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**REACTION OF INCONEL 690 AND 693 IN IRON PHOSPHATE MELTS:
ALTERNATIVE GLASSES FOR WASTE VITRIFICATION**

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EXECUTIVE SUMMARY

The corrosion resistance of candidate materials used for the electrodes (Inconel 690 & 693) and the melt contact refractory (Monofrax K-3) in a Joule Heated Melter (JHM) has been investigated at the University of Missouri-Rolla (UMR) during the period from June 1, 2004 to August 31, 2005. This work was supported by the U.S. Department of Energy (DOE) Office of Biological and Environmental Research (DE-FG02-04ER63831).

The unusual properties and characteristics of iron phosphate glasses, as viewed from the standpoint of alternative glasses for vitrifying nuclear and hazardous wastes which contain components that make them poorly suited for vitrification in borosilicate glass, were recently discovered at UMR. The expanding national and international interest in iron phosphate glasses for waste vitrification stems from their rapid melting and chemical homogenization which results in higher furnace output, their high waste loading that varies from 32 wt% up to 75 wt% for the Hanford LAW and HLW, respectively, and the outstanding chemical durability of the iron phosphate wasteforms which meets all present DOE requirements (PCT and VHT). The higher waste loading in iron phosphate glasses, compared to the baseline borosilicate glass, can reduce the time and cost of vitrification considerably since a much smaller mass of glass will be produced, for example, about 43% less glass when the LAW at Hanford is vitrified in an iron phosphate glass according to PNNL estimates.

In view of the promising performance of iron phosphate glasses, information is needed for how to best melt these glasses on the scale needed for practical use. Melting iron phosphate glasses in a JHM is considered the preferred method at this time because its design could be nearly identical to the JHM now used to melt borosilicate glasses at the Defense Waste Processing Facility (DWPF), Westinghouse Savannah River Co. Therefore, it is important to have information for the corrosion of candidate electrode and refractory materials in iron phosphate melts in a JHM.

During the period from June 1, 2004 to August 31, 2005, the corrosion resistance of coupons of Inconel 690 & 693 metals and Monofrax K-3 refractory, partially submerged in several iron phosphate melts at 950-1200°C, has been investigated to determine whether iron phosphate glasses could be melted in a JHM equipped with such electrodes and refractory in the same manner as now being used to melt borosilicate glass. These representative iron phosphate melts, which contained 30 wt% Hanford

LAW and 40 wt% Idaho SBW simulants, did not corrode the Inconel 690 to any greater extent than what has been reported for Inconel 690 in the borosilicate melt in the JHM at DWPF. Inconel 693 appeared to be an even better candidate for use in iron phosphate melts since its corrosion rate (1.8 to 25.4 $\mu\text{m}/\text{day}$) was only about one half that (5.4 to 45.4 $\mu\text{m}/\text{day}$) of Inconel 690. The dynamic corrosion measured for the candidate refractory, Monofrax K-3, by iron phosphate melts is quite encouraging since the measured corrosion (0.011 to 0.132 mm/day at 9.2 rpm) is less than the corrosion (0.137 mm/day) that has been reported in the JHM used to melt borosilicate glass at DWPF.

During the period covered by this final report, the results of the research on iron phosphate glasses have been described in seven technical papers and have been presented at one national meeting. In addition to the principal investigator, one research professor and one undergraduate research aide were supported by this project.

1. INTRODUCTION AND RESEARCH OBJECTIVES

The vitrification of nuclear waste to form a chemically durable glass is considered the most effective way to immobilize and permanently dispose of these potentially mobile and biologically dangerous wastes. The U.S. Department of Energy (DOE) currently approves only borosilicate type glasses for such use. However, many of the liquid and solid wastes, presently awaiting disposal at Hanford, WA and elsewhere, have more complex and diverse chemical compositions than originally anticipated when borosilicate glasses were chosen for this application. These wastes often contain components such as phosphates, sulfates, chrome oxide, and heavy metals which can severely limit the waste loading because they are either poorly soluble or chemically incompatible in borosilicate glasses [1,2]. In the case of Hanford Low Activity Waste (LAW), there are certain waste compositions where the waste loading in borosilicate glasses could be as little as 5 wt%, i.e., 95 wt% of the borosilicate wasteform will consist of additives and the volume of the vitrified wasteform will be several times larger than the volume of the starting waste.

With support from the Environmental Management Science Program, DOE [3,4], the University of Missouri-Rolla has investigated novel iron phosphate glasses as an alternative host matrix for vitrifying nuclear and other hazardous wastes that are not well suited for borosilicate glasses. Iron phosphate glasses appear to offer a practical way to accelerate the clean up of nuclear wastes, especially those stored at Hanford because of their faster melting, excellent chemical durability, and higher waste loading, 32 wt% [5-7] and up to 75 wt% [8-10] for the Hanford LAW and HLW, respectively. Iron phosphate glasses have the potential to greatly reduce the cost and time for the clean up effort. In a recent Pacific Northwest National Laboratory Report [6], it was estimated that the mass of glass needed to vitrify the Hanford LAW would be reduced by approximately 43%, compared to the baseline borosilicate glass, by vitrifying the LAW in an iron phosphate glass at a waste loading of 27 wt% which has already been demonstrated. This higher waste loading would translate into a huge reduction in the time and cost to vitrify just this one waste.

Melting iron phosphate glasses in a Joule Heated Melter (JHM) is considered the preferred method at this time because its design could be nearly identical to the JHM now in use to melt borosilicate glasses at the Defense Waste Processing Facility (DWPF), Westinghouse Savannah River Co. Knowledge of the corrosion resistance of

the glass-contact materials in the JHM is of considerable importance to the vitrification technology. The objective of the present research was to investigate the corrosion resistance of Inconel 690 & 693 and Monofrax K-3 in iron phosphate melts. Inconel 690 & 693 and Monofrax K-3 are candidate materials for the electrodes and melt contact refractory, respectively in a JHM.

2. CORROSION RESISTANCE OF CANDIDATE METALS

Inconel 690 was chosen since it is the current electrode material being used in the JHM at DWPF to melt borosilicate glass. Inconel 693 was chosen since it is a modified version of Inconel 690, see Table 1, that was expected to offer a higher corrosion resistance and longer service life.

Table 1. Composition and selected physical properties of Inconel 690 and 693 [11].

		Inconel 690*	Inconel 693*
Composition (wt%)	Nickel	58.0 min.	53.0 min.
	Chromium	27-31	27.0-31.0
	Iron	7-11	2.5-6.0
	Aluminum		2.5-4.0
	Niobium		0.5-2.5
	Manganese	0.50 max.	1.0 max.
	Titanium		1.0 max.
	Copper	0.50 max.	0.5 max.
	Silicon	0.50 max.	0.5 max.
	Carbon	0.05 max.	0.15 max.
	Sulfur	0.015 max.	0.01 max.
	Physical property	Density (g/cm ³)	8.19
Melting range (°C)		1343-1377	1317-1367
Electrical resistivity (μΩ·m)		1.148	1.168

* Inconel 690 and 693 samples were supplied in the annealed condition by Special Metals Corporation [11].

2.1. Preparation of Glass

The melt compositions were chosen from among those considered most likely to be used to vitrify the LAW at Hanford and the SBW at the Idaho National Laboratory. Iron phosphate glasses were prepared which contained 30 wt% of the high sulfate Hanford LAW simulant or 40 wt% of the SBW simulant since these compositions had been studied extensively and had been demonstrated to meet DOE's PCT and VHT

requirements [3-10,12]. The overall LAW, SBW simulant and batch compositions are given in Table 2. The appropriate amounts of the raw materials were mixed in a sealed plastic container for 30 minutes to produce a homogeneous mixture. This mixture was put in an alumina crucible and melted at 950-1000°C for 2 hours (minimal corrosion of the alumina crucible) in an electric furnace in air. Each melt was stirred 3 to 4 times with a fused silica rod over a period of 30 minutes to insure chemical homogeneity, and then poured onto the surface of a clean steel plate. The quenched glass was used for the corrosion tests.

Table 2. Nominal composition (wt%) of Hanford LAW simulant, Idaho SBW simulant and iron phosphate wasteforms (glasses) containing 30 wt% LAW (IP30LAW, IP30LAW-A, IP30LAW-C) or 40 wt% SBW (IP40SBW) [5,12].

	LAW simulant	SBW simulant	IP30LAW	IP30LAW-A	IP30LAW-C	IP40SBW
Al ₂ O ₃	4.4	27.8	1.3	11.3	1.3	10.9
B ₂ O ₃	-	0.4	-	-	-	0.1
CaO	-	2.2	-	-	-	0.9
Cl	0.6	0.9	0.2	0.2	0.2	0.3
Cr ₂ O ₃	0.4	0.2	0.1	0.1	3.1	0.1
F	1.6	0.8	0.5	0.5	0.5	0.3
Fe ₂ O ₃	-	1.4	20.0	10.0	17.0	10.3
K ₂ O	-	7.6	-	-	-	3.0
MgO	-	0.4	-	-	-	0.2
MnO	-	0.8	-	-	-	0.3
Na ₂ O	75.3	52.3	22.6	22.6	22.6	20.5
P ₂ O ₅	7.7	1.6	52.2	52.2	52.2	51.7
SiO ₂	0.5	-	0.2	0.2	0.2	-
SO ₃	9.5	3.6	2.9	2.9	2.9	1.4
Total	100.0	100.0	100.0	100.0	100.0	100.0

2.2. Corrosion Tests and Results

Specimens (~14 mm × ~9 mm × ~7 mm) of Inconel 690 and 693 were cut from larger pieces of each metal using a diamond saw and then each surface was polished to 600 grit SiC paper. The dimensions of each specimen were measured and recorded. Fifty grams of the as-made iron phosphate glass was re-melted in an alumina crucible at 950-1000°C for 30 minutes and then one Inconel specimen, which had been preheated to 950-1000°C, was partially submerged in the melt (to simulate a partially submerged electrode in a JHM). After 7 days, the crucible was removed from the furnace and the

Inconel sample was removed from the melt and immediately quenched in water. After cleaning and drying the Inconel sample, its dimensions at the melt line were measured.

The corrosion rate of Inconel 690 and 693 was determined from the initial and final dimensions of the samples after the 7-day test. The overall corrosion rate (calculated by assuming a constant rate from time = 0) at the melt line was 1.8 to 25.4 $\mu\text{m}/\text{day}$ for the Inconel 693 and was 5.4 to 45.4 $\mu\text{m}/\text{day}$ for the Inconel 690 depending on the melt composition and temperature (Figure 1). With the exception of two values for Inconel 690, all the values are smaller than the 32.6 $\mu\text{m}/\text{day}$ rate reported [13] for the Inconel 690 insert from the DWPF melter pour spout at $\sim 1000^\circ\text{C}$. The corrosion rates for Inconel 693 were about one half of those for Inconel 690, indicating that Inconel 693 was more chemically resistant to the iron phosphate melts.

Melt Line Corrosion Rate of Inconel 690 & 693 Alloys in Iron Phosphate Melts

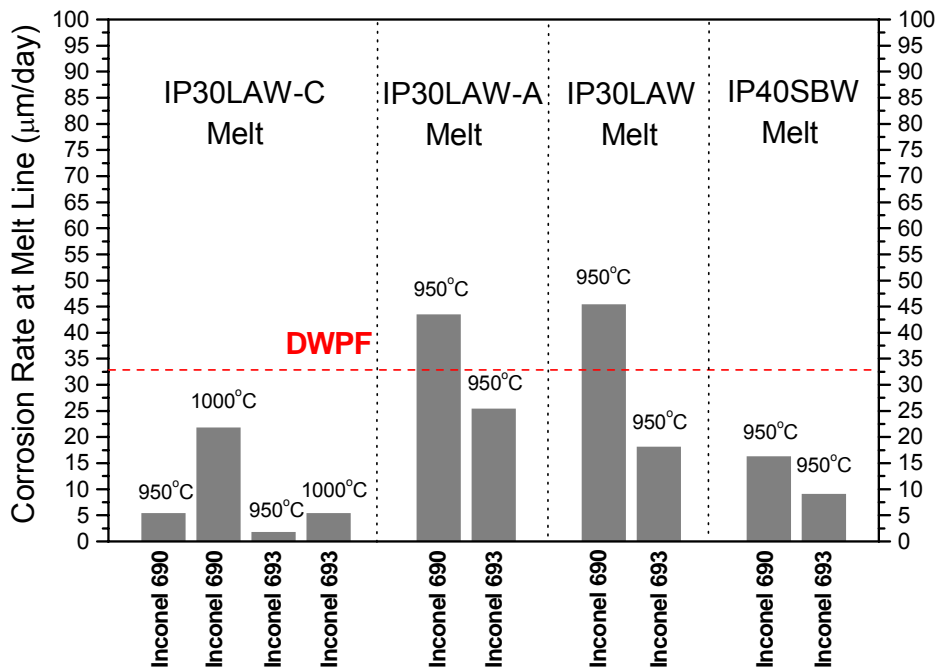


Figure 1. Melt line corrosion rate of Inconel alloys in iron phosphate melts. The red horizontal line, labeled DWPF, denotes the corrosion rate of 32.6 $\mu\text{m}/\text{day}$ that has been reported [13] for the Inconel 690 insert from the DWPF melter pour spout at $\sim 1000^\circ\text{C}$.

3. CHEMICAL CORROSION/EROSION OF OXIDE REFRACTORY

3.1. Corrosion Tests

The corrosion/erosion of the commercially available chrome-alumina refractory, Monofrax K-3, was investigated for the same iron phosphate melts and at the similar conditions used for the metal corrosion experiments. The phosphate melt compositions were those containing 30 wt% of the LAW (IP30LAW-C) or 40 wt% of the SBW (IP40SBW), see Table 2.

A dynamic corrosion procedure, see Figures 2 and 3, was used for the corrosion/erosion tests. The dynamic measurement is an accelerated test and is preferred over the static measurement since the dynamic method better simulates the conditions (convective flow of glass over the refractory wall) of the refractory in service.



Figure 2. External view of the dynamic corrosion test apparatus.

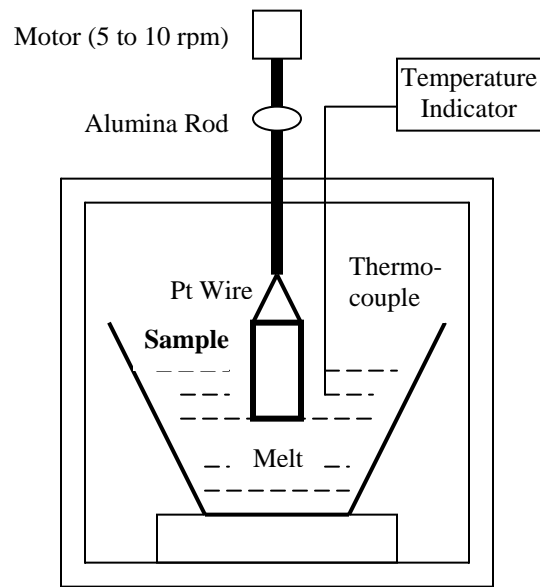


Figure 3. Schematic of the apparatus for measuring dynamic corrosion of a refractory in a high temperature melt.

Cylindrical rods of the Monofrax K-3, 15 to 20 mm in diameter and 50 to 60 mm in length, were core-drilled from commercially prepared (Monofrax, Inc.) blocks. A cylindrical rod was connected to one end of an alumina rod using platinum wire. The other end of the alumina rod was fastened in a chuck attached to the drive shaft of a variable speed motor. Once the melt was at the desired temperature, the motor and

refractory sample were lowered until the lower portion of the refractory was immersed in the melt and the top of the refractory rod extended 25 to 30 mm above the melt. The refractory rod was rotated at 9.2 rpm in the melt for 7 days at 950°C, 1100°C, and 1200°C. At the end of the corrosion test, the refractory rod was raised clear of the melt, held above the melt inside the furnace for 2 hours to allow any adhering melt to drip back into the crucible, and then transferred to an another furnace for slow cooling. After cutting the corroded rod along its longitudinal cross section, the diameter of the corroded rod was measured at the melt line. The dynamic corrosion rate (mm/day) was calculated using the equation:

$$\text{CR (corrosion rate)} = [D - \frac{1}{2}(d_1 + d_2)] / 2 \cdot t \quad (1)$$

where D is the starting diameter of the rod at the melt line, d_1 and d_2 are the average diameter of the two halves of the sectioned rod at the melt line and t is the duration of the test.

3.2. Results and Discussion

The dynamic corrosion rate (rotating refractory rods) for the commercially available Monofrax K-3 refractory partially immersed in different iron phosphate melts (containing up to 22.6 wt% Na₂O) was typically less than the 0.137 mm/day rate used in the design of the DWPF melter, red line in Figure 4. It should be noted that the IP30LAW-C and IP40SBW glasses are normally melted at 950-1000°C rather than at 1100°C or 1200°C as used for the measurements given in Figure 4. Even at these higher than needed temperatures, the Monofrax K-3 refractory has a corrosion rate below 0.137 mm/day. The melt line (red arrows in Figure 5) on the external surface of Monofrax K-3 refractory rods was barely visible after the 7-day, dynamic corrosion test suggesting that Monofrax K-3 refractory was resistant to the corrosion/erosion of the melts.

Dynamic Corrosion Rate of Monofrax K-3 Refractory in Iron Phosphate Melts

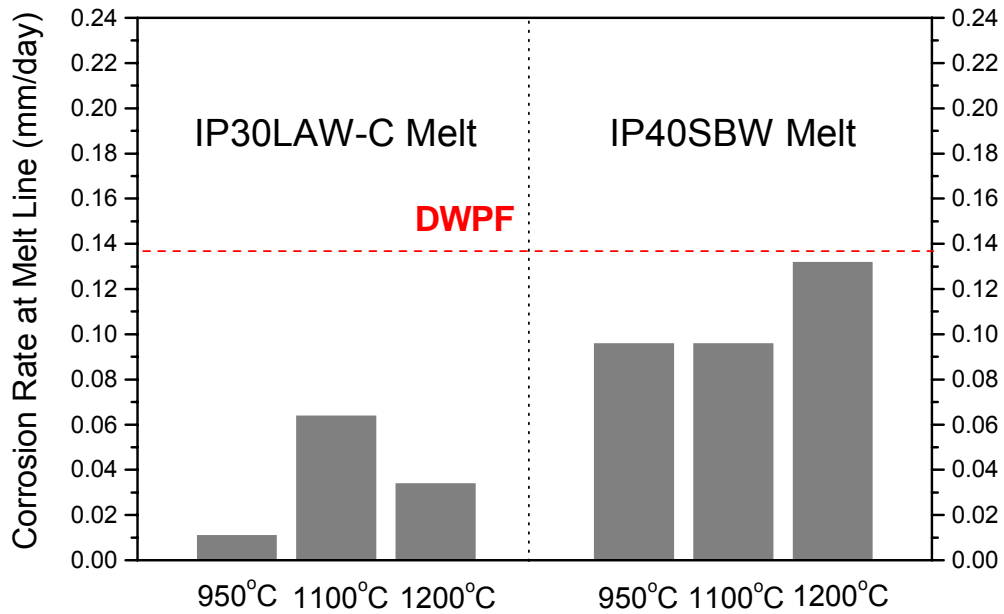


Figure 4. Dynamic corrosion rate of Monofrax K-3 refractory in iron phosphate melts. The red horizontal line, labeled DWPF, denotes a corrosion rate of 0.137 mm/day which was used in designing the Monofrax K-3 refractory lining in the DWPF melter at 1150°C [14].



Figure 5. External surface of a Monofrax K-3 refractory rod after partial immersion and rotation at 9.2 rpm in the IP30LAW-C iron phosphate melt at 1100°C for 7 days. The melt line indicated by red arrows was hardly visible.

A further indication that commercial refractories should provide an acceptable service life in a JHM melting iron phosphate glasses is the experience reported [15] from Russia where nuclear waste has been vitrified in sodium-alumino phosphate glasses for many years. Sodium-alumino phosphate melts are by nature chemically corrosive so they are expected to chemically attack commercial refractories significantly more than iron phosphate melts. Even so, sodium-alumino phosphate glasses have been successfully melted in Russia for up to six years in a JHM lined with commercial AZS refractories. While the experience in Russia for melting sodium-alumino phosphate glasses in a JHM is an indirect indication of the behavior expected for the less chemically corrosive iron phosphate melts, that experience combined with our own measurements of the dynamic corrosion resistance of the Monofrax K-3 refractory by iron phosphate melts indicate that commercial chrome-alumina refractories should be satisfactory as the glass contact refractory and will have an acceptable service life in a JHM melting iron phosphate glass.

4. RELEVANCE AND IMPACT

The iron phosphate melts did not corrode the Inconel 690 to any greater extent than what has been reported for Inconel 690 in the borosilicate melt in the JHM at DWPF. Furthermore, Inconel 693 may be an even better candidate for use in iron phosphate melts since its corrosion rate was only about one half that of Inconel 690. The data from the dynamic corrosion experiments of the candidate refractory, Monofrax K-3, by iron phosphate melts (at the melting temperature and above) are encouraging since the observed corrosion was much lower than expected, based on experience with other phosphate melts, and was less than the corrosion that has been observed in the JHM used to melt borosilicate glass at DWPF.

It is extremely important that the reader understand that iron phosphate glasses have unique properties which place them in a special category of phosphate glasses. Our previous work has shown that iron phosphate glasses have an excellent chemical durability at high waste loadings and can be melted at low temperatures (typically 900-1150°C) in short periods of time. This existing knowledge and the corrosion rates from the present study indicate that iron phosphate glasses and their wastefoms should be a highly effective and low cost alternative to borosilicate glasses, especially for those

wastes which contain components that are poorly soluble in or chemically incompatible with borosilicate glasses.

5. PUBLICATIONS

The following 7 papers on iron phosphate glasses have either been published or are in press during the period (June 1, 2004 to August 31, 2005) covered by this final report.

1. A. S. Aloy, R. A. Soshnikov, A. V. Trofimenko, D. E. Day, C. W. Kim, and D. Gombert, "Iron-Phosphate Glass (IPG) Waste Forms Produced Using Induction Melter with Cold Crucible", *In Scientific Basis for Radioactive Waste Management XXVII*, Mater. Res. Soc. Symp. Proc. 807 (2004) 187-192.
2. W. Huang, D. E. Day, C. S. Ray, C. W. Kim, and A. Moguš-Milanković, "Vitrification of High Chrome Oxide Nuclear Waste in Iron Phosphate Glasses", *J. Nucl. Mater.* 327 (2004) 46-57.
3. C. W. Kim, D. Zhu, D. E. Day, et al., "Iron Phosphate Glass for Immobilization of Hanford LAW", *Ceramic Transactions* 155 (2004) 309-318.
4. W. Huang, D. E. Day, C. S. Ray, C. W. Kim, and S. T. Reis, "Properties and solubility of chrome in iron alumina phosphate glasses containing high level nuclear waste", *Glass Science and Technology* 77 (2004) 203-210.
5. D. Zhu, C. W. Kim, and D. E. Day, "Corrosion behavior of Inconel 690 and 693 in an iron phosphate melt", *J. Nucl. Mater.* 336 (2005) 47-53.
6. C. W. Kim, D. Zhu, and D. E. Day, "Corrosion resistance of metal electrodes in an iron phosphate melt", *Ceramic Transactions* 168 (2005) 59-68.
7. W. Huang, D. E. Day, C. S. Ray, and C. W. Kim, "High temperature properties of an iron phosphate melt containing high chrome nuclear waste", *Journal of Nuclear Materials* (in press).

6. PRESENTATIONS

1. S. Jung, "Monofrax K-3 refractory corrosion in iron phosphate waste glass", American Ceramic Society 107th Annual Meeting, Baltimore, Maryland, April 10-13, 2005.

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induction melting (CCIM) techniques”, *Journal of Nuclear Materials* 322 (2003) 152-164.

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