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

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Collaborators

X-Ray Absorption Spectroscopy (EXANES/EXAFS)

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Lawrence Berkeley National Laboratory and Stanford Synchrotron Radiation Laboratory

Neutron and High Energy X-Ray Scattering and Raman Spectroscopy

Marie-Louise Saboungi, Yaspal Badyal, Dean Heaffner, and Marcos Grimsditch

Argonne National Laboratory

Radiation Damage Studies

Bill Weber

Pacific Northwest National Laboratory

Electron Spin Resonance Studies

David Griscom

Naval Research Laboratory

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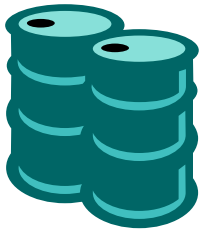
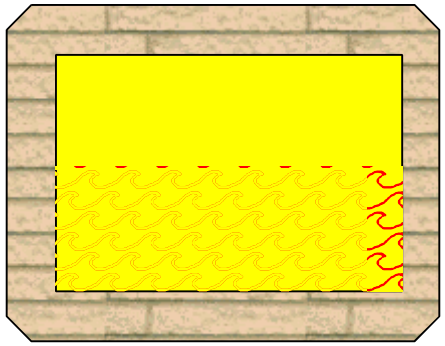
Vitrifying High Level Waste in an Iron Phosphate Host Matrix

Radioactive waste
High in phosphates, halides, and heavy metals like U, Cs, Sr, Pu, and Bi



Additives:
Fe_2O_3/Fe_3O_4
P_2O_5/Phosphoric acid

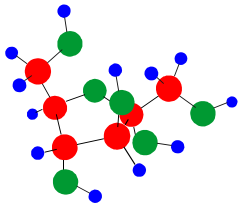
Melting



Composition (wt%):
15 - 40 Fe_2O_3//Fe_3O_4
30- 60 P_2O_5/Phosphoric acid
Up to 50% HLW
Melts @ 950 - 1200°C in 1-2 hrs.
Viscosity: 1-5 poise

Vitrified Waste Form

Up to 50 wt% HLW
All properties meet DOE standards
Density ~3.2 g/cm^3
Glass transition ~ 500°C
Crystallization ~ 600°C



Waste elements occupy "empty spaces" within the Fe-O-P network

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Scientific Rationale

Certain high level wastes (HLW) in the U.S. contain components such as phosphates and halides which make them poorly suited for disposal in borosilicate glasses. Current plans call for vitrifying even these problematic waste feeds in borosilicate glasses by pre-treating/diluting the original waste feed to compensate for the incompatibility. However, these pre-treatment processes and larger waste volumes can add billions of dollars to the nuclear waste disposal effort. Such additional costs may be avoided by developing a small number of alternative host matrices which are better suited for vitrifying those waste feeds which are incompatible with borosilicate glasses. Iron phosphate glasses appear to be a technically feasible alternative to borosilicate glasses for vitrifying several HLWs. The objective of this research is to gather more information on the binary iron-phosphate glasses and simulated iron phosphate waste forms so that a comprehensive scientific assessment can be made of their usefulness in nuclear waste disposal.

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Iron Phosphate Glasses at a Glance

Batch Composition	$40Fe_2O_3$-$60P_2O_5$ (mol%)
Meting Conditions	1-2 hrs. @ 1000-1100EC
Chemical Durability[a]	10^{-9} g/cm^2/min
Thermal Expansion Coefficient	1×10^{-5} EC^{-1}
Density	3 g/cm^3
Glass Transition Temperature	500EC

[a] From weight loss in distilled water @90EC over 16 days.

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Iron Phosphate Waste Forms Containing Up to 50 wt% of Certain HLWs Possess Excellent Chemical Durability.

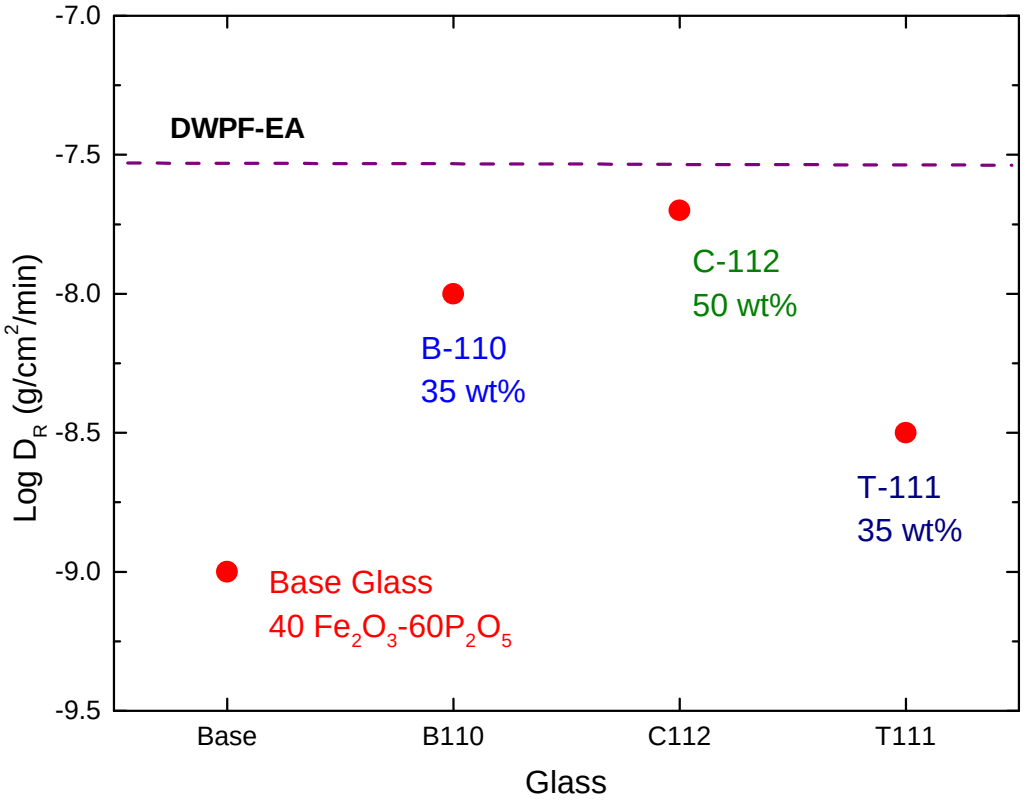

Figure. Dissolution rate (@90EC in distilled water for 16 days) of several iron phosphate waste forms containing sludges from Hanford. C-112, B-110 and T-111 are waste tank designations. The dissolution rate of an environmental assessment standard glass used at DWPF is also shown.

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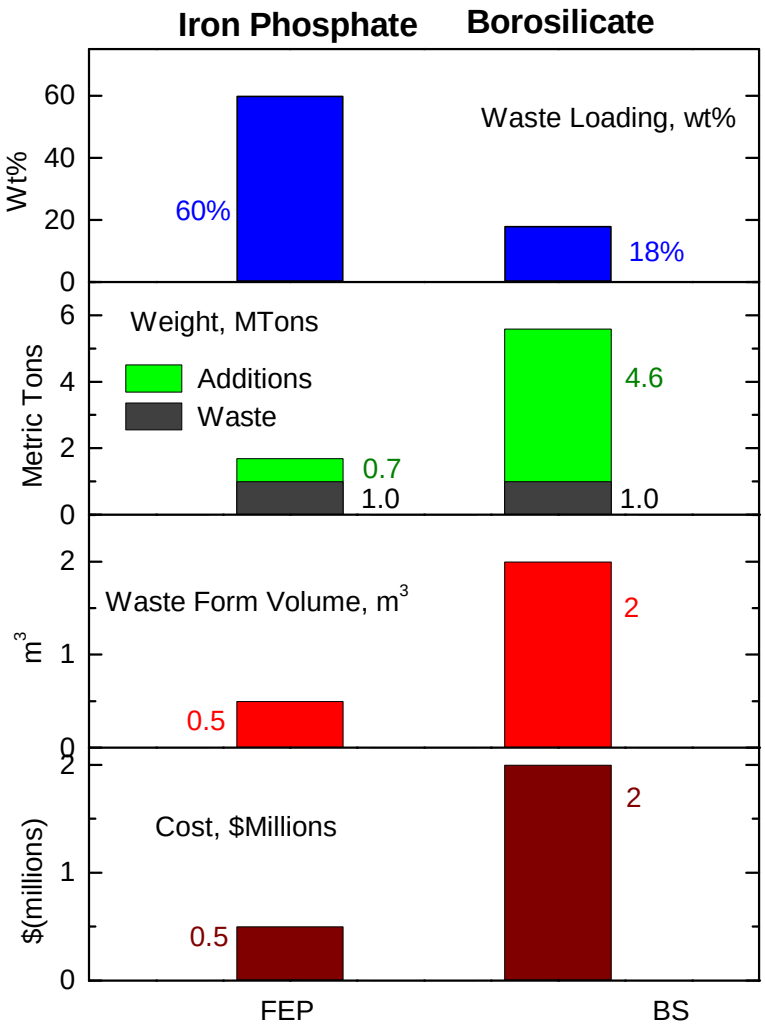
Iron Phosphate Glass is a Better Host Matrix for Vitrifying Selected High Level Nuclear Wastes.

Figure: A comparison of iron phosphate and borosilicate waste forms containing one metric ton of sludge from tank C-112 from Hanford. A 2 wt% solubility limit of P_2O_5 in borosilicate glasses and a vitrification cost of $1M/m^3 is assumed.



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Iron Phosphate Waste Forms - Selected Properties

Table. Selected properties of three iron phosphate waste forms containing 30wt% waste from tanks B-110, C-112, and T-111 from Hanford site.

Waste Form	Log D_R[a] ($g/cm^2/min$)	Density (g/cm^3)	T_s[b](EC)	T_c[c](EC)	a[d] ($\times 10^{-7}$/EC)
B-110	-8.35	3.18	542	612	136.4
C-112	-8.56	3.36	571	642	132.5
T-111	-8.97	3.31	547	629	94.3

[a] Measured from weight loss in distilled water @ 90EC for 16 days.

[b] Softening temperature. [c] Crystallization temperature. [d] Thermal expansion coefficient.

A sample of C-112 waste glass mentioned above. → Contact us for a sample

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Objectives of this research project are to investigate...

- Ideal compositions and processing conditions
- Chemical durability
- Glass forming and crystallization characteristics
- Redox equilibria
- Atomic structure
- Glass manufacturing procedures
- Other properties such as density, electrical conductivity, and Thermal expansion coefficient

...of iron phosphate glasses and their simulated waste forms so that a comprehensive scientific assessment can be made of their usefulness in nuclear waste disposal.

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Experimental Techniques

- **Glass Melting**

  Batches are melted in air or under controlled atmospheres for 1 to 24 hrs. at temperatures ranging from 950 to 1450 EC

- **Glass Manufacturing Procedures**

  Investigate suitable refractories and melting techniques

- **Chemical Durability Measurements**

  Dissolution rate is obtained by measuring the weight loss of 1x1x1 cm samples in distilled water @90EC over 16 days

- **Differential Thermal Analysis (DTA)**

  Glass forming and crystallization characteristics

- **X-Ray Diffraction**

  Identification of products of forced devitrification

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Experimental Techniques Contd.

- **Mössbauer Spectroscopy**
  Redox equilibria and coordination and bonding of iron ions

- **X-ray Photoelectron Spectroscopy (XPS)**
  Bonding of oxygen ions

- **Raman and Infra-Red Spectroscopy**
  Phosphorus-Oxygen network

- **X-Ray Absorption Spectroscopy (EXAFS/XANES)**
  Spacial arrangement of atoms/short range order

- **Neutron and High Energy X-Ray Scattering**
  Spacial arrangement of atoms/long range order

- **Electron Spin Resonance Spectroscopy (ESR)**
  Iron-Oxygen bonding

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Glass Forming and Crystallization Characteristics

Glass transition temperature ~ 550°C.

Crystallizes around 625°C.

Most waste components such as UO_2, Bi_2O_3, SrO, and MoO_3 suppress crystallization and enhance glass formation.

Waste components such as Cs_2O and Na_2O tend to produce sharper crystallization peaks but they do not adversely lower the glass transition and crystallization temperatures.

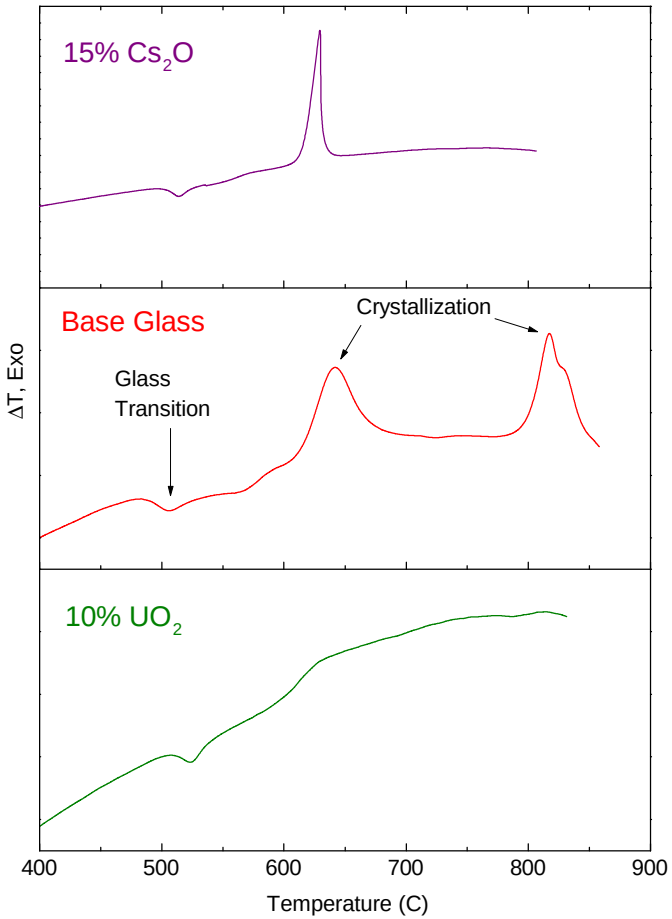

Figure. DTA thermograms for three iron phosphate glasses.

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Glass Manufacturing Suitable Refractories

Several commercial refractories can be used to melt iron phosphate waste forms.

Chrome refractories appear to be the best suited for iron phosphate melts.

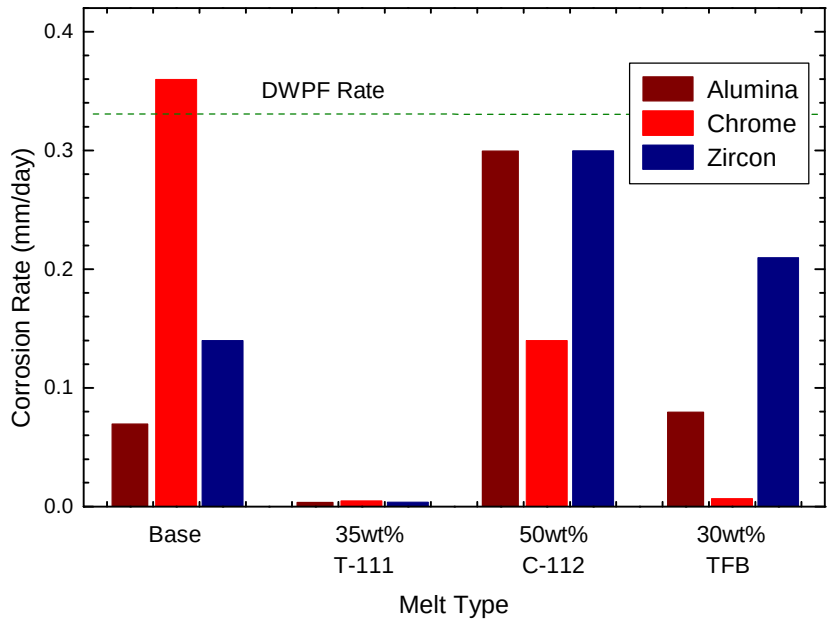

Figure. Corrosion rate of three commercial refractories in four iron phosphate melts. Base glass composition is $40Fe_2O_3$-$60P_2O_5$ (mol%). T-111 and C-112 are waste compositions from Hanford. TFB is an average waste composition from tank farm B at Hanford. The corrosion rate labeled DWPF was used in designing the refractory lining in the DWPF melter at the Savannah River site. Tests were conducted at 1200, 1100, 1200, and 1000EC for Base, T-111, C112, and TFB melts, respectively.

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Redox Equilibria in Binary Iron Phosphate Glasses

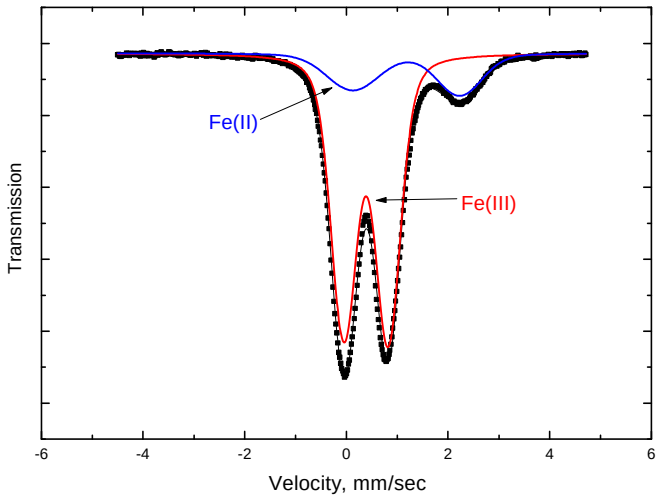

Figure. Room temperature Mössbauer spectrum of an iron phosphate glass of batch composition $40Fe_2O_3$-$60P_2O_5$ (mol%) melted at 1150EC clearly shows the presence of both Fe(II) and Fe(III).

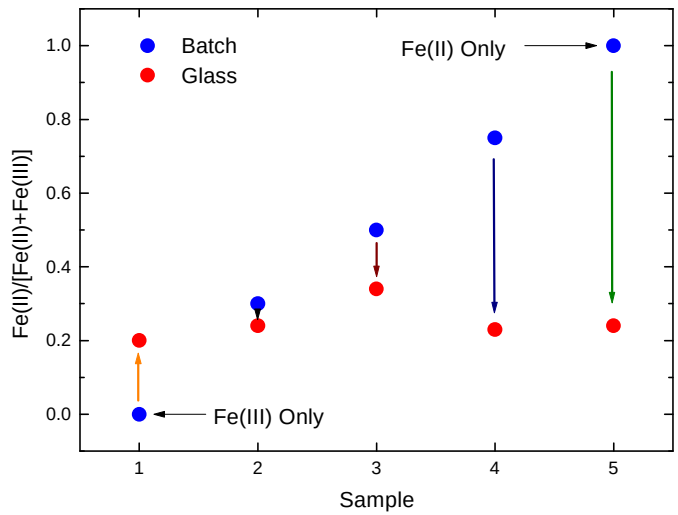

Figure. Irrespective of the iron valence in the batch, the Fe(II) fraction in the glass is in the 0.2-0.3 range when melted in air at ~1250EC. Fe/P ratio is 0.67 for samples shown above.

When melted in air at ~1250EC for 1-2 hrs., iron phosphate glasses reach a redox equilibria corresponding to a Fe(II) fraction of 0.2-0.3. The Fe(II) fraction can be increased either by increasing the melting temperature or by melting in a reducing atmosphere. Glass forming ability of melts decreases rapidly if the Fe(II) fraction is forced above 0.5.

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Structural Features-Iron Coordination

Table. Mössbauer hyperfine parameters obtained at 295 K for an iron phosphate glass of batch composition $40Fe_2O_3$-$60P_2O_5$ (mol%).

Parameter	Fe^{2+}	Fe^{3+}
Isomer shift, *mm/s*	1.01	0.42
Quadrupole splitting, *mm/s*	2.63	0.83

Average coordination of iron ions is distorted octahedral. However, some tetrahedrally coordinated iron ions can not be ruled out. This observation is supported by EXAFS studies.

Hyperfine parameters are independent of the type (see Figure on right) and the concentration of waste components indicating that **the local environment around iron ions is not affected by the addition of waste components.**

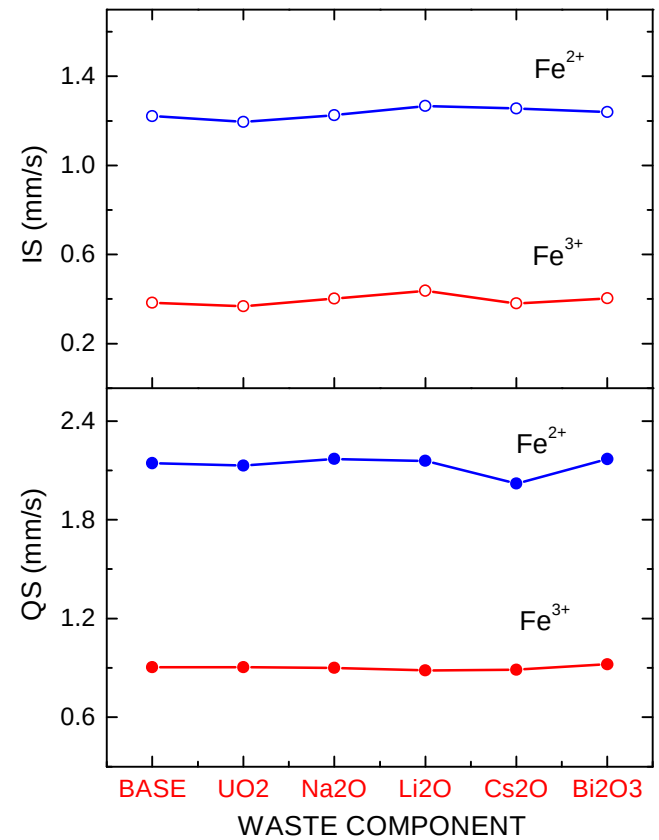

Figure. Dependence of the hyperfine parameters on the type of waste component in iron phosphate glasses. The waste component content in each glasses is 10 mol%.

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Valence State of Iron Ions in Iron Phosphate Glasses Containing Common Nuclear Waste Components.

Most common nuclear waste components do not adversely affect the redox equilibria in iron phosphate glasses.

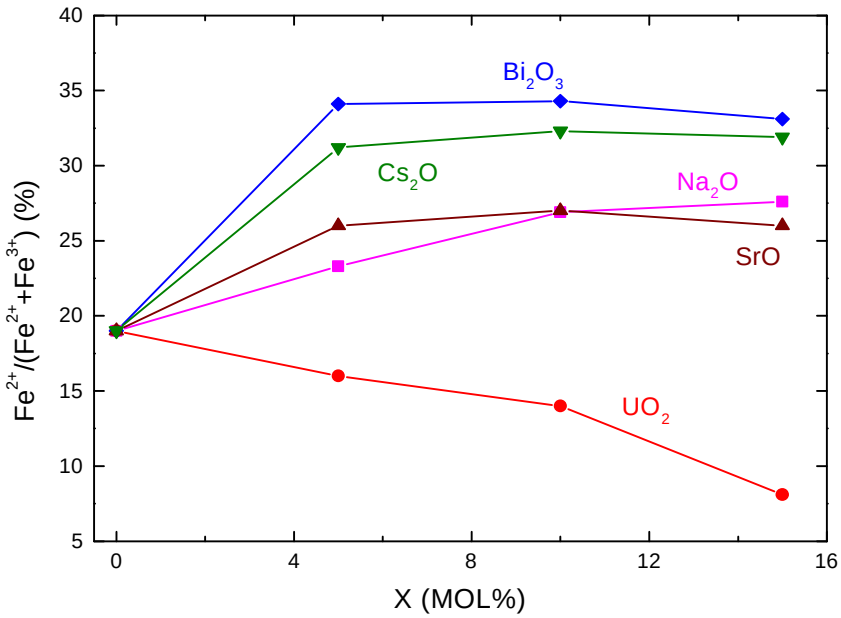

Figure. Dependence of iron valence on the waste component (MO) content in (100-x)(40Fe_2O_3-60P_2O_5)-x(MO) glasses melted in air.

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Structural Features - Oxygen Bonding

The poor chemical durability of non-iron-containing phosphate glasses can be attributed to the abundance of bridging oxygens (BOs) which are linked via easily hydrated -P-O-P- links.

In contrast, X-ray photoelectron spectra show that only a minority, about 26%, of oxygen ions in iron phosphate glasses are bridging, see Figure on right. This may be basis for the excellent chemical durability of iron phosphate glasses.

None of the common waste components such as Cs_2O, UO_2, Bi_2O_3, and Na_2O increase the fraction of BOs above 35%.

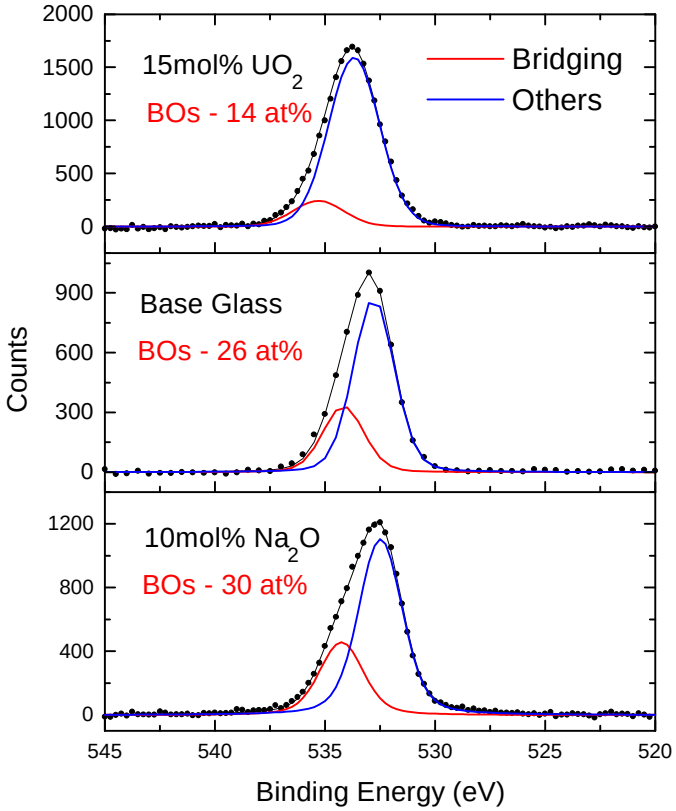

Figure. O1s XPS spectra for iron phosphate glasses containing UO_2 or Na_2O. Base glass composition is $31Fe_3O_4$-$69P_2O_5$ (mol%).

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Structural Features

Several spectroscopic techniques suggest that the atomic structure of iron phosphate glasses may share short range similarities with that of $Fe_3(P_2O_7)_2$, the compound which crystallizes when a binary iron phosphate glass of approximate batch composition $40Fe_2O_3$-$60P_2O_5$ (mol%) is heat treated at ~600EC for 24h.

The structure of $Fe_3(P_2O_7)_2$ is characterized by:

- All phosphorus ions taking part in $P_2O_7^{4-}$ groups.
- Fe(II) and Fe(III) in six-fold coordination with surrounding oxygen ions.
- Fe-O clusters interconnected via $P_2O_7^{4-}$ groups.
- Only a small fraction, 14%, of bridging oxygens.

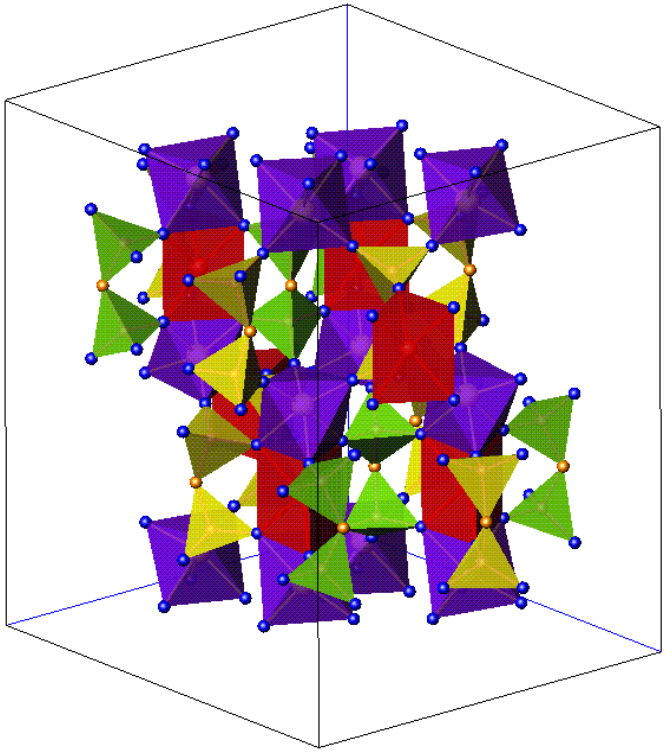

Figure. Crystal structure of $Fe_3(P_2O_7)_2$.
Purple - $Fe(III)O_6$ octahedra
Red - $Fe(II)O_6$ trigonal prisms
Green/Yellow - PO_4 tetrahedra

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Structural Features
Phosphorus - Oxygen Network

Raman spectra indicate that the P-O network is dominated by $P_2O_7^{4-}$ dimer units.

Addition of waste components does not appreciably disturb the P-O network, see Figure.

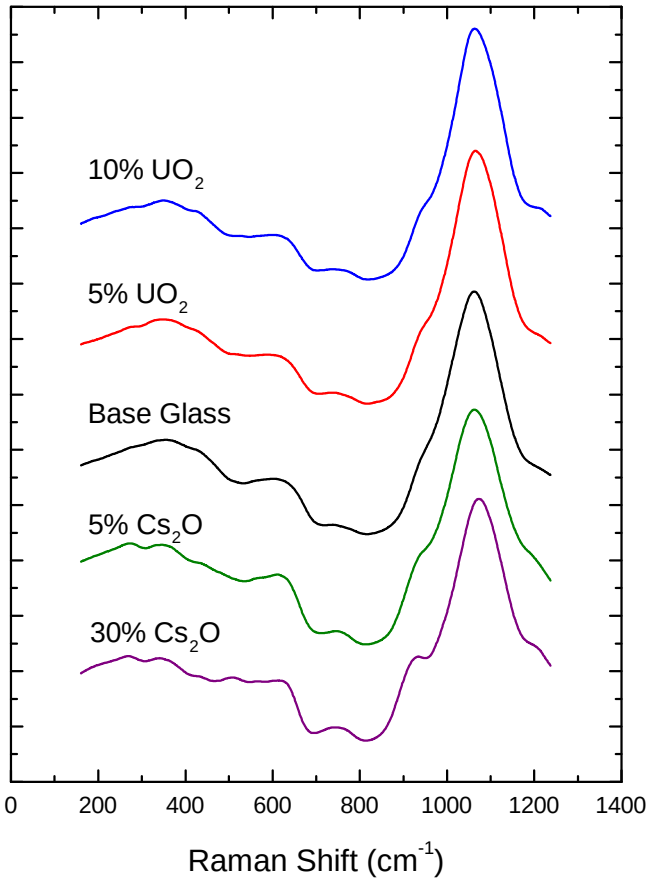

Figure. Raman spectra of iron phosphate glasses containing UO_2 and Cs_2O. Base glass composition is $40Fe_2O_3$-$60P_2O_5$ (mol%).

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Structural Features
Local Environment Around Iron Ions

Fe K-edge EXAFS data suggest that the iron ions are 5-6 coordinated with near neighbor oxygens.

Major features in the Fourier transform (FT) of $k^3x(k)$ from EXAFS data do not change when waste components are added, see Figure.

Waste elements appear to be excluded from the near neighborhood of iron ions.

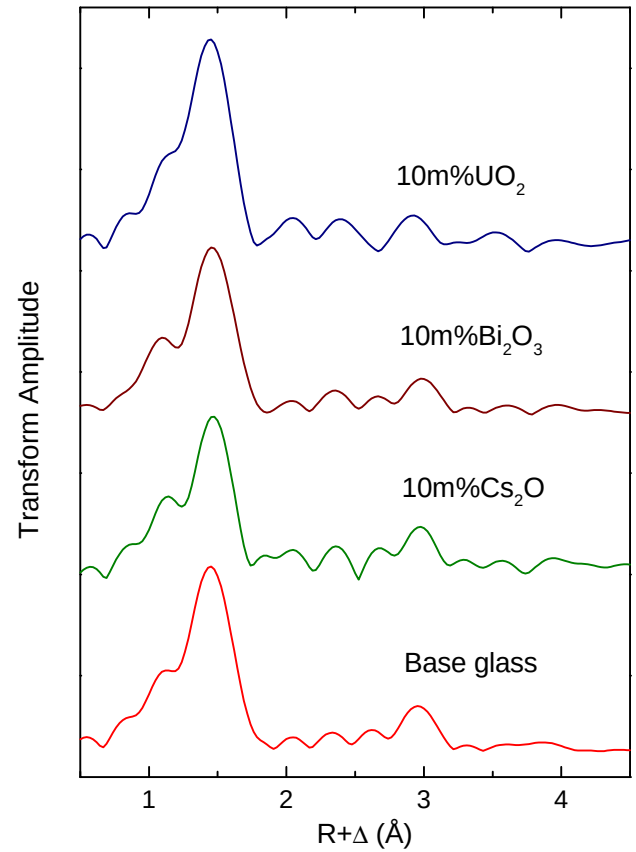

Figure. Fourier transform (FT) of $k^3x(k)$ from EXAFS data for iron phosphate glasses containing waste components. Base glass composition is $40Fe_2O_3$-$60P_2O_5$ (mol%).

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Structural Features
Long Range Structure

Neutron and High Energy X-ray scattering data strongly suggests that the waste elements are situated away from FeO_6 and PO_4 polyhedra.

For example, two new peaks corresponding to interatomic distances of 2.3 and 3.7 Å appear in T(r) plots, see Figure, as UO_2 is added to the base glass. The peak at 2.3Å is due to U-O pairs. **The peak at 3.7 Å is most likely due to U-P and/or U-Fe pairs suggesting that U ions are far removed from Fe and P ions.**

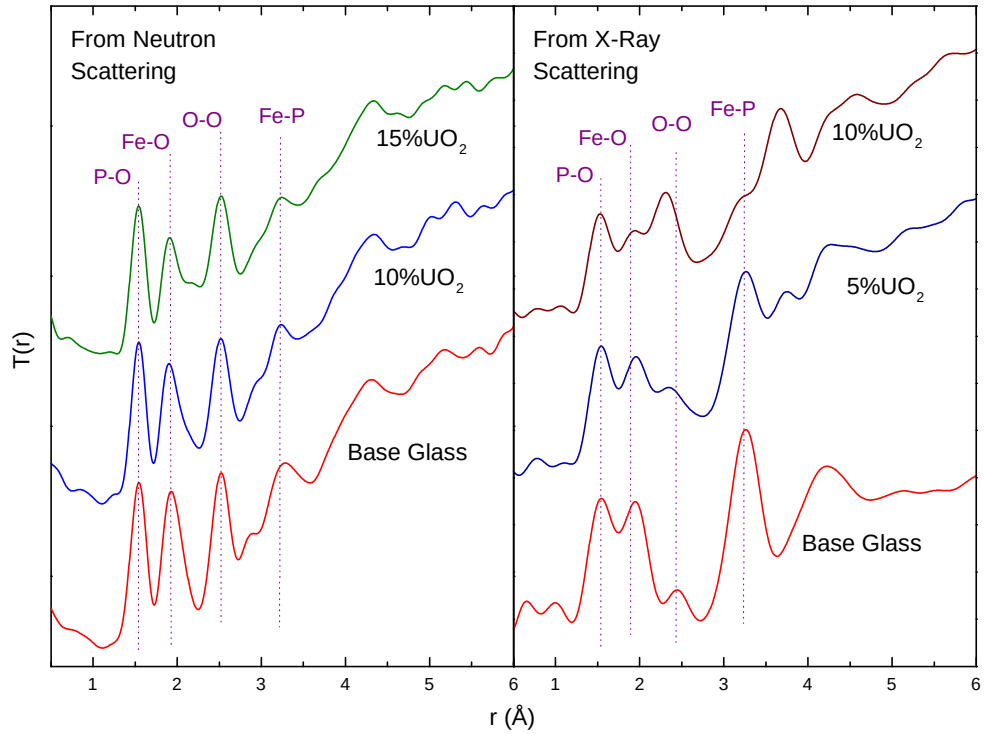

Figure. Total correlation functions from neutron and high energy X-ray scattering data for several iron phosphate glasses containing UO_2. Base glass composition is $40Fe_2O_3$-$60P_2O_5$ (mol%).

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Structural Features
Where are the Waste Elements?

$Fe_3(P_2O_7)_2$, which share structural features with iron phosphate glasses, has voids capable of hosting large ions such as Cs, see Figure.

Because iron phosphate glasses are less dense than their crystallized samples, it is reasonable to expect interstitial "voids" in the glass structure as well.

Addition of waste elements does not extensively disturb the Fe-P-O network in iron phosphate glasses suggesting that the waste elements may occupy the above mentioned empty spaces in the Fe-P-O network.

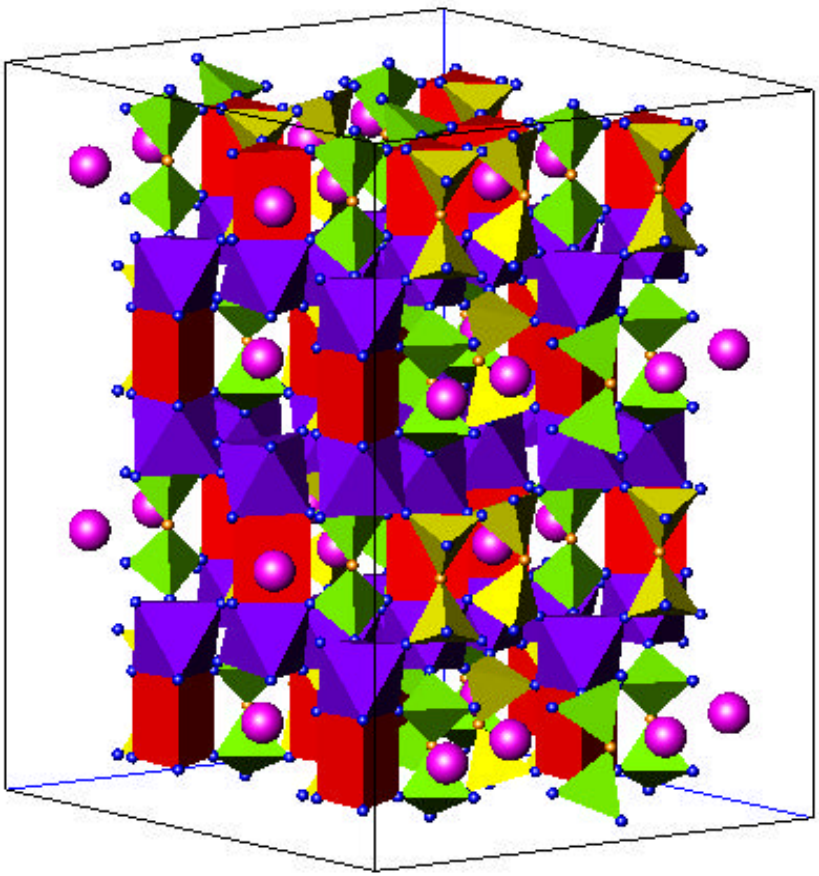

Figure. The structure of $Fe_3(P_2O_7)_2$ showing voids, purple spheres, which are capable of hosting a large atom such as Cs.

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Summary: Iron Phosphate Waste Forms

- Host up to 50 wt% HLWs which are high in phosphates, halides, and heavy metals like U, Cs, Pu, Sr, and Bi. Use of iron phosphate glasses to vitrify certain HLWs which are poorly suited for borosilicate glasses may result in much smaller waste volumes.

- May be melted at 950-1200 EC in 1-2 hrs. using commercially available refractories.

- Physical and chemical properties such as the chemical durability and glass transition temperature meet current DOE standards.

- Waste elements appear to occupy “voids” in the host matrix structure without adversely disturbing the Fe-O-P network.

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Publications: as of July 1998

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- "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.
- "Structural Study of Iron Phosphate Glasses," A. Mogus-Milankovic, B. Pivac, K. Furiƒ, and D. E. Day, Phys. Chem. Glasses **38** (1997) 74.
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- "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance and Evolved Gas Mass Spectroscopy," D. I. Giscom, C. I. Merzbacher, N. E. Bibler, H. Imagawa, M. Mesko, and G. K. Marasinghe, Nucl. Instr. and Meth. **B141** (1998) 600.
- "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, Ceramic Transactions, **93** (In Press).
- "Iron Redox Equilibria and Crystallization of Iron Phosphate Glasses" C. S. Ray, X. Fang, M. Karabulut, G. K. Marasinghe, and D. E. Day, Ceramic Transactions, **93** (In Press).
- "Corrosion of Selected Refractories by Iron Phosphate Melts," F. Chen and D. E. Day, Ceramic Transactions, **93** (In Press).
- "Chemical Durability, Crystallization, and Iron Redox Equilibria of Iron Phosphate Glasses," C. S. Ray, X. Fang, M. Karabulut, G. K. Marasinghe, and D. E. Day, J. Non-Cryst. Solids (In Press).

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PROJECT INFORMATION

http://www.umr.edu/~gkmars/emsp.html