

Table 1. Simplified compositions (wt%) of several radioactive tank sludges at Hanford site which are not well suited for disposal in borosilicate glass.

	Tank Designation[a]			
Component	B-110	C-106	C-112	T-111
Fe_2O_3	30.6	16.8	15.0	26.3
P_2O_5	1.7	1.3	14.1	3.6
Na_2O	14.4	22.1	7.1	5.6
Al_2O_3	2.7	17.7	4.2	1.1
Bi_2O_3	25.8	-	-	29.8
SiO_2	23.4	34.7	2.5	11.3
UO_2	-	-	30.5	3.3
CeO_2	-	-	-	-
Other	1.6	7.4	26.6	19.0

[a] Numbers refer to different radioactive waste tanks from the Hanford site.

Several other waste components such as chlorides, fluorides, and oxides of heavy metals such like Cs, Sr, Zn, Zr, Cr, and Bi are also ill-suited for vitrification in borosilicate glasses. In all such cases, the waste feed needs extra dilution during vitrification resulting in larger waste volumes. If one is to avoid such large waste glass volumes generated due to waste components poorly soluble in borosilicate glasses, the waste stream must be pre-treated prior to vitrification in order to remove the unfavorable components. However, such pre-treatment processes are expensive and also add further risks to the disposal process. *Examples like these make it clear that no single type of glass will ever be totally satisfactory and cost effective for all of the many different nuclear waste feeds now in existence.* The solution to such problems is to develop a small number of different types of glasses which provide the optimum means of vitrifying the wide spectrum of nuclear waste compositions now in existence.

Preliminary research conducted at the University of Missouri-Rolla (UMR) in the early 90s indicated that a new family of iron phosphate glasses may be better suited for vitrifying certain nuclear wastes. This preliminary work [4-6], done in collaboration with scientists from *Pacific Northwest National Laboratory*, *Westinghouse Savannah River Laboratory*, and *Lawrence Berkeley National Laboratory*, suggested that iron phosphate glasses could be developed as a lowcost and highly effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. A comprehensive evaluation of the viability of using iron phosphate glasses in nuclear waste vitrification, however, required additional information on the atomic structure, valence states, nature of bonding, structure-property relationships, crystallization kinetics, and optimized melt processing. Obtaining such information was the overall objective of this research project.

C. BACKGROUND

Prior to detailing our research on iron phosphate glass nuclear wasteforms, it is prudent to review the role other phosphate glasses have played in the U.S. nuclear waste vitrification program. From our perspective, it is intriguing to note that the first attempt to vitrify nuclear waste was made in the 1960s utilizing a phosphate host matrix [7]. Because of the large quantity of sodium present in the wastes considered at that time, the final wasteform was a high-sodium phosphate glass in which the radionuclides were dissolved. Even though sodium phosphate glasses presented several advantages such as lower melting temperatures and shorter melting times as compared to borosilicate glasses, problems with sodium phosphate wasteforms soon became evident. Sodium phosphate melts are chemically corrosive and must be melted in furnaces lined with platinum. In addition, the chemical durability of sodium phosphate glasses was poor and yielded unacceptably high radionuclide leach rates in durability tests. Sodium phosphate glasses are also susceptible to devitrification resulting in phases whose durability is even worse than that of the parent glass. Mainly because of such problems with the sodium phosphate glasses, all phosphate glasses were dropped from the pool of potential host matrices in the early 1970s.

Lead-iron phosphate glasses (LIP) developed in 1984 [7,8] were a marked improvement over sodium phosphate glasses in many aspects. LIP melts were much less corrosive and had low melting temperatures and short melting times comparable to the sodium phosphate melts. LIP glass based wasteforms do not easily devitrify and their chemical durability rivals that of borosilicate glasses. However, the low waste loading (approximately 10 wt%), low durability of their crystallized counterparts, and the limited experience melting phosphate glasses led to the lead-iron phosphate glasses being dropped from consideration for vitrification of nuclear waste.

At the time when potential alternative host glasses such as LIP glasses were dropped from active consideration, the nuclear waste management community was beginning to view borosilicate glasses as the "one size fits all" host matrix. This view resulted mainly from two reasons. First, the amount of data available at the time for nuclear wastes that contained components incompatible with borosilicate glasses was much less than now. Second, the borosilicate glasses were a well-known system for which efficient melting technologies had been developed over several decades. Adopting the better known borosilicate based glasses was viewed as a low risk approach for vitrifying nuclear waste.

By the early 1990s, however, as the true diversity and chemical complexity of the nuclear wastes in the US became more apparent and as the range of nuclear wastes tested in borosilicate glasses widened, the potential problems of the incompatibility of certain wastes with borosilicate glasses became more evident. A logical solution to this problem is to have alternative host matrices available that are better suited for vitrifying such problematic wastes, i.e. "**to match the glass to the waste**." It was under these circumstances, that the Environmental Management Science Program (EMSP) funded research at UMR in 1996 to evaluate the feasibility of using iron phosphate glasses for nuclear waste vitrification.

D. RESEARCH OBJECTIVES

As mentioned above, the overall goal of this research project was to collect the scientific information essential to develop iron phosphate glass based nuclear wasteforms. The specific objectives of the project were:

1. Investigate the structure of binary iron phosphate glasses and it's dependence on the composition and melting atmosphere: Understand atomic arrangements and nature of the bonding. Establish structure-property relationships. Determine the compositions and melting conditions which optimize the critical properties of the base glass.

2. Understand the structure of iron phosphate wasteforms and it's dependence on the composition and melting atmosphere: Investigate how the waste elements are bonded and coordinated within the glass structure. Establish structure-property relationships for the waste glasses. Determine the compositions and melting atmosphere for which the critical properties of the waste forms would be optimum.

3. Determine the role(s) played by the valence states of iron ions and it's dependence on the composition and melting atmosphere: Understand the different roles of iron(II) and iron(III) ions in determining the critical properties of the base glass and the waste forms. Investigate how the iron valence and its significance depend on the composition and melting atmosphere.

4. Investigate glass forming and crystallization processes of the iron phosphate glasses and their waste forms: Understand the dependence of the glass forming and crystallization characteristics on overall glass composition and valence states of iron ions. Identify the products of devitrification and investigate the critical properties of these crystalline compounds which may adversely affect the chemical and physical properties of the waste forms.

E. EXPERIMENTAL

Sample Preparation: Approximately 350 crucible-melted (50-100 g samples), binary iron phosphate glasses, iron phosphate glasses containing varying amounts of one or more common nuclear waste components such as Na_2O, Bi_2O_3, Cs_2O, UO_2, SrO, and MoO_3, and several glasses containing simulated wastes from the *Hanford, Savannah River,* and *Idaho Falls* sites were prepared. The majority of the samples were melted in air in alumina crucibles at -1200°C for 1.5 to 2 hrs. However, the melting conditions of selected samples were varied so as to investigate the effects of melting temperature, time, and atmosphere on the atomic structure and critical properties (chemical durability) of the glasses. Each melt was quenched by pouring into 1cm x 1cm x 5cm steel molds at room temperature. The rectangular samples were immediately transferred to a furnace and annealed at 475°C for approximately 3 hrs. The absence of crystalline phases in the annealed samples were confirmed X-ray diffraction technique. The chemical compositions of selected samples were determined by inductively coupled plasma spectroscopy (ICP).

Chemical Durability: The chemical durability of all of the samples was investigated by measuring the weight loss of cubic samples of known dimensions immersed in distilled water at 90°C for 8 or 16 days. Details of these techniques have been published elsewhere [1]. The chemical durability of selected samples was measured also by the product consistency test (PCT), ASTM C-1285-94. In this method, -100 +200 mesh powders were placed in deionized water at 90°C for seven days. The chemical composition of the solutions were then analyzed using ICP.

Redox Equilibria: The valence state of iron ions was measured using Mössbauer spectroscopy. The Mössbauer spectra were measured on a ASA600 spectrometer at room temperature (295 K) using a 50 mCi rhodium matrix cobalt-57 source. Each spectrum was fit with approximately eight broadened paramagnetic doublets. Details of this fitting procedure and its merits have been previously discussed [2].

Atomic Structure: The atomic structure of binary iron phosphate glasses and those containing simulated waste was investigated using a multitude of techniques. Iron-oxygen coordination was investigated using Mössbauer spectroscopy. X-ray absorption spectroscopy (XAS), conducted at the *Stanford Synchrotron Radiation Laboratory* in collaboration with scientists from the *Lawrence Berkeley National Laboratory*, was used to probe the short range order around iron ions and selected waste ions. The structural role of oxygen ions was investigated using X-ray photoelectron spectroscopy (XPS). Raman spectra, measured at the *Materials Science Division, Argonne National Laboratory (ANL)* , were used to probe the phosphorous-oxygen network. Short and intermediate range order in these glasses were investigated using high energy x-ray and neutron scattering at ANL [ANL].

Glass forming and crystallization characteristics: Properties such as the glass transition and crystallization temperatures were investigated by differential thermal analysis (DTA). Products of crystallization were identified by x-ray diffraction (XRD).

Glass processing: Preliminary information essential to large scale glass processing such as the corrosion rate of commercial refractories and heating elements and joule heating parameters were measured.

F. RESULTS [9-26]

F.1. Glass compositions [13,22,25]: In general, the iron phosphate glasses investigated in this project can be grouped in to three categories, binary iron phosphate glasses, those containing one or two waste components, and iron phosphate glasses containing selected simulated waste compositions from U.S. nuclear waste sites. For the purpose of this report, unless otherwise noted, all compositions will be given as mol%.

Table 2. Batch compositions and waste loading of selected iron phosphate glasses containing one or two waste components.

Batch Composition (mol%)	Waste loading (wt%)
$40Fe_2O_3$-$60P_2O_5$	Base glass
$32Fe_2O_3$-$48P_2O_5$-$20UO_2$	31
$20Fe_2O_3$-$60P_2O_5$-$20Bi_2O_3$	44
$32Fe_2O_3$-$48P_2O_5$-$20Na_2O$	10
$28Fe_2O_3$-$42P_2O_5$-$30Cs_2O$	44
$32Fe_2O_3$-$48P_2O_5$-$20SrO$	48
$32Fe_2O_3$-$48P_2O_5$-$10UO_2$-$10Na_2O$	22
$32Fe_2O_3$-$48P_2O_5$ -$10Bi_2O_3$-$10Na_2O$	31
$32Fe_2O_3$-$48P_2O_5$-$10UO_2$-$10CaO$	22
$32Fe_2O_3$-$48P_2O_5$ -$10Cs_2O$-$10Na_2O$	24

Binary iron phosphate glasses are made by melting homogenized batches of composition xFe_2O_3-(100-x)P_2O_5 (x. 50) for 1.5 to 2 hrs. followed by quenching in air in steel molds. In general, the required melting temperature increases with x. Batches for which x > 30 (Fe/P>0.5) can be melted at temperatures between 950 and 1050EC. Batches containing smaller iron contents must be melted in the 1050 to 1250 EC range. ICP analysis of selected glasses suggest that a considerable amount of phosphorus is lost during melting at low iron concentrations ($x < 20$ or $Fe/P < 0.25$). For example, two batches with x equal to 5 ($Fe/P = 0.05$) and 15 ($Fe/P = 0.18$) resulted in glasses having Fe/P ratios of 0.25 and 0.31, respectively. At higher iron contents ($30 < x < 50$), however, the phosphorus loss during melting, if any, is too small to be detected by ICP analysis. As described below, the binary iron phosphate batch compositions relevant to nuclear waste vitrification belong to the approximate Fe/P ratio range of 0.3 - 0.7, i.e. $23 < x < 40$ in terms of the compositional notation xFe_2O_3-$(100-x)P_2O_5$. For the purpose of this report, an iron phosphate glass of batch composition $40Fe_2O_3$-$60P_2O_5$ (mol%) will be referred to as the base glass.

Glasses in the second and third categories can be made from batches in which the waste/waste components are added to the base glass composition or from batches in which Fe_2O_3 in the base glass composition is partially replaced by waste/waste components. The maximum waste loading in the glasses obviously depend on the chemical composition of the waste. In the case of iron phosphate glasses containing only a single waste component, for example, the approximate solubility limits of Na_2O, Cs_2O, UO_2, and Bi_2O_3 are 10, 45, 35, and 44 wt %, respectively. Table 2 gives several examples of batch compositions for iron phosphate glasses containing one or two waste components.

F. 2. Raw materials [10,12]: The vast majority of the samples investigated herein were synthesized using Fe_2O_3 and P_2O_5 as the sources of iron and phosphorus, respectively. However, it must me noted that other iron and phosphorus containing raw materials can be used without any reservations. For example, Fe_3O_4, which is a low cost alternative to Fe_2O_3, can be used without adversely affecting the redox equilibria or the physical and chemical properties of the samples. Similarly, using $(NH_4)H_2PO_4$ or H_3PO_4 as the source of phosphorus avoids the problems that may crop up due to the hygroscopic nature of P_2O_5. Another raw material of interest that can provide both iron and phosphorus is the industrial waste that is being generated during the iron (and zinc) phosphating process for improved corrosion protection and paint adhesion to metal parts (vehicles, office furniture, household appliances, etc). Large quantities of these iron and zinc phosphating wastes (exact amount is unknown but estimated to be several thousand tons per year) are currently being buried in landfills across the US. These iron and zinc phosphating industrial wastes could be a low cost raw material providing all of the iron oxide and phosphate needed for the iron phosphate waste vitrification program.

F.3. Chemical Durability [21,25,26]: One of the most important properties a nuclear wasteform must have is an excellent chemical durability. The chemical durability is measured in terms of the dissolution rate (D_R) of the wasteform in a selected liquid. In general, a nuclear wasteform is required to have a net dissolution rate (@ 90EC in distilled water) less than 10^{-7} (log D_R = -7)

Table 3. Batch compositions (wt%) of glasses containing 35 wt% simulated wastes from three Hanford tanks.

Component	Sample (Tank Designation)[9]		
	P(B-110)	Q(C-112)	R(T-111)
P_2O_5	46.3	45.2	45.5
Fe_2O_3	30	30	30
Al_2O_3	0.9	1.5	0.4
Bi_2O_3	9.0	-	10.4
CaO	0.5	5.6	1.2
La_2O_3	-	-	1.8
Mn_2O_3	-	-	3.6
NiO	-	3.3	-
PbO	-	0.4	-
SiO_2	8.2	1.0	4.0
Na_2O	5.0	2.5	2.0
UO_2	-	10.7	1.2

Table 4. Normalized elemental mass release from iron phosphate wasteforms and a borosilicate glass as measured by Product Consistency Test (PCT). Elements for which the mass release was less than 0.1 $mg/m^2.d$, i.e. Al, Bi, La, Fe, Mn, Ni, Pb, and U, are not listed.

Element	Normalized Mass Release ($mg/m^2.d$)				
	35 wt% C-112	35 wt% T-111	35 wt% B-110	Base Glass	CVS-IS[a]
B	-	-	-	-	242
Ca	1.99	20.91	6.80	-	-
Cs	-	-	-	-	13
Li	-	-	-	-	192
Mo	-	-	-	-	300
Na	17.91	5.98	26.17	-	178
P	0.59	0.45	0.95	0.36	-
Si	21.59	2.61	6.16	-	57

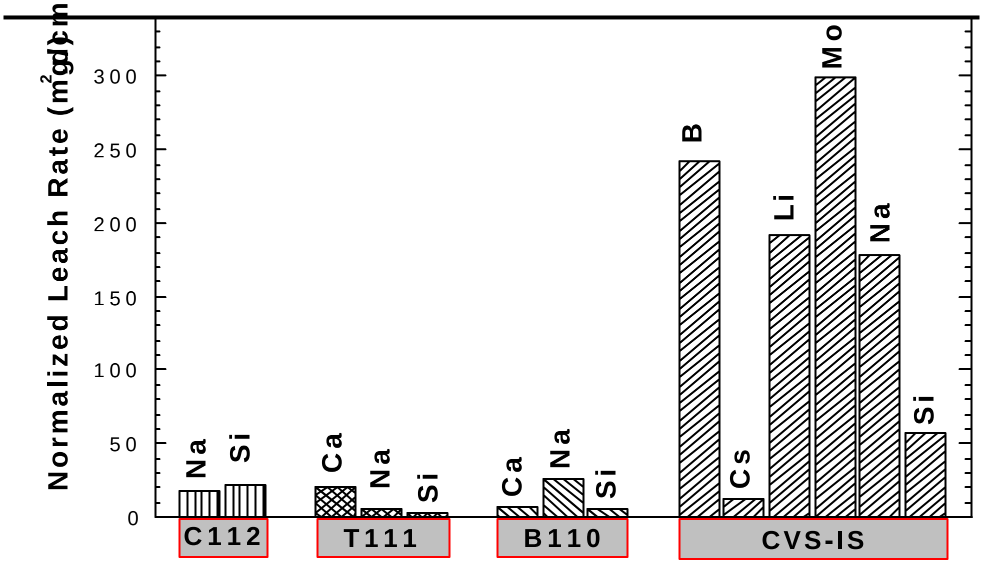

Fig. 1. PCT determined normalized elemental mass release from three iron phosphate wasteforms containing 35 wt% simulated wastes from Hanford tanks C-112, T-111, and B-110. CVS-IS is a borosilicate glass provided by PNNL. Only those elements for which the mass release is greater than 2 mg/m².d are shown.

D_R[b] (g/cm².min)	1.3×10^{-10}	1.0×10^{-10}	1.6×10^{-10}	3.3×10^{-11}

[a] Standard glass of composition 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 (wt%). Provided by Pacific Northwest National Laboratory.[3]

[b] Dissolution rate (net weight loss) calculated by summing the individual elemental leach rates in Table III. Note that D_R values are given in g/m².d for comparison with previously published. g/cm²/min.

Table 5. Dissolution rates of selected iron phosphate glasses calculated from the weight loss of bulk samples kept for 16 days in 90EC distilled water.

Sample	Batch Composition (mol%)	Dissolution Rate (g/cm².min)
5A	$40Fe_2O_3$-$60P_2O_5$	2.0×10^{-9}
5B	90A-$5UO_2$-$5Na_2O$	7.7×10^{-9}
5C	85A-$5UO_2$-$10Na_2O$	3.1×10^{-9}
5D	80A-$10UO_2$-$10Na_2O$	1.1×10^{-9}
5E	90A-$5Bi_2O_3$-$5Na_2O$	7.7×10^{-10}
5F	85A-$5Bi_2O_3$-$10Na_2O$	4.4×10^{-9}
5G	80A-$10Bi_2O_3$-$10Na_2O$	1.2×10^{-8}

5H	90A-5UO_2-5CaO	6.7×10^{-10}
5J	90A-5Cs_2O-5Na_2O	1.2×10^{-9}
5K	80A-10Cs_2O-10Na_2O	6.6×10^{-9}
5L	90A-5CaO-5Na_2O	2.6×10^{-9}
5M	80A-10CaO-10Na_2O	1.7×10^{-8}
5N	35 wt% C-112	3.8×10^{-8}
5O	35 wt% T-111	2.8×10^{-8}
5P	35 wt% B-110	7.7×10^{-9}

The dissolution rates of the iron phosphate glasses and their nuclear wasteformsinvestigated herein are well within the DOE requirements and are several orders of magnitude better than those of most non-iron-containing phosphate glasses. The Product Consistency Test (PCT, ASTM C-1285-94), which measures the leach rate of ions from powders in distilled water, is a common standardized test used to determine the chemical durability of a material, especially one being considered for waste vitrification. Figure 1 compares the PCT results for three iron phosphate wasteforms containing 35 wt% nuclear wastes, see Table 3, to those of a borosilicate waste glass standard. The measured leach rates are given also in Table 4. Even though the iron phosphate glasses in Fig. 1 contains up to ten different cations, the leach rates of only two or three cations are large enough to be compared with those for the borosilicate glass. It is especially worth noting that the leach rates of the dominant ions in the glass, iron and phosphorus, are too small to be shown in Fig. 1. The elemental leach rates given in Table 4 correspond to net dissolution rates [20] in the order of 10^{-10} g/cm^2/min, see last row of Table 4.

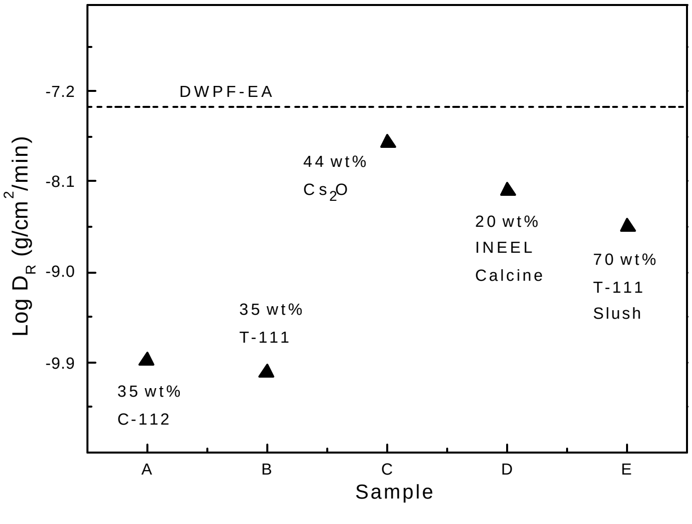

Fig. 2. Dissolution rates (D_R), in distilled water at 90EC, measured for five iron phosphate wasteforms containing varying amounts of simulated wastes or a waste component. Samples A-D are fully vitrified glasses. Sample E is a partially vitrified wasteform mentioned in sections F.6. Data for samples A and B are from PCT tests. Data for the other samples are from weight loss experiments. DWPF-EA is a borosilicate glass standard provided by SRL.

Table 5 gives the dissolution rates measured by the weight loss technique, a simpler and less precise technique compared to the PCT test, for several iron phosphate glasses including the three glasses mentioned in the previous paragraph. A comparison of net dissolution rates listed in Tables 4 and 5 for the glasses containing Hanford waste indicates that the weight loss technique yields over estimated dissolution rates. Note that even the over estimated dissolution rates listed in Table 5 are smaller than that generally required of a nuclear wasteform (10^{-7} g/cm^2/min).

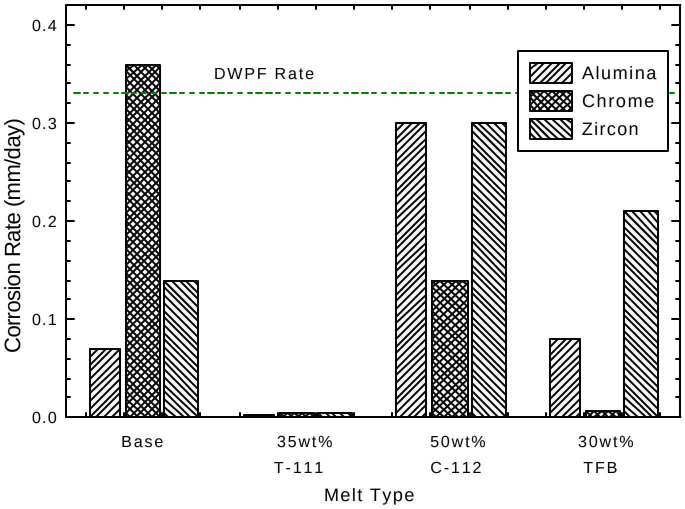

Fig. 3. Corrosion rates (1100-1200EC) of three common refractories in four different iron phosphate melts. Melt labeled "Base" is a binary iron phosphate melt of composition $40Fe_2O_3$-$60P_2O_5$ (mol%). The composition of the simulated waste TFB is similar to the average composition in tanks at the Tank Farm B at Hanford [20].

F.4. Waste Loading [22,25]: A high waste loading is desirable because it reduces the waste volume and, therefore, the overall cost of waste vitrification and disposal. At the present time, the borosilicate wasteforms being produced at DWPF contain about 28 wt% waste. When the wastes contain heavy metals that are poorly soluble in a borosilicate glass or phosphates which can cause phase separation, the waste loading in a borosilicate wasteform can be 10 wt% or less. Iron phosphate glasses, on the contrary, can contain in excess of 35 wt% of such wastes and still have an excellent chemical durability. In the case of wastes containing large amounts of phosphates such as waste from tank C112 in Hanford, the waste loading in a fully vitrified iron phosphate glass can be as high as 50 wt%. In addition, "partially vitrified" iron phosphate wasteforms containing up to 70 wt% wastes have also been prepared with an equally good chemical durability, see sample E in Fig. 2.

F.5. Glass Melting [20]: Iron phosphate glasses can be melted at temperatures as low as 1000EC in as little as 1.5 hrs. In contrast, the borosilicate glasses currently being processed at the DWPF are melted at 1150EC for times > 24 hrs. The lower melting temperature and, especially, the shorter melting time for iron phosphate glasses translate into considerable energy savings and smaller furnaces for the same output. In addition, shorter melting times mean that smaller, less expensive, furnaces can be used. Unlike other phosphate glasses which are melted in platinum lined furnaces because of their corrosiveness towards common refractories, preliminary experiments at UMR show that iron phosphate glasses can be melted using commercially available refractory materials such as alumina, mullite, or zircon, see Fig 3.

F.6. Alternative Melting Techniques: Not all waste streams may justify vitrification by continuous melting. Especially when the waste quantity is relatively small, an alternative melting process such single pass melting can be more cost effective. In this technique, a ceramic container (a ceramic tube with one end closed and the other end sealed) containing the batch is slowly passed through the hot zone of a furnace at a pre-determined rate. Melting and quenching of the waste occurs in the container without contaminating the furnace. Because of the short melting time and single use, corrosion of the refractories is slight and of little concern. The low viscosity (300 to 600 centipoise) is an advantage for such no-flow melting processes because chemical homogeneity is achieved very quickly. With this technique, fully vitrified iron phosphate wasteforms containing in excess of 40 wt% of simulated waste from tank farm B at Hanford have been prepared in less than two hrs. It should be noted that the chemically durable ceramic tube (mullite or alumina) provides another chemical barrier protecting the durable glass wasteform inside from chemical attack.

F.7. Glass Forming/Crystallization Characteristics [12,13,15,25]: The DTA curves for binary iron phosphate glasses contain an endothermic transition around 500EC due to the glass transition and two exothermic peaks near 650 and 800EC that correspond to crystallization [12], see Fig. 4. In general, the high temperature exothermic peak is suppressed in iron phosphate glasses containing waste components. The addition of alkali and alkaline earth oxides leads to sharper crystallization peaks which indicates less resistance to crystallization when heat treated at the appropriate temperatures. In contrast, the addition of heavy metal oxides such as UO_2 increases the crystallization temperature and makes the glass more resistant to crystallization. In some

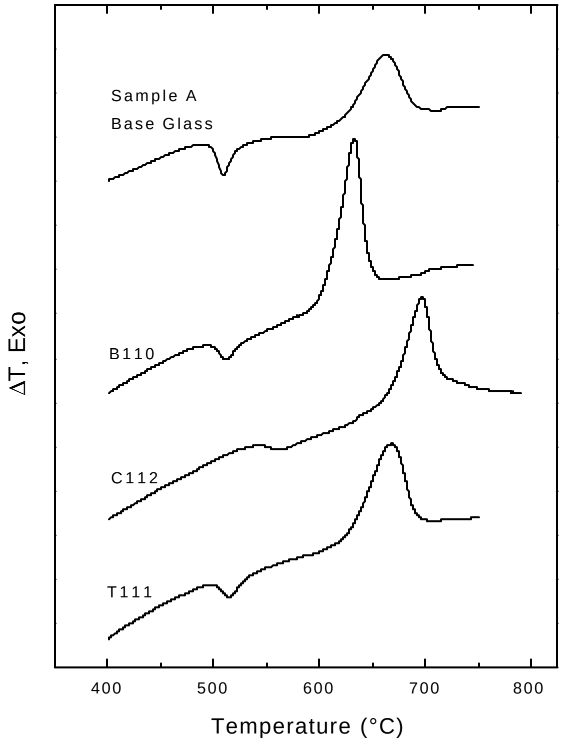

Fig. 4. Differential thermal analysis data for the base glass and three other iron phosphate glasses which contain 35 wt% waste from Hanford tanks B110, C112, and T111.

uranium-containing iron phosphate glasses, the DTA curve does not show a crystallization peak [22]. None of the waste components/simulated wastes investigated herein reduce the glass transition and crystallization temperatures below 500 and 600EC, respectively, see Fig. 4. Note that the measured crystallization temperature is above the 400EC minimum specified by the Department of Energy [12,15].

F.8. Redox Equilibria [10,12,13,15,22]: Knowledge of the redox conditions in nuclear waste glass melts is important due to two reasons. First, extreme oxidizing conditions can promote the formation of foam on the melt surface which in turn diminishes the heat transfer and lowers the melting rates. Second, extreme reducing conditions can cause the formation of metallic phases which can settle to the melter floor and potentially cause a short between the electrodes in an electric furnace. The iron(II)/iron(III) ratio in a waste glass, which can be accurately determined by Fe-57 Mössbauer spectroscopy, is used to determine and control the general oxidation state of the glass during melting [27], see Fig. 5.

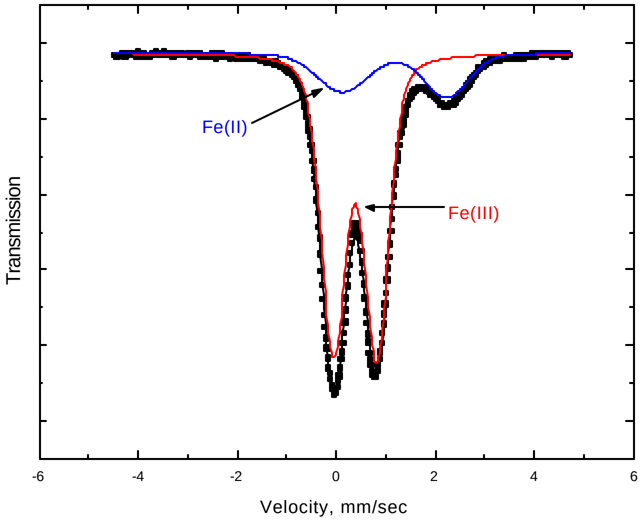

Fig. 5. Mössbauer spectrum measured at 295 K for an iron phosphate glass of batch composition 40Fe_2O_3-60P_2O_5 (mol%) melted at 1150EC. The areas under the envelops assigned to Fe(II) and Fe(III) can be used to calculate their relative occupancy.

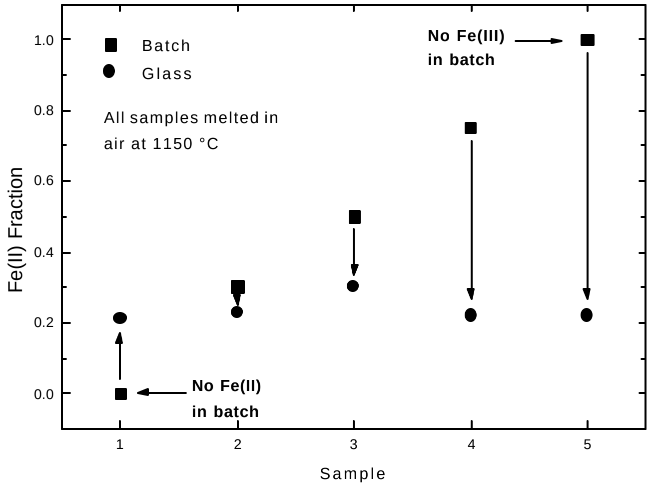

Fig. 6. Change in Fe(II) fraction of binary iron phosphate batches due to melting. The Fe(II) fraction in the batch was set by using either FeO, Fe_2O_3, Fe_3O_4, or a combination of them. P_2O_5 was used as the source of phosphorus.

For a given source of phosphorus (P_2O_5, $(NH_4)H_2PO_4$, or H_3PO_4) and when melted in air at approximately 1150EC using either FeO, Fe_2O_3, Fe_3O_4 or a combination thereof as the source of iron, binary iron phosphate melts reach a redox equilibria corresponding to a Fe(II) fraction, Fe(II)/[Fe(II)+Fe(III)], between 0.2 and 0.35 irrespective of the iron valence state in the batch, see Fig. 6 [10,12]. The use of $(NH_4)H_2PO_4$, which is known to act as a reducing agent, usually leads to Fe(II) fractions at the upper end of that range.

Table 6 shows the effect of melting atmosphere on the redox equilibria of the melts. The similarity in the iron valence of samples 6A, 6B, and 6C, which had the same batch composition but were melted in air, nitrogen, and oxygen, respectively, suggests that the process by which the redox equilibria is reached is independent of the oxygen content in the melting atmosphere. However, the large fraction of Fe(II) in samples 6D, 6E, and 6F indicates that the Fe(II) content in the glass can be increased above that found in glasses melted in air, oxygen, or nitrogen by melting in reducing atmospheres such as forming gas ($90N_2$-$10H_2$, at%).

Table 6. Batch composition and processing conditions of the glasses studied. Note that the Fe/P atomic ratio is the same (. 0.67) for all compositions listed.

Sample	Batch Composition (mol%)	Melting Atmosphere	Fe(II) Fraction
6A	$40Fe_2O_3$-$60P_2O_5$	Air	0.20
6B	As in sample A	Nitrogen	0.22
6C	As in sample A	Oxygen	0.21
6D	As in sample A	70%Forming gas[a]-30%Air	0.31
6E	As in sample A	90%Forming gas-10%Air	0.40
6F	As in sample A (Crystallized)	Forming gas	0.48

[a] Forming gas is a mixture of $90N_2$ and $10H_2$ (at%).

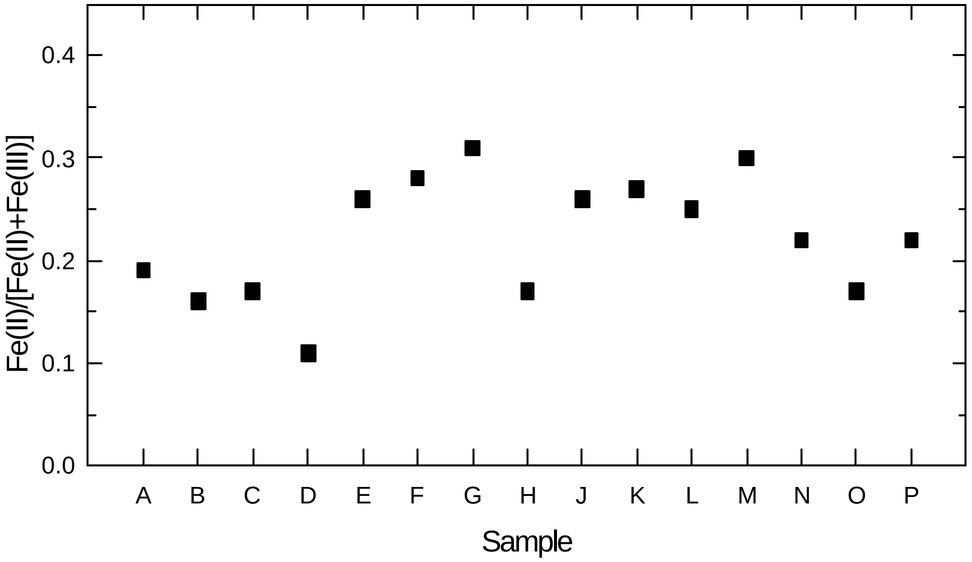

Fig. 7. Iron (II) fractions determined by room temperature Mössbauer spectroscopy for the glasses listed in Table 5.

Crystallization of sample 6F whose Fe(II) fraction is 0.48 illustrates the sensitivity of the glass forming ability of the melts to the iron valence [12]. In general, the melts tend to crystallize when quenched in air as described in the experimental section if the Fe(II) fraction is greater than 0.45.

Another factor that affects the redox equilibria of the melts is the melting temperature. The Fe(II) fraction in the resulting glass appears to increase linearly with melting temperature. When melted in air, melting temperatures above 1400 EC lead to Fe(II) contents that promote crystallization [15]. From a practical point of view, how the addition of nuclear waste influences the redox equilibria is more important. As for glasses containing a single waste component [13], UO_2 or MoO_3 reduces the Fe(II) fraction in the glass, as compared to the base glass, whereas Na_2O, Cs_2O, SrO, and Bi_2O_3 cause the Fe(II) to increase. In the case of samples containing both reducing and oxidizing waste components [25] the latter appears to prevail. It is important to note that none of the waste components or simulated wastes we investigated cause the Fe(II) fraction to reach a level that affects the glass forming ability of the melts, see Fig 7.

F.9. Atomic structure [9,17,19,21,22,24]: Knowledge of the atomic structure of a nuclear waste glass is essential to understanding the origin of its properties crucial to nuclear waste vitrification and for predicting its long term stability. Prior to discussing the structure of iron phosphate glasses, it is necessary to review the atomic structure of more common phosphate glasses. P_2O_5 glasses are made of $(PO_4)^{-3}$ tetrahedra which are linked via -P-O-P- bonds, see Fig. 8(a). The three oxygens in a $(PO_4)^{-3}$ tetrahedron bonded via

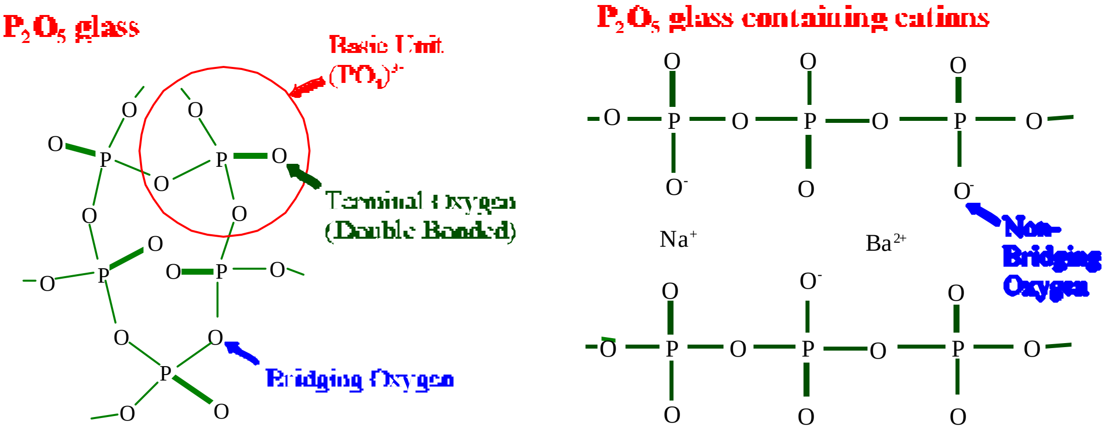

Fig. 8. Illustrations of the atomic structure of (a). a P_2O_5 glass and (b). an alkali/alkaline earth phosphate glass.

-P-O-P- links are called bridging oxygens (BOs). The one oxygen double bonded to the phosphorus is called a terminal oxygen. The -P-O-P- links are known to hydrate easily. As a result, P_2O_5 glasses, in which 75% of the oxygens are bridging, are hygroscopic and dissolve readily under moist conditions.

Addition of cations result in the partial depolymerization of the network forming -P-O-M- (M / cation) type links at the expense of easily hydrated -P-O-P- bonds. Consequently, the chemical durability of phosphate glasses containing cations is several orders of magnitude better than that of a P_2O_5 glass. The oxygen ions taking part in -P-O-M- bonds, and sometimes the terminal (-P=O) oxygens, are referred to as non-bridging oxygens (NBOs). In general, a cation may occupy one of two types of sites in a glass structure. Ions such as Na^+ and Ca^{2+} occupy “network modifying” positions between the -P-O- chains, see Fig 8(b). Other cations such as Al^{3+} or Bi^{3+} , however, may occupy “network forming” positions by substituting for a phosphorus ion in a -P-O-P- chain.

The atomic structure of a glass lacks the long range order present in a crystalline material. For this reason, a complete picture of the atomic structure of a glass can be put together only by independently investigating various structural units that combine to form the glass network. In the case of iron phosphate glasses and their wasteforms, the different structural features investigated were the following.

1. The structural role of iron ions: The environment around iron ions were studied using Mössbauer and x-ray absorption spectroscopies.
2. The -P-O- network: Whether the -P-O- network is formed by isolated monomers (PO_4^{-3}), isolated dimers $P_2O_7^{-4}$, longer $P_nO_{2n+1}^{-(n+2)}$, or a combination thereof was investigated using Raman spectroscopy.
3. The structural role of oxygen: The nature of oxygen bonding, whether as bridging, non-bridging, or a combination thereof was investigated using x-ray photoelectron spectroscopy.
4. The structural role of waste ions: The environment around waste ions such as U^{4+} and Cs^+ was investigated using x-ray absorption spectroscopy.
5. Short and intermediate range order in the glasses were investigated using high energy x-ray and neutron scattering.

The Fe-57 Mössbauer hyperfine parameters, isomer shift and quadrupole splitting, depend mostly on the near neighbor coordination environment around iron ions [28]. Based on published [17,22] hyperfine parameters of crystalline materials, we conclude that the average coordination of iron ions in iron phosphate glasses is closer to octahedral than to tetrahedral. A realistic interpretation of this conclusion is that the majority of iron ions are octahedrally coordinated while the rest are tetrahedrally coordinated. Figure 9 shows that the hyperfine parameters, whose approximate uncertainty is ±0.05mm/s, are quite independent of the type (and the concentration as other data has shown, see references 13, 22, and 25] of the waste components. We conclude that the addition of waste components does not affect the local environment around iron ions to an extent which can be detected by Mössbauer spectroscopy.

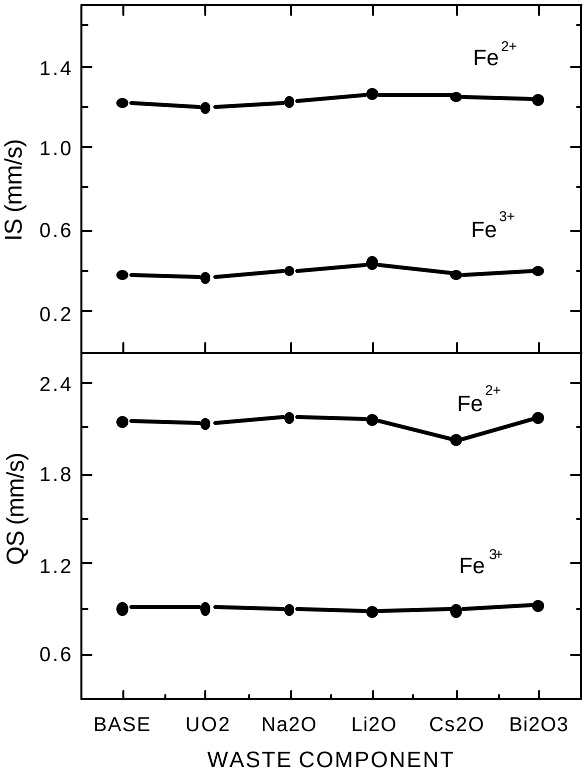

Fig. 9. Room temperature Mössbauer parameters for the base iron phosphate glass and several others containing 10 mol% of a waste component. Note that the variation in a given parameter is well within the error of measurement.

The Fe K-edge X-ray-absorption spectrum measured for sample A shown in Fig. 10 is typical of those measured for other samples. Information about the coordination environment of iron ions was obtained by fitting the raw Fe K-edge EXAFS data. As seen in Table 7, EXAFS fits yield three iron-oxygen distances [19,22]. The average iron-oxygen coordination for interatomic distances $d_{Fe\text{-}O} < 2.4$Å is in the 5 to 5.5 range. Note that this average coordination number is in agreement with that obtained from Mössbauer spectroscopy. Iron ions are also coordinated with 4 to 6 phosphorus ions at an approximate iron-phosphorus distance of 3.3 Å. Detailed analysis show that approximately 60% of the iron ions are octahedrally/distorted-octahedrallly coordinated whereas the other iron ions are tetrahedrally coordinated. Iron-phosphorus coordination observed at ca. 3.3 Å is due to the $(PO_4)^{-3}$ polyhedra which surround iron ions. The low iron-iron coordination numbers suggest that the FeO_n polyhedra are far removed from each other. Detailed analysis of EXAFS data show that the environment around iron ions in glasses containing waste/waste components is quite similar to that in the base glass.

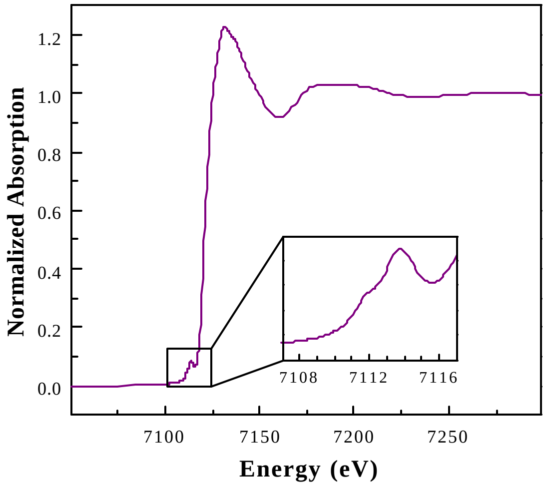

Fig. 10. Iron K-edge X-ray absorption spectrum for the base glass. In addition to the extended x-ray absorption fine structure of this spectrum, the pre-edge (inset) feature also gives structural information [11].

Table 7. Average structural parameters obtained by fitting the k and k^3 weighted EXAFS data for samples C, E, and G. <*N*> is the number of neighbor atoms in each shell. The error in R is ±0.01 D for the first Fe-O shell and ± 0.02 D for the other coordination shells. The error in <N> is ± 20%.

Shell	Base Glass		Sample 7A[a]		Sample 7B[a]		Sample 7C[a]	
	<N>	R(D)	<N>	R(D)	<N>	R(D)	<N>	R(D)
Fe-O_s	3.47	1.90	2.81	1.87	3.6	1.93	3.36	1.9
Fe-O_m	0.91	2.1	1.88	1.97	1.85	2.04	1.4	2.06
Fe-O_l	0.61	2.31	0.58	2.22	0.47	2.33	0.48	2.3
Fe-Fe	0.22	3.22	0.35	3.20	0.15	3.2	0.15	3.21
Fe-P_s	3	3.17	2.7	3.16	2	3.17	2.6	3.18
Fe-P_l	3	3.43	3.1	3.45	1.91	3.44	1.33	3.45

[a] Batch compositions (mol%): 7A: $25Fe_2O_3$-$60P_2O_5$-$15UO_2$, 7B: $28Fe_2O_3$-$42P_2O_5$-$30Cs_2O$, 7C: Base glass composition + ($10UO_2$ and $10Na_2O$)

The O1s spectra of iron phosphate glasses are best fit with two-Voigt peaks, see Fig. 11. As described elsewhere [17], the peak at the lower binding energy is assigned to non-bridging oxygens (NBOs) and the other peak is assigned to the bridging oxygens (BOs). Table 8 gives the BO fractions [BO/(BO+NBO)] and the energy separation between the two Voigt peaks for selected samples. Note that the majority, roughly about three fourths, of the oxygens in the base glass are non-bridging. The relatively low BO fraction suggests that -P-O-P- bonds are not a major feature in the atomic structure of these glasses. Even though a small fraction of the NBOs are terminal oxygens, the vast majority are bonded via -Fe-O-P- links. As compared to the base glass, glasses containing waste components have smaller BO fractions. In general, the addition of alkaline cations appear to have the most effect on

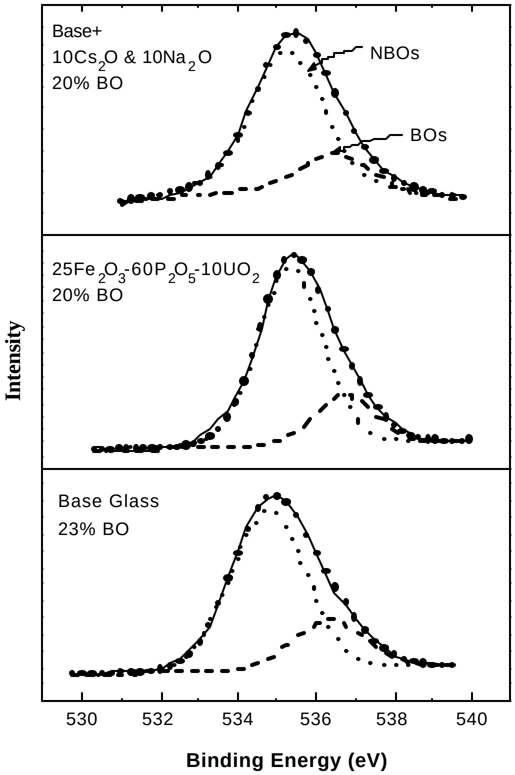

Fig. 11. XPS spectra of three iron phosphate glasses showing peaks assigned to bridging (BO) and non-bridging (NBO) oxygens.

the BO fraction.

Table 8. The fraction of bridging oxygens (BOs) and the separation between the Voigt peaks representing the bridging and non-bridging oxygens (NBOs) in five iron phosphate glasses as determined using X-ray photoelectron spectroscopy.

Batch Composition	BO Fraction (± 5%)	ÄE (eV)
Base Glass (BG)	0.23	1.7
$25Fe_2O_3$-$60P_2O_5$-$15UO_2$	0.20	1.6
$20Fe_2O_3$-$60P_2O_5$-$20Bi_2O_3$	0.20	1.4
$28Fe_2O_3$-$42P_2O_5$-$30Cs_2O$	0.17	1.5
BG +($10Cs_2O$ and $10Na_2O$)	0.21	1.4

Figure 12 shows the Raman spectra measured on some of the samples. The Raman spectrum of the base glass is characteristic of a structure dominated by dimer $(P_2O_7)^{4-}$ units [22,25]. Quite likely, a considerable fraction of the oxygens responsible for the BO contribution to the XPS spectra is due to the dimer $(P_2O_7)^{-4}$ groups. The addition of waste components result in only small changes in the Raman spectra. As seen in Fig. 12, the band at approximately 750 cm^{-1} assigned to dimer units and the band at 950 cm^{-1} assigned to $(PO_4)^{-3}$ monomer units are slightly larger in the spectra for glasses containing waste components as compared to the spectrum of the base glass.

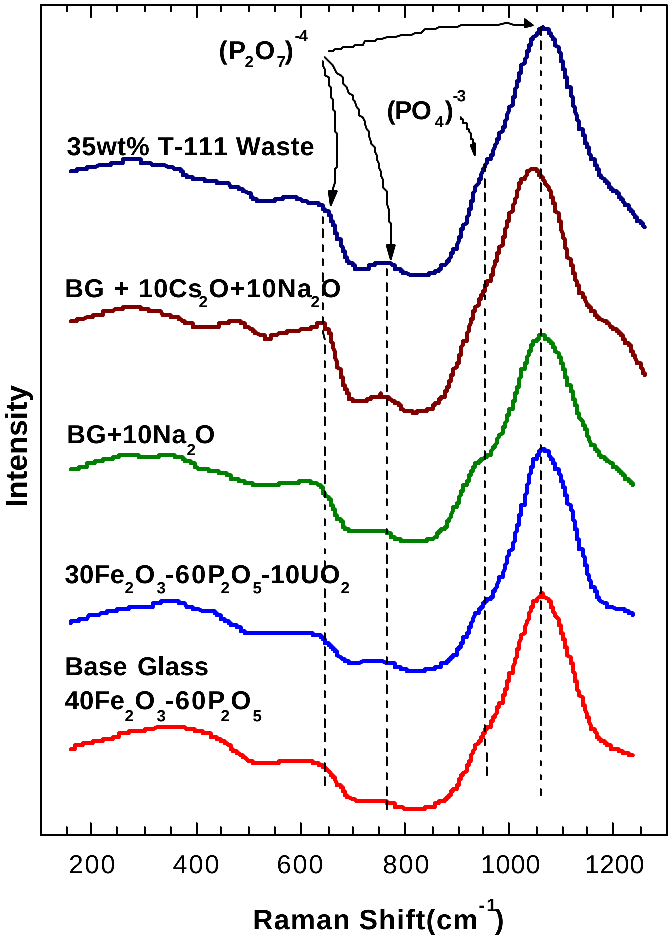

Fig. 12. The major features of Raman spectra of iron phosphate glasses of varying compositions are quite similar.

Total correlation functions, T(r), obtained from neutron and high energy X-ray scattering data for several UO_2 containing samples are

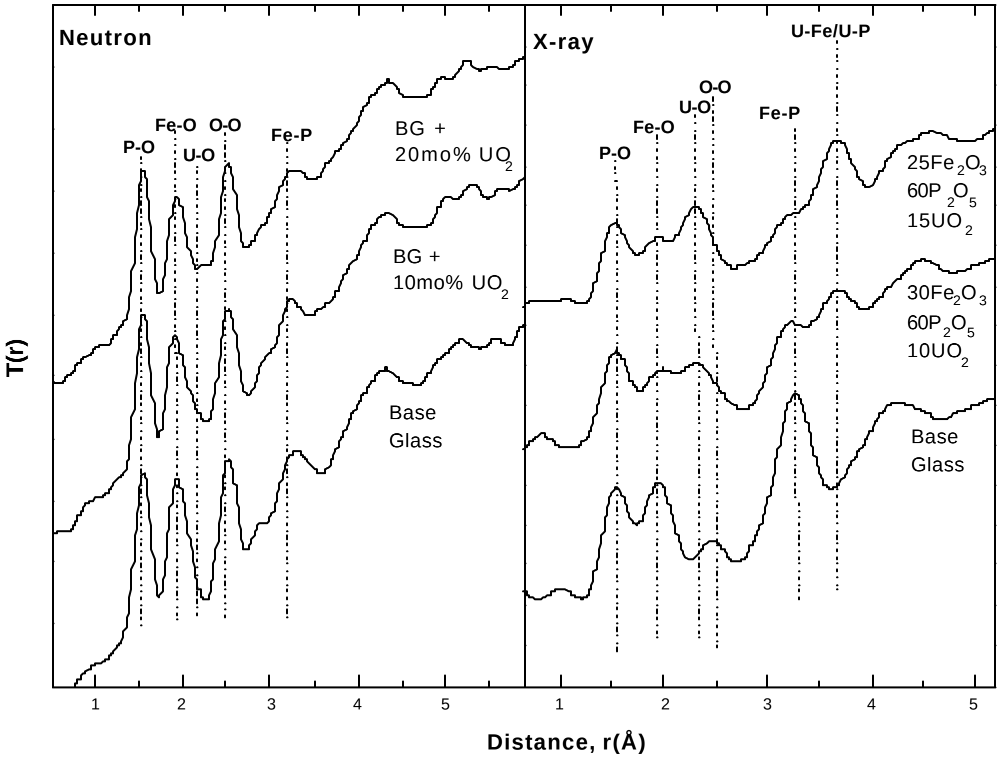

Fig. 13. Total correlation functions obtained from neutron (left) and high energy X-ray (right) scatterin data for several iron phosphate glasses containing UO_2.

shown in Fig. 13 [21,24]. Peaks at approximately 1.5, 1.9, 2.4, and 3.3 Å are assigned to P-O, Fe-O, O-O, and Fe-P pairs, respectively. The addition of UO_2 results in two new peaks, most apparent in the T(r) plot for X-ray scattering data, at 2.3 and 3.7 Å. Based on the interatomic distances observed in uranium phosphates such as $U_2P_2O_9$, the peak at 2.3 Å can be attributed to U-O pairs. The peak at 3.7 Å is most likely due to U-P and/or U-Fe pairs. Note that the peak positions of T(r) plots do not depend, within errors of measurement, on the sample composition indicating that the near neighbor interatomic distances are not appreciably altered by the addition of UO_2. Based on the 3.7 Å distance observed for U-P and/or U-Fe pairs, we conclude that the uranium ions are situated outside the second coordination shell of iron and phosphorus ions.

Based on the structural features described above, the structure of iron phosphate glasses can be thought of as isolated Fe(II)-O_n and Fe(III)-O_n polyhedra linked via a -P-O- network dominated by $P_2O_7^{4-}$ units. The waste elements appear to occupy interstitial atomic voids without appreciably disturbing the -Fe-O-P- network. This insensitivity of the -Fe-O-P- network to the addition of a nuclear waste ions may be the reason for the apparent immunity of chemical properties such as the chemical durability to the additional waste components [22].

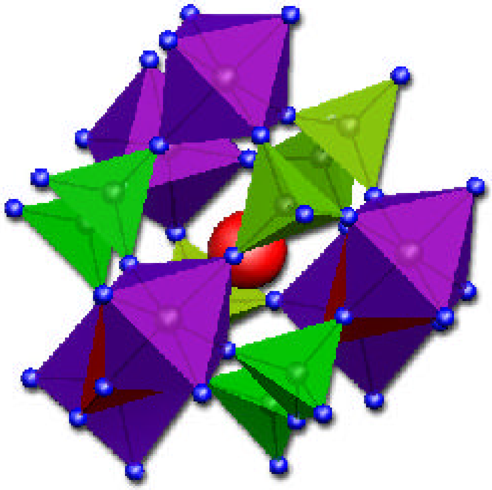

Fig. 14. A computer generated model of a uranium ion (red) encapsulated among the PO_4 tetrahedra (green) and FeO_n (n ~ 5-6) polyhedra (purple).

An in depth analysis of the crystalline structure of $Fe_3(P_2O_7)_2$ helps explain some of the observed structural features in these iron phosphate glasses. $Fe_3(P_2O_7)_2$ crystallizes from the base glass when appropriately heat treated [29]. Even though the structure of the base glass need not be identical to that of $Fe_3(P_2O_7)_2$, it is reasonable to expect general similarities between the crystal and glass structures. Fe(II) ions in crystalline $Fe_3(P_2O_7)_2$ are in trigonal prism coordination with its six near neighbor oxygens. Each of the six-fold coordinated Fe(II) ions is sandwiched between two Fe(III) ions in distorted octahedral (Fe(III) ion is off center) coordination with oxygen ions. The $(Fe_3O_{12})^{-16}$ clusters consisting of the Fe(II) trigonal prism and the two Fe(III) octahedra are connected via pyrophosphate groups, i.e., $(P_2O_7)^{-4}$. Only a minority, 14%, of the oxygens take part in a -P-O-P- bond. Other oxygen atoms are bonded via -Fe-O-P- links.

The average oxygen packing, determined by the average volume per oxygen atom, in $Fe_3(P_2O_7)_2$ is one of the lowest among comparable phosphates [24]. A small packing fraction generally is indicative of loosely packed structure having a considerable volume of empty space among atoms. A careful analysis of the $Fe_3(P_2O_7)_2$ crystal structure shows that it contains interstitial voids large enough to accomodate ions as large as U^{4+} and Cs^+, see Fig 14 . The density of the base glass and its crystalline counterpart are similar, ~3.1 g/cm^3, which suggest that similar voids may also exist in the glass structure. Such voids in glass structure can explain why the Fe-O-P network in glasses containing waste components is similar to that in the base glass. As the glass is quenched from the melt, the Fe-O-P network may form with voids that can be occupied by waste ions such as U^{4+}.

G. SUMMARY OF RESULTS

In collaboration with scientists from *Argonne, Lawrence Berkeley, Lawrence Livermore, and Pacific Northwest National Laboratories*, and the *Westinghouse Savannah River* and *Naval Research* laboratories, our extensive investigation of iron phosphate glasses and their nuclear wasteforms has identified the following advantages of using iron phosphate glasses as an alternative host matrix for vitrifying a variety of nuclear wastes.

! **High Chemical durability**: The chemical durability of iron phosphate vitrified wasteforms is comparable to, and in many instances, better than that of most comparable borosilicate glass based wasteforms. Product Consistency Tests (PCT) show that the quantity of ions leached from iron phosphate wasteforms is as little as one tenth of the quantity leached from borosilicate wasteforms. In addition, iron phosphate wasteforms will inherently buffer any aqueous solution which they come into contact with, thereby, slowing down the corrosion process. On the contrary, the alkali ions released from the corrosion of borosilicate glass waste forms causes a rapid increase in the pH of the aqueous solution, thereby, accelerating the corrosion process

! **Higher waste loading or smaller waste volume**: Considerable amounts, up to 50 wt% in certain cases, of simulated wastes have been vitrified in iron phosphate glasses compared to the roughly 28 wt% now being vitrified in borosilicate glasses at the Defense Waste Processing Facility (DWPF) at Savannah River. When the waste contains large amounts of components such as phosphates and heavy metal oxides like, Bi_2O_3, UO_2, ZrO_2, the waste loading in iron phosphate wasteforms can be up to three times higher than that for borosilicate glasses. Equally durable, “partially vitrified” iron phosphate wasteforms containing up to 70 wt% of simulated wastes containing large amounts of Al_2O_3 and ZrO_2 (calcine waste at Idaho Falls) have also been prepared..

! **Lower melting temperatures and shorter melter times**: Iron phosphate glasses can be melted at 950-1100EC compared to the 1150EC for the borosilicate glasses now being melted at the DWPF. Because of their high fluidity and rapid homogenization, melting times are only 1 to 2 hrs. compared to 24 hrs. or more for borosilicate glasses. The residence time of the borosilicate melt in the DWPF melt is typically more than 48 hrs. Lower melting temperatures and shorter melting times lead to less expensive and safer melting processes and mean that smaller furnaces can be used for the same given output.

! **Higher density reduces waste volume**: The density of iron phosphate wasteforms, typically 3.2 g/cm^3, is approximately 25% higher than that of borosilicate wasteforms. Consequently, the volume of an iron phosphate wasteform of a given weight will be about 25% smaller than that for a borosilicate-based wasteform. When combined with their previously mentioned higher waste loading, glassy iron phosphate wasteforms could have a volume that is up to 70% smaller than that of a comparable borosilicate wasteforms.

! **Accommodating (flexible) atomic structure and redox equilibria:** The iron phosphate glasses have an atomic structure that easily accommodates ions of widely different size and charge. Radio nuclides such as Cs^+, Sr^{2+} and U^{4+} ions occupy interstitial atomic voids in the iron phosphate host glass without adversely modifying the atomic structure or the physical and chemical properties. Extreme reducing or oxidizing conditions in melts can cause problems in the melters. Irrespective of the starting composition, iron phosphate melts when melted in air reach a redox equilibria corresponding to a Fe(II)/Fe(III) ratio of 0.15 to 0.5.

! **Utilization of industrial phosphating wastes:** Recent results suggest that the current industrial waste being produced from the iron and zinc phosphating treatment of metal surfaces (for corrosion protection and paint adhesion) can be a low cost raw material for vitrifying nuclear wastes in an iron phosphate glass. Large amounts, estimated at > 3000 tons/yr., of these iron and zinc phosphating wastes are currently being buried in land fills, but this could be eliminated by using them as a source of P_2O_5 and iron oxide in glassy iron phosphate wasteforms.

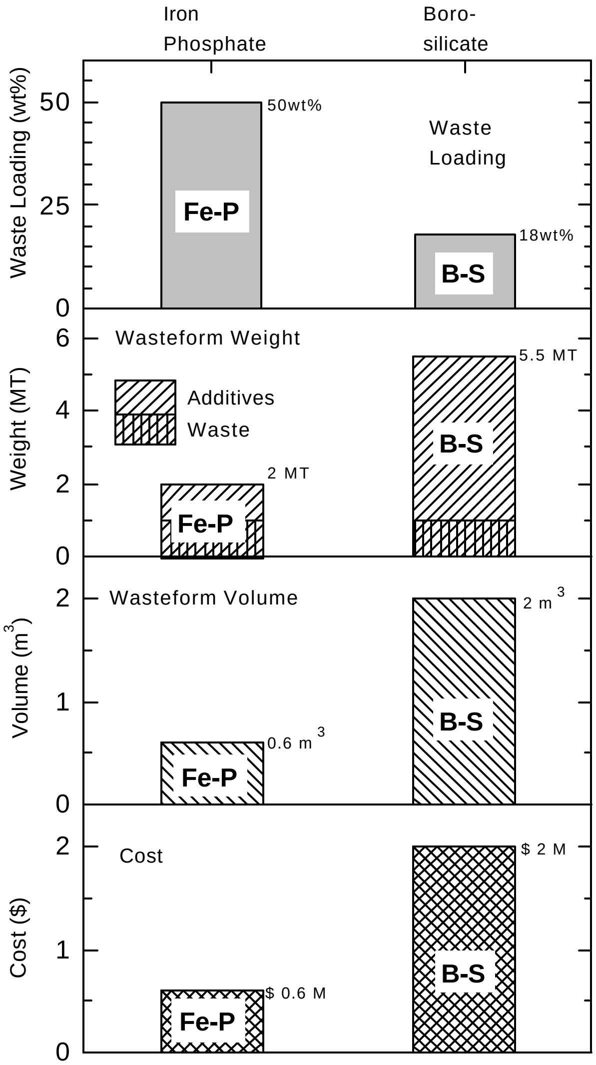

Fig. 15. A comparison of iron phosphate (Fe-P) and borosilicate (B-S) wasteforms containing one metric ton of waste from Hanford tank C-112 (see Table 1). A maximum phosphate solubility of 2 wt% in borosilicate glasses is assumed. The waste volumes is calculated based on densities of 2.8 and 3.2 g/cm³ for borosilicate and iron phosphate glasses, respectively. The cost of vitrification is assumed to be \$1M/m³.

I. RELEVANCE AND IMPACT

It is a known fact that some of the nation's nuclear wastes are not well suited for vitrifying in borosilicate glasses. Special procedures designed to successfully vitrify such problematic wastes in borosilicate glasses can add billions of dollars to the DOE's cost of cleaning up the former nuclear weapons production facilities. The iron phosphate glasses developed at the University of Missouri-Rolla appear to be an excellent alternative host matrix for vitrifying many of the nuclear wastes that contain components poorly suited for borosilicate glasses. The use of alternative host matrices such as iron phosphate glasses for selected wastes may potentially save the DOE a considerable amount of money, see Fig. 15.

It must be noted that a typical phosphate glass might be considered an unlikely candidate for vitrifying nuclear waste because these low melting glasses usually have an unacceptably poor chemical durability. Based on our knowledge of the properties of phosphate glasses at the time, these glasses were excluded several decades ago from the pool of potential host glasses considered for the US vitrification program.

On a global scale however, considerable amounts of high level nuclear waste have been vitrified in phosphate glasses. An alkali-alumino-phosphate glass has been used in the Russian nuclear waste disposal program for decades [30,31]. Unlike the US, which started large scale vitrification within the past ten years, the Russians have been vitrifying nuclear waste in alumino-phosphate glasses for much longer. The chemical durability of the Russian alumino-phosphate glasses is inferior to that of the borosilicate glass being used in the US, but the Russians have clearly demonstrated that phosphate glasses can be successfully melted on a scale needed for waste vitrification. In the period 1987 to 1995, more than 1800 metric tons of high level wasteforms was processed at “Mayak” facility in South Ural using a sodium alumino phosphate glass [31].

It is extremely important for the reader to understand that the iron phosphate glasses developed at UMR are unlike other types of phosphate glasses with the possible exception of the chemically durable lead iron phosphate (LIP) glasses developed [7,8] at the Oak Ridge National Laboratory (ORNL). Compared to LIP glasses, however, the iron phosphate host matrices can accommodate larger quantities of nuclear wastes. The chemical durability and other important properties of the iron phosphate glasses are far superior to those of all other known phosphate glasses including the alumino-phosphate glasses used in Russia. In many respects (chemical durability, maximum waste loading, and low melting temperature), iron phosphate glasses appear to be as good as or even better than borosilicate glasses for vitrifying certain nuclear wastes.

I. PROJECT PRODUCTIVITY

It is a pleasure to note that we met all of the objectives stated in the proposal submitted in response to RPF 96-10. In addition, we investigated several other factors regarding iron phosphate glasses such as their effect on commercial refractories. Successful collaborations with several national laboratories resulted in an unexpectedly large quantity of data and, as a result, a non-funded extension was secured to complete the data analysis.

J. PERSONNEL SUPPORTED

Student Training: Support was provided to two graduate students who completed their Ph.D. thesis, "Structure and Properties of Iron Phosphate Glasses: A Novel Host Matrix for the Vitrification of High Level Nuclear Wastes" (Mevlut Karabulut, Dec. 1999) and "Properties of Iron Phosphate Glasses" (Xiangyu Fang, May 2000). In addition, three undergraduates were employed as research aides during the project.

Faculty: The Principal Investigators of this project, Drs. Delbert E. Day and Chandra Ray were supported at the levels of 0.167 FTE and 0.75 FTE, respectively. In addition, Dr. Kanishka Marasinghe (Res. Asst. Prof), was supported at the 0.5 FTE level.

K. REFEREED PUBLICATIONS

The research from this EMSP project has been published in the following 18 refereed publications. Five additional publications are in review or in press.

1. "Structural Features of Iron-Phosphate glasses," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, W. B. Yelon, C. H. Booth, P. G. Allen, and D. K. Shuh, J. Non-Cryst. Solids 222 (1997) 144.
2. "Redox Characteristics and Structural Properties of Iron Phosphate Glasses:A Potential Host Matrix for Vitrifying of High Level Nuclear Waste," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, C. H. Booth, P. G. Allen, and D. K. Shuh, Environment Issues and Waste Management Technologies III: Ceramic Transactions 87 (1998) 261.
3. "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance, Mössbauer, and Evolved Gas Mass Spectroscopy," D. L. Griscom, C. I. Merzbacher, N. E. Bibler, H. Imagawa, S. Uchiyama, A. Namiki, G. K. Marasinghe, M. Mesko, and M. Karabulut, Nucl. Instr. and Meth. B 141 (1998) 600.
4. "Iron Redox and Crystallization of Iron Phosphate Glasses," C. S. Ray, X. Fang, M. Karabulut, G. K. Marasinghe, and D. E. Day, Environment Issues and Waste Management Technologies IV:Ceramic Transactions, 93 (1999) 187.
5. "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, P. G. Allen, J. J. Bucher, D. K. Shuh, Y. Badyal, M. L. Saboungi, M. Grimsditch, S. Shastri,

and D. Heaffner, Environment Issues and Waste Management Technologies IV:Ceramic Transactions, 93 (1999) 195.

6. “DC Conductivity and Polarization in Iron Phosphate Glasses,” A. Mogus-Milankovic, D.E. Day and B. Santic, Phys. Chem. Glasses 40 (2) 69-74 (1999).
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L. INTERACTIONS

Collaborations: The following productive collaborations were established and remain active.

Pacific Northwest National Laboratory [8,24] : Drs. Bruce Bunker (now at Sandia) and Lou Balmer provided information for sludge compositions in various tank farms, especially for wastes considered good candidates for iron phosphate glasses. Iron phosphate glasses were provided to Dr. Bill Weber for radiation damage studies. Dr. Pavel Hrma provided useful data for borosilicate glasses.

Westinghouse Savannah River Company [15]: Dr. William G. Ramsey provided information for sludge compositions and evaluated iron phosphate glasses which contained uranium and plutonium. Undergraduate and graduate students from UMR worked part time at the Savannah River Laboratory with Drs. Carol Jantzen, William Miller, and others.

Lawrence Berkeley National Laboratory (LBNL) [7,9,12,18,20,23]: Drs. David Shuh, N. M. Edelstein, and Corwin Booth of the Actinide Chemistry Division provided experimental and theoretical support for x-ray absorption (EXAFS/XANES) studies conducted at the Stanford Synchrotron Radiation Laboratory (SSRL). Personnel from UMR visited both SSRL and LBNL to conduct experiments and to be trained in data analysis.

Lawrence Livermore National Laboratory (LLNL) [7,9,12,18,20,23]: Dr. Pat Allen provided experimental and theoretical support for x-ray absorption (EXAFS/XANES) studies.

Argonne National Laboratory (ANL) [12,19,20,22]: Drs. Marie-Louise Saboungi and Yaspal Badyal provided experimental and theoretical support for neutron scattering studies conducted at the *Intense Pulsed Neutron Source* (IPNS). Dr. Dean Heaffner provided access to the *Advanced Photon Source*

(APS) for high energy x-ray scattering studies and Dr. Marcos Grimsditch provided experimental and theoretical support for Raman spectral studies. Personnel from UMR visited ANL to conduct experiments and to be trained in data analysis

Naval Research Laboratory (NRL)[10]: Dr. David Grisscom conducted Electron Spin Resonance spectral and Gas Evolved Mass Spectroscopy studies on iron phosphate glasses provided by UMR.

Ruder Boskovic Institute, Zagreb, Croatia [13,17]: Dr. Andrea Mogus-Milankovic measured Raman/IR spectra and AC/DC conductivity of iron phosphate glasses we provided.

Presentations: The results of this EMSP project were presented at numerous national and international conferences such as the meetings of the American Ceramics Society, American Physical Society, University Conference on Glass Science, and at the EMSP workshops in Chicago and Atlanta.

M. FUTURE WORK

All of our existing knowledge of iron phosphate glasses and their wasteforms indicates that they can be a highly effective and low cost alternative to borosilicate glasses, especially for those wastes which are contain components that are poorly soluble in or chemically incompatible with borosilicate glasses. However, the high priority wastes that are likely to cause problems in borosilicate melts need to be better identified and property data needs to be acquired for iron phosphate wasteforms made from these wastes. In addition, we currently lack the scientific and technical knowledge base that is needed to design and construct the furnaces needed for melting iron phosphate glasses on a production scale. The logical next step is to 1). work closely with personnel at Hanford, Savannah River, and Idaho sites to identify and characterize the high priority problematic waste feeds, 2). research and develop optimized melting and processing methods for vitrifying the problematic wastes in iron phosphate glasses, and 3). investigate the structure-property relationships of the vitrified iron phosphate wasteforms containing the problematic wastes.

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