ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

T. Zachry

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

IRON PHOSPHATE GLASSES FOR VITRIFYING DOE HIGH PRIORITY NUCLEAR WASTES

C. W. Kim and D. E. Day
Department of Ceramic Engineering and the Graduate Center for Materials Research,
University of Missouri-Rolla, Rolla, MO 65409-1170
cheol@umr.edu, Fax: 573-341-2071

Iron phosphate glasses have been studied as an alternative glass for vitrifying Department of Energy (DOE) high priority wastes. The high priority wastes were the Low Activity Waste (LAW) and the High Level Waste (HLW) with high chrome content stored at Hanford, WA and the Sodium Bearing Waste (SBW) stored at the Idaho National Engineering and Environmental Laboratory (INEEL). These wastes were recommended by Tanks Focus Area because their high sodium, high sulfate, high phosphate, and high chrome content (Table 1) can seriously reduce the maximum waste loading in borosilicate glasses[1]. All three of these high priority wastes have been successfully vitrified, at high waste loadings, in iron phosphate glasses which have an excellent chemical durability. The research results and identified advantages for vitrifying these three wastes in iron phosphate glasses are summarized below.

Table 1. Simplified composition (wt%) of nuclear wastes containing large amounts of sulfate (LAW and SBW), phosphate (LAW and HLW), or chrome (HLW) that are poorly soluble in borosilicate glasses.

Oxide (wt%)	LAW*	HLW**	SBW***
Al_2O_3	4.4	21	27.8
B_2O_3	-	-	0.4
Bi_2O_3	-	4	-
CaO	-	5	2.2
Cl	0.6	-	0.9
Cr_2O_3	0.4	4	0.2
F	1.6	-	0.8
Fe_2O_3	-	12	1.4
K_2O	-	-	7.6
La_2O_3	-	1	-
MgO	-	-	0.4
MnO	-	-	0.8
Na_2O	75.3	24	52.3
P_2O_5	7.7	3	1.6
SiO_2	0.5	10	-
SO_3	9.5	-	3.6
U_3O_8	-	10	-
ZrO_2	-	6	-
Total	100.0	100	100.0

* Hanford Low Activity Waste (LAW): LAW compositions with SO_3 concentrations above 7 wt% were averaged & simplified[2].
** Hanford High Level Waste (HLW) containing high chrome: Blended composition from clusters #3, 4, 6, 7, 8, 10 and 14[1].
*** Simplified composition of Sodium Bearing Waste (SBW) at INEEL [1].

Higher Waste Loading (Smaller Wasteform Volume)

Large amounts of simulated wastes (32 wt% for LAW, 40 wt% for SBW and 75 wt% for HLW) have been successfully vitrified in iron phosphate glasses (Figure 1). For the Hanford LAW and INEEL SBW, it is unlikely that the waste loading in iron phosphate glasses will be limited by the SO_3 content of the wastes as is currently the case[3] in borosilicate glasses. If the sulfate content of the LAW did not limit its waste loading in

the glass then the amount of glass produced at Hanford could be reduced by as much as 43%[2].

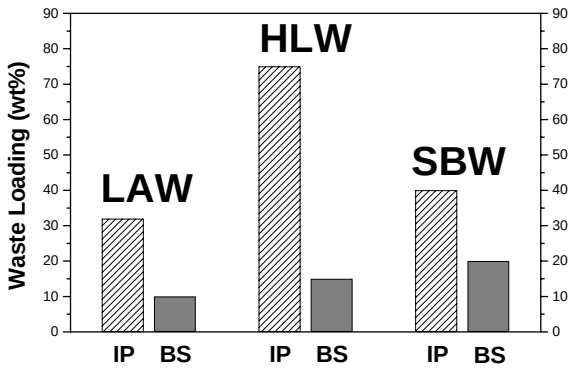

Figure 1. A comparison of the waste loading achieved in iron phosphate (IP) and that calculated for borosilicate (BS) glass wasteforms for the high priority wastes. The waste loading in BS glass was calculated based on the low sulfate, < 1 wt% SO_3, (for LAW and SBW) and the low chrome, < 1 wt% Cr_2O_3, (for HLW) solubility in BS glasses using the simplified composition given in Table 1.

Excellent Chemical Durability

Vitrified iron phosphate wasteforms satisfy all known DOE requirements for aqueous chemical durability based on the Product Consistency Test (PCT) and Vapor Hydration Test (VHT), see Figure 2. Some iron phosphate wasteforms partially crystallize when slowly cooled or heat treated to simulate Canister Centerline Cooling, but the chemical durability of these partially crystallized wasteforms is excellent and meets all DOE requirements.

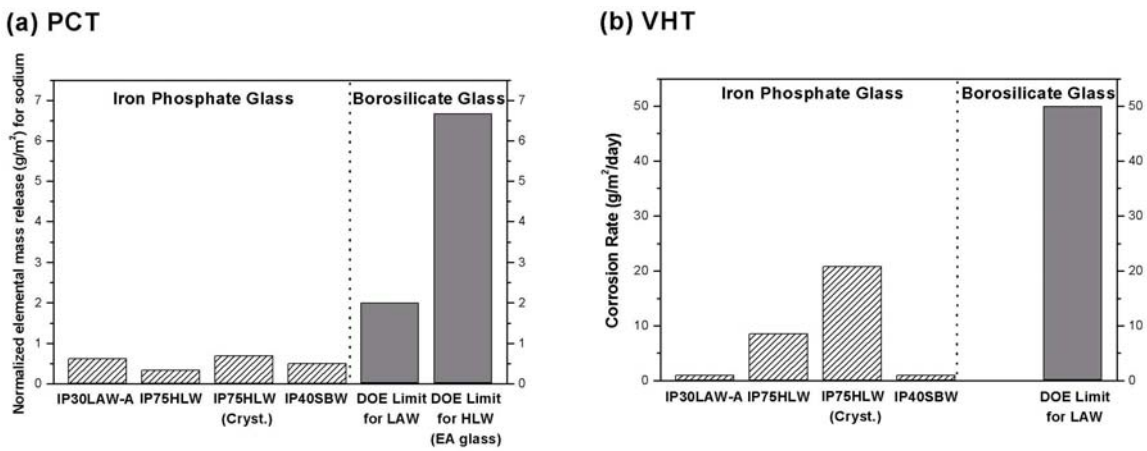

Figure 2. (a) Normalized elemental mass release (g/m^2) after PCT for sodium from iron phosphate glassy and deliberately crystallized wasteforms containing 30, 75 and 40 wt% of simulated LAW, HLW and SBW, respectively. (b) VHT corrosion rate (g/m^2/day) for the same iron phosphate wasteforms. DOE specifications for PCT and VHT are given for comparison, but currently, there is no DOE specification for VHT for HLW.

Lower Melting Temperatures and Shorter Melting Times

Iron phosphate glasses can be melted as low as 950-1000°C compared to the 1150°C for the borosilicate glasses now being melted at the Defense Waste Processing Facility (DWPF). Because iron phosphate melts are fluid at their melting temperature (viscosity 200 to 900 centipoise), they rapidly become homogeneous and their melting times can be as short as a few hours (< 4 hours) compared to the > 48 hour residence time for borosilicate melts (viscosity 4,500 to 9,000 centipoise) in the DWPF joule heated melter (JHM). Also, because of their lower viscosity, there is less tendency for an insulating foam, which reduces the melting rate, to form on the surface of an iron phosphate melt during melting. Lower melting temperatures and shorter melting times lead to less expensive and safer melting processes and mean that smaller furnaces can be used for any given output.

Minimum Corrosion of Refractory and Electrode Materials

Commercial refractories, such as high purity alumina, AZS, zircon, silica and chrome refractories, are corroded very little by iron phosphate melts, even after being in contact with the melt for several days at temperatures well above the “normal” melting temperature. For still unidentified reasons, these refractory oxides are only poorly “wet” by iron phosphate melts. The corrosion of Inconel 690 and 693 has been investigated using samples partially and fully submerged in an iron phosphate melt that contained 30 wt% of the Hanford LAW, see Table 1, at 1025°C for 155 days. The weight loss for the partially submerged Inconel 693 was only 2.5% (that corresponds to < 0.7 µm/day), which is comparable to the corrosion that has been observed for the Inconel 690 electrodes in the JHM used to melt borosilicate glass at DWPF. These preliminary results suggest that Inconel 693 is a candidate for the electrodes in a JHM melting iron phosphate glasses.

Flexible Atomic Structure and Redox Equilibria

Iron phosphate glasses have an atomic structure that easily accommodates ions of widely different size and charge. An idealized structure of iron phosphate glasses is shown in Figure 3 and consists of FeO_6 octahedra and trigonal prisms joined together by pyrophosphate (P_2O_7) groups. The outstanding chemical durability of the iron phosphate glasses is attributed to the small number of P-O-P bonds which are more easily hydrolyzed than the more numerous Fe-O-P bonds which dominate the structure. Radionuclides such as ^{137}Cs, ^{90}Sr, ^{234}U and transuranic ions occupy interstitial sites in the iron phosphate host glass without adversely modifying the atomic structure or the physical and chemical properties (Figure 3).

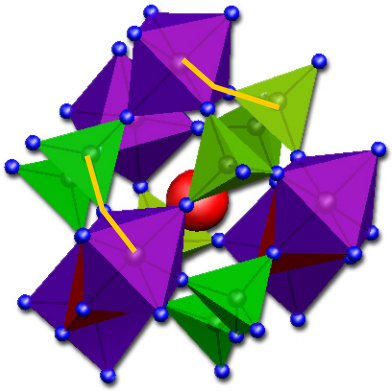

Figure 3. Waste elements (red) occupy interstitial sites among PO_4 tetrahedra (green) and FeO_n (n ~5-6) polyhedra (purple and brown) without appreciably affecting the -Fe-O-P- network. The glass structure is dominated by hydration resistant -Fe-O-P- bonds (yellow).

Inexpensive Raw Materials

The number of additives that are added to a particular nuclear waste to form a glass with acceptable properties obviously depends upon the waste composition, but iron phosphate glasses typically require fewer additives than borosilicate glasses. In many cases, only a source of phosphate (such as phosphoric acid, rock phosphate or industrial phosphate waste) and a source of iron oxide (as-mined iron ore) need to be added to the nuclear waste. These raw materials are all inexpensive. One attractive raw material is the phosphate waste currently being generated by metal fabricators (automotive, construction equipment, appliance and office furniture manufacturers) which use a metal conversion process to improve the corrosion resistance of iron and steel. An estimated 12,000 tons/yr of iron and zinc phosphate waste is currently generated from this conversion process and buried in landfills. Many of these wastes have been determined to be an excellent source of iron oxide and phosphate for iron phosphate glass wasteforms. Using these wastes as a raw material in vitrifying nuclear waste would be a doubly beneficial use of these wastes and would eliminate the need to dispose of them in our Nation's landfills.

CONCLUSIONS

The documented high waste loading, low melting temperature, rapid furnace throughput (short melting time) and outstanding chemical durability of iron phosphate glasses indicate that these alternative glasses offer an opportunity to significantly accelerate the clean up effort, thereby reducing the time and cost of vitrifying these high priority nuclear wastes.

ACKNOWLEDGEMENTS

This work was supported by the Environmental Management Science Program (EMSP) of the U.S. Department of Energy (DOE) under contract FG07-96ER45618.

REFERENCES

1. J. M. Perez, Jr., D. F. Bickford, D. E. Day, D. S. Kim, S. L., Lambert, S. L. Marra, D. K. Peeler, D. M. Strachan, M. B. Triplett, J. D. Vienna and R. S. Wittman, “High-Level Waste Melter Study Report”, PNNL-13582, Pacific Northwest National Laboratory, Hanford, WA (2001).
2. D. S. Kim, W. C. Buchmiller, M. J. Schweiger, J. D. Vienna, D. E. Day, C. W. Kim, D. Zhu, T. E. Day, T. Neidt, D. K. Peeler, T. B. Edwards, I. A. Reamer and R. J. Workman, “Iron Phosphate Glass as an Alternative Waste-Form for Hanford LAW”, PNNL-14251, Pacific Northwest National Laboratory, Richland, WA (2003).
3. J. D. Vienna, W. C. Buchmiller, J. V. Crum, D. D. Graham, D. S. Kim, B. D. MacIsaac, M. J. Schweiger, D. K. Peeler, T. B. Edwards, I. A. Reamer and R. J. Workman, “Glass Formulation Development for INEEL Sodium-Bearing Waste”, PNNL-14050, Pacific Northwest National Laboratory, Richland, WA (2002).