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IRON PHOSPHATE GLASSES: AN ALTERNATIVE FOR VITRIFYING CERTAIN NUCLEAR WASTES

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EXECUTIVE SUMMARY

The unusual properties and beneficial 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), have been investigated by the University of Missouri-Rolla with support from the Environmental Management Science Program (EMSP), DOE [DE-FG07-96ER45618].

During the past year, the corrosion resistance of Inconel 690 and 693 coupons submerged in an iron phosphate melt at 1050°C for up to 155 days has been investigated to determine whether iron phosphate glasses could be melted in a Joule Heated Melter (JHM) equipped with such electrodes in the same manner as now being used to melt borosilicate glass. Substituting iron phosphate glasses for borosilicate glasses could significantly reduce the time and cost for clean up due to the higher waste loading possible in iron phosphate glass.

The iron phosphate melt, which contained 30 wt% of the Hanford Low Activity Waste (LAW), did not corrode the Inconel 690 to any greater extent than what has been reported for Inconel 690 electrodes in the borosilicate melt in the JHM at the Defense Waste Processing Facility. Furthermore, Inconel 693 appeared to be an even better candidate for use in iron phosphate melts since its corrosion rate (0.7 μm/day) was only about one half that (1.3 μm/day) of Inconel 690.

In the past year, the results of the research on iron phosphate glasses have been described in nine technical papers and one report and have been presented at four international and national meetings.

This grant will terminate on September 30, 2004. However, the investigation of the corrosion resistance of Inconel 690 and 693 will continue till January 31, 2005 on Contract DE-FG02-04ER63831.

1. INTRODUCTION

The vitrification of liquid nuclear waste in a chemically durable glass is considered the most effective way to 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 wastes, presently awaiting disposal at Hanford, WA, Idaho National Engineering and Environmental Laboratory (INEEL), ID, and elsewhere, have more complex and diverse chemical compositions than originally anticipated. 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 below 5 wt%, i.e., 95 wt% of the borosilicate wasteform will consist of additives.

With support from the Environmental Management Science Program (EMSP), DOE [DE-FG07-96ER45618], the University of Missouri-Rolla (UMR) has developed [Patent: U.S. 5,750,824; 12 May 1998] novel iron phosphate glasses as an alternative host matrix for vitrifying nuclear and other hazardous wastes that are not well suited for use in borosilicate glasses. Based upon the promising results to date, iron phosphate glasses appear to offer a practical way to accelerate the clean up of nuclear wastes, especially those stored at Hanford and INEEL. Because of their faster melting, excellent chemical durability, and higher waste loading, 32 wt% for the Hanford LAW [3-5], 48 wt% for the INEEL Sodium Bearing Waste (SBW) [6,7], and 75 wt% for the Hanford HLW [8,9], iron phosphate glasses have the potential to greatly reduce the cost and time for the clean up effort.

While the potential performance of iron phosphate glasses is very promising, we currently lack certain scientific and technical information about how to best melt these glasses on the scale needed for practical use. Melting iron phosphate glasses in a Joule Heated Melter (JHM) is considered the preferred method to investigate 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.

The objective of the research during the past year (June 1, 2003 to May 31, 2004) was to continue to investigate the type and extent of reaction(s) that may occur between iron phosphate melts and Inconel 690 and 693 which are candidate materials for the electrodes in a JHM.

2. RESEARCH PROGRESS

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 might offer a higher corrosion resistance and longer service life.

Table 1. Composition and selected physical properties of Inconel 690 and 693 [10].

		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	7.77
	Melting range (^oC)	1343-1377	1317-1367
	Electrical resistivity ($\mu\Omega\cdot m$)	1.148	1.168

2.1. Preparation of Glass

An iron phosphate glass was prepared which contained 30 wt% of the high sulfate Hanford LAW simulant and 70 wt% glass forming additives Fe_2O_3 and P_2O_5. The overall LAW 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 1050°C for 2 hours in an electric furnace in air. The 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 and iron phosphate batch containing 30 wt% LAW simulant.

	LAW simulant	Batch
Al_2O_3	4.4	1.3
Cl	0.6	0.2
Cr_2O_3	0.4	0.1
F	1.6	0.5
Fe_2O_3	0.0	20.0
Na_2O	75.3	22.6
P_2O_5	7.7	52.2
SiO_2	0.5	0.2
SO_3	9.5	2.9
Total	100.0	100.0

2.2. Corrosion Tests

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 polished to 600 grit SiC paper. The dimensions and weight of each specimen were measured and recorded.

Fifty grams of the as-made iron phosphate glass was re-melted in an alumina crucible at 1050°C for 30 minutes and then one Inconel specimen, which had been preheated to 1050°C, was submerged in the melt. After a prescribed time, 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 weight was measured and the sample again submerged in the melt in the crucible and the corrosion test continued. The iron phosphate melt was replenished every 7 days with new as-made glass to minimize any compositional changes over the entire period of the test.

The weight of each specimen (initial weight 7.07 and 6.29 g for Inconel 690 and 693, respectively) was measured every 7 days, from which the weight loss of the sample was calculated as a function of time. The ratio of the weight difference (initial weight minus weight of specimen after a certain time interval) divided by the initial weight was defined as a percent weight loss at a given testing time. The corrosion tests were terminated after 155 days, whereupon, the final dimensions of each specimen were measured.

2.3. Weight Loss

The total weight loss after being submerged in the iron phosphate melt for 155 days was 14 and 8% for the Inconel 690 and 693 sample, respectively (Figure 1). The calculated weight loss rate for the two samples as a function of time is shown in Figure 2. The weight loss and its rate for Inconel 693 were about one half of that for Inconel 690, indicating that Inconel 693 was more chemically resistant to the melt.

The rate of weight loss for Inconel 690 and 693 was higher at the early stage of the corrosion test, and then gradually decreased with time. At the conclusion of the 155-day test, the weight loss rate was roughly two thirds and one third that of the initial rate for Inconel 690 and 693, respectively. This behavior is consistent with a chemically protective layer forming on the external surface of the metal during the test.

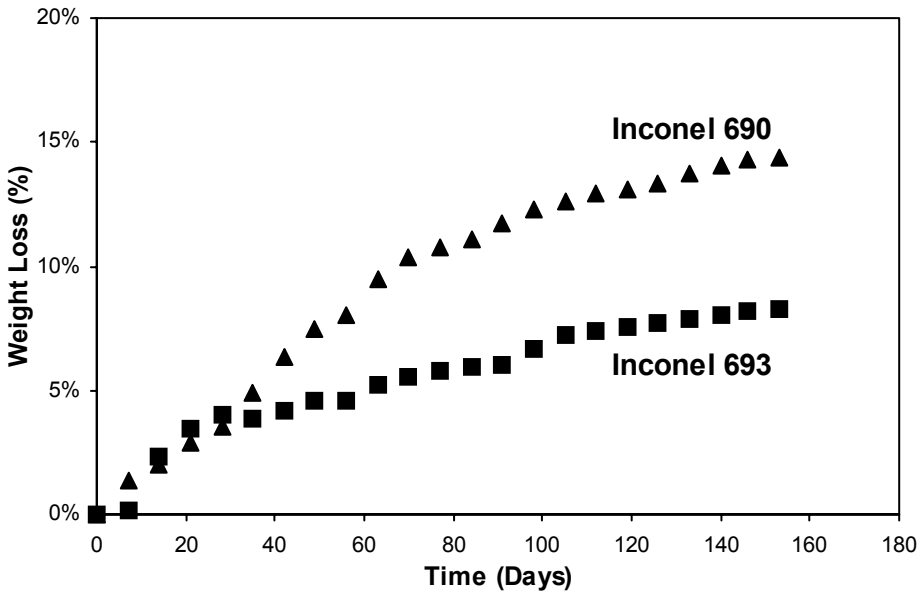


Figure 1. Weight loss (%) of the submerged Inconel 690 and 693 samples as a function of time in an iron phosphate melt containing 30 wt% Hanford LAW at 1050°C. Estimated error is represented by size of data points.

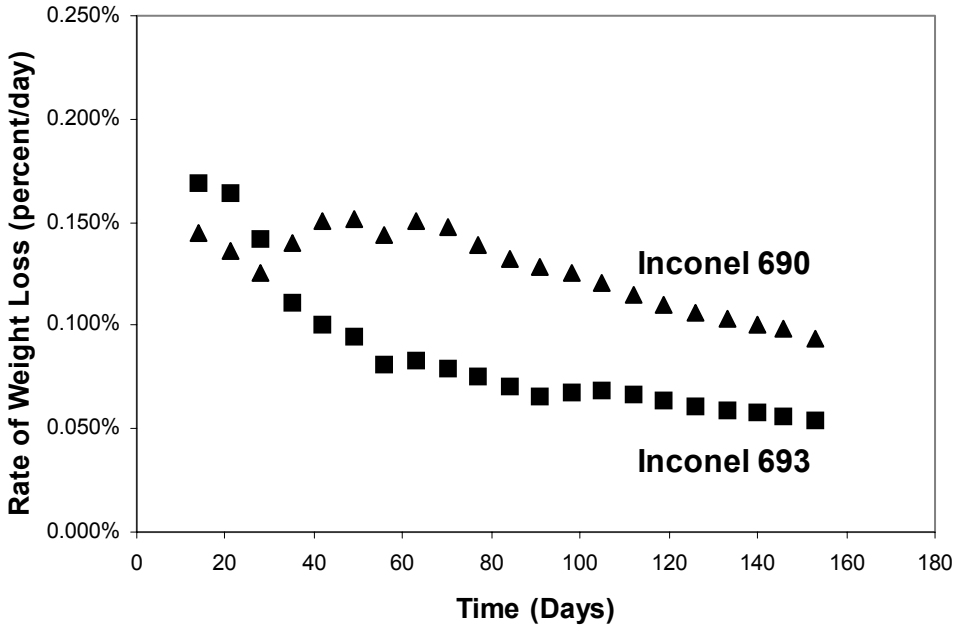


Figure 2. Rate of weight loss (%/day) of the submerged Inconel 690 and 693 samples as a function of time in the iron phosphate melt containing 30 wt% Hanford LAW at 1050°C. Estimated error is represented by size of data points.

The corrosion rate of Inconel 690 and 693 was also determined by measuring the initial and final dimensions of the samples after the 155-day test. The overall corrosion rate (calculated by assuming a constant rate from time = 0) was 1.3 and 0.7 μm/day for the submerged Inconel 690 and 693 sample, respectively. These values are significantly smaller than the 6.5 μm/day rate reported [11] for the Inconel 690 electrodes in a JHM being used to melt borosilicate glass at 1150°C in the DWPF at Savannah River. The typical appearance of the cross section of the submerged Inconel 693 sample after 155 days is shown in Figure 3.

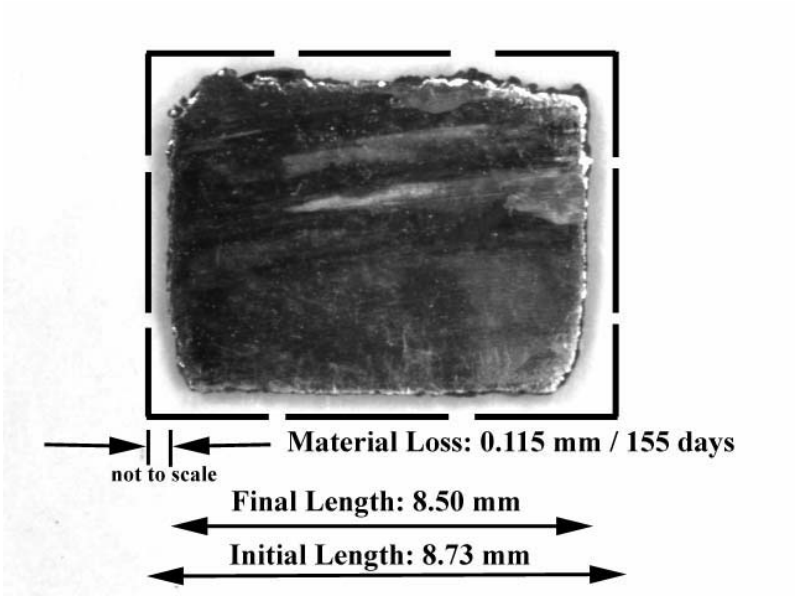
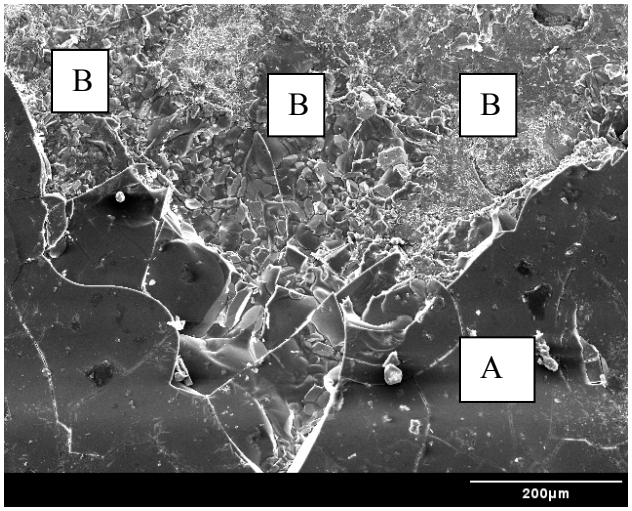


Figure 3. Cross sectional view of the Inconel 693 sample after the corrosion test at 1050°C for 155 days (0.115 mm/155 days = 0.7 μm/day). Note box around sample not to scale.

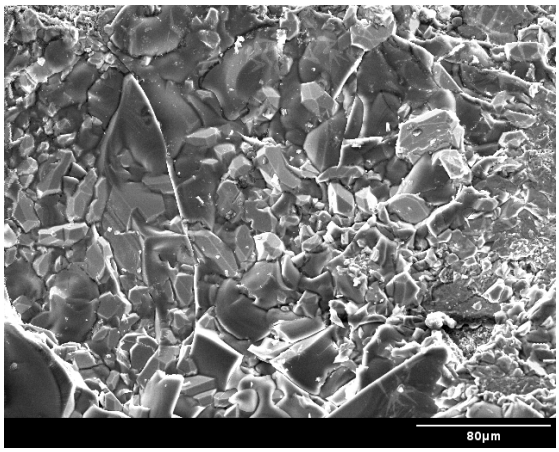
2.4. Corrosion Products

Only one alteration phase or corrosion product was found at the external surface of the Inconel 690 sample submerged for 155 days in the iron phosphate melt containing 30 wt% Hanford LAW simulant. SEM micrographs and EDS spectra for this Fe-rich solid solution of $(Fe, Cr)_2O_3$ phase are shown in Figure 4. Similarly, there was one main alteration phase at the surface of the Inconel 693 sample, but it was composed of crystals having two different morphologies (Figure 5). There were smaller grain-like crystals such as those in Figure 5(b) (Cr-rich solid solution of $(Fe, Cr)_2O_3$) and larger platy crystals, Figure 5(c), (Fe-rich solid solution of $(Fe, Cr)_2O_3$). The presence of only the Fe-rich phase in the Inconel 690 sample may be due to its higher iron content (7-11 wt%) compared to the lower iron content (2.5-6.0 wt%) of Inconel 693, see Table 1. This suggests that iron corrodes more easily than chromium and that substituting other components such as Al, Nb, and Ti for Fe in Inconel 693 (Table 1) enhances its corrosion resistance.

(a)



(b)



(bb)

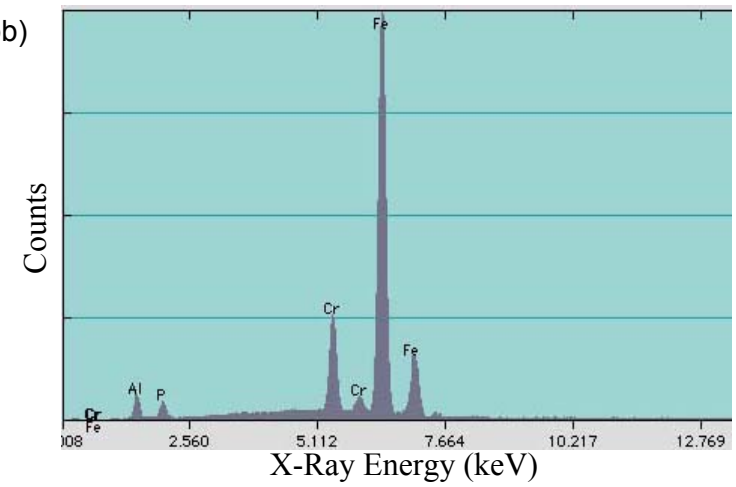


Figure 4. (a) SEM micrograph of the external surface of the Inconel 690 sample after the 155-day corrosion test. A: residual glass attached to the surface; B: Fe-rich solid solution $(Fe, Cr)_2O_3$ alteration phase. (b) Close-up view of the Fe-rich $(Fe, Cr)_2O_3$ phase in area B. (bb) EDS spectra for the Fe-rich $(Fe, Cr)_2O_3$ phase.

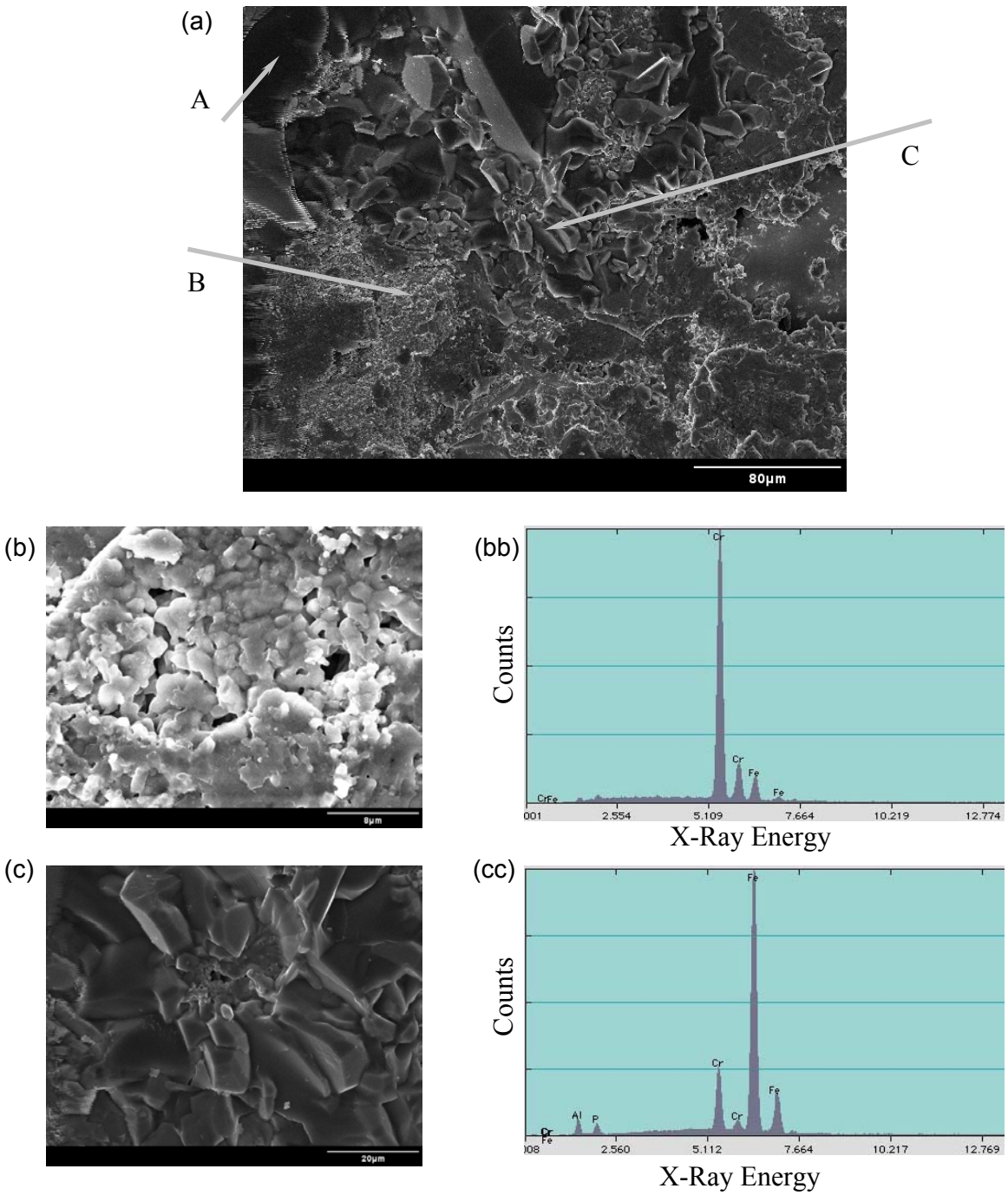
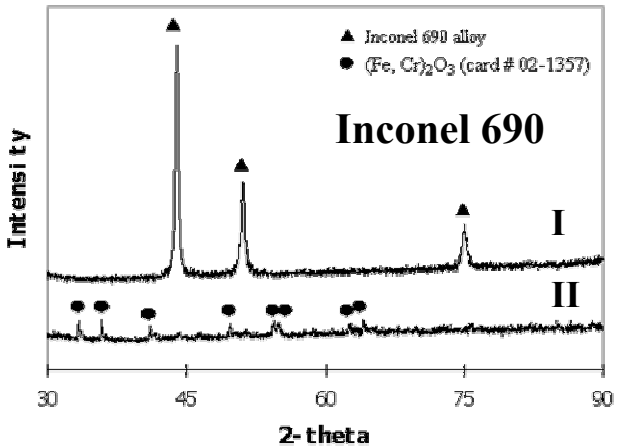


Figure 5. (a) SEM micrograph of the surface of the Inconel 693 sample after the corrosion test. A: residual glass attached to the surface; B: Cr-rich solid solution (Fe, $Cr)_2O_3$ alteration phase; C: Fe-rich solid solution (Fe, $Cr)_2O_3$ alteration phase. (b) Close-up view of the Cr-rich (Fe, $Cr)_2O_3$ phase in area B. (bb) EDS spectra for the Cr-rich (Fe, $Cr)_2O_3$ phase. (c) Close-up view of the Fe-rich (Fe, $Cr)_2O_3$ phase in area C. (cc) EDS spectra for the Fe-rich (Fe, $Cr)_2O_3$ phase.

The XRD spectra of Inconel 690 and 693 before and after the corrosion test are shown in Figure 6. The XRD Peaks for the Inconel 690 and 693 samples before corrosion were consistent with FCC alloys as expected. Diffraction peaks from the corroded samples of Inconel 690 and 693 corresponded to those for $(Fe, Cr)_2O_3$ (JCPDS-ICDD card # 02-1357). It should be noted that the diffraction peaks corresponding to the fresh Inconel alloys were also detected on the external surface of the corroded Inconel 693 sample (Figure 6(b)-II), while these peaks were absent on the corroded Inconel 690 surface. The thinner alteration layer (~20 μm) on the external surface of Inconel 693, compared to the ~40 μm thick layer on the Inconel 690 sample, indicates that the Inconel 693 was corroded less than 690, which is consistent with the presence of the diffraction peaks corresponding to the fresh Inconel alloy.

(a)



(b)

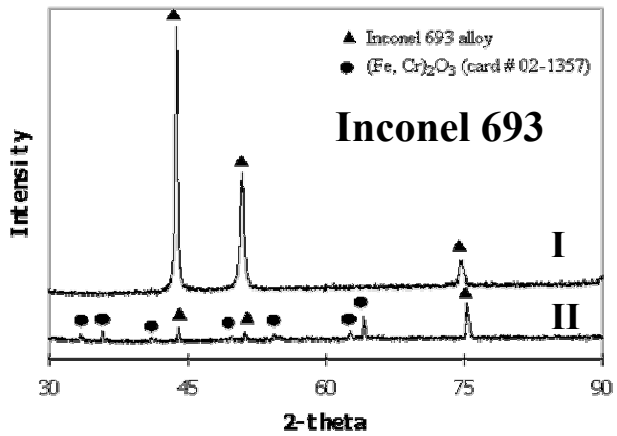


Figure 6. (a) XRD spectra for the Inconel 690 sample before (I) and after (II) the corrosion test. (b) XRD spectra for the Inconel 693 sample before (I) and after (II) the corrosion test.

No Ni-containing phase, such as $NiCr_2O_4$ (a Ni/Cr containing spinel) or $NiFe_2O_4$ (a Ni/Fe containing spinel), was detected on the surface of the corroded Inconel 690 and 693 samples, even though Ni was the main component (> 53 wt%) in each metal. However, Ni was detected by X-ray fluorescence in the glasses after corrosion tests. These results suggest that all the Ni lost from the Inconel samples go into the glass melt rather than forming an alteration phase on the metals.

3. SUMMARY

The overall corrosion rate of Inconel 690 and 693 submerged for 155 days in an iron phosphate melt containing 30 wt% Hanford LAW stimulant at 1050°C was small, 1.3 and 0.7 μm/day for Inconel 690 and 693, respectively. The corrosion resistance of Inconel 693 was about twice that of Inconel 690 in the iron phosphate melt as measured by the weight loss and dimensional changes.

The surface of both Inconels at the completion of the corrosion test was depleted in Ni and composed of a layer of $(Fe, Cr)_2O_3$, which appeared to act as a chemically protective layer on the metals.

These preliminary results are encouraging since the iron phosphate melt did not corrode the Inconel 690 to any greater extent than what has been reported for Inconel 690 electrodes 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.

4. PUBLICATIONS

The following ten papers on iron phosphate glasses have either been published or in press during the 12 month period covered by this progress report.

1. C. W. Kim, D. Zhu, and D. E. Day, “Corrosion resistance of metal electrodes in an iron phosphate melt”, *Ceramic Transactions* (in press).

2. 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 HLW”, *Glass Science and Technology* (in press).

3. A. S. Aloy, R. A. Soshnikov, A. V. Trofimenko, D. Gombert, D. E. Day, and C. W. Kim, “Iron-phosphate glass (IPG) waste forms produced using Induction Melter with Cold Crucible”, *In* Scientific Basis for Nuclear Waste Management XXVII (in press).

4. C. W. Kim, D. Zhu, D. E. Day, D. S. Kim, J. D. Vienna, D. K. Peeler, T. E. Day, and T. Neidt, “Iron phosphate glass for immobilization of Hanford LAW”, *Ceramic Transactions* 155 (2004) 309-318.

5. 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”, *Journal of Nuclear Materials* 327 (2004) 46-57.

6. C. W. Kim, C. S. Ray, D. Zhu, D. E. Day, D. Gombert, A. Aloy, A. Moguš-Milanković, and M. Karabulut, “Chemically durable iron phosphate glasses for vitrifying sodium bearing waste (SBW) using conventional and cold crucible induction melting (CCIM) techniques”, *Journal of Nuclear Materials* 322 (2003) 152-164.

7. C. W. Kim and D. E. Day, “Immobilization of Hanford LAW in iron phosphate glasses”, *Journal of Non-Crystalline Solids* 331 (2003) 20-31.

8. D. S. Kim, W. C. Buchmiller, 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).

9. C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, “Iron phosphate glasses for vitrifying sodium bearing waste”, *Ceramic Transactions* 143 (2003) 329-336.

10. W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, “Solubility of high chrome nuclear wastes in iron phosphate glasses”, *Ceramic Transactions* 143 (2003) 347-354.

As of the date of this report, more than sixty technical papers on iron phosphate glasses have been published since EMSP started supporting this work in 1996.

5. PRESENTATIONS

1. C. W. Kim, D. Zhu, and D. E. Day, “Corrosion resistance of metal electrodes in an iron phosphate melt”, American Ceramic Society 106th Annual Meeting, Indianapolis, Indiana, April 18-21, 2004.

2. C. W. Kim and D. E. Day, “Iron phosphate glasses for vitrifying DOE high priority nuclear wastes”, Environmental and Waste Management: Advances through the Environmental Management Science Program, 227th American Chemical Society Meeting, Anaheim, California, March 28-April 1, 2004.

3. C. W. Kim, D. E. Day, and A. S. Aloy, “Iron phosphate glasses for nuclear waste vitrification”, Alternative Nuclear Waste Forms, Engineering Conferences International, Alaska, U.S.A., January 18-23, 2004 (invited).

4. 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”, MRS 2003, Scientific Basis for Radioactive Waste Management XXVII, Kalmar, Sweden, June 15-18, 2003.

6. REFERENCES

1. S. L. Lambert and D. S. Kim, “Tank Waste Remediation System High-Level Waste Feed Processability Assessment Report”, PNNL #WHC-SP-1143, Pacific Northwest National Laboratory, Hanford, WA (1994).
2. 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).
3. C. W. Kim and D. E. Day, “Immobilization of Hanford LAW in Iron Phosphate Glasses”, *J. Non-Cryst. Solids* 331 (2003) 20-31.
4. D. S. Kim, W. C. Buchmiller, 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, R. J. Workman, “Iron Phosphate Glass as an Alternative Waste-Form for Hanford LAW,” *PNNL-14251*, Pacific Northwest National Laboratory, Richland, WA (2003).
5. C. W. Kim, D. Zhu, D. E. Day, D. S. Kim, J. D. Vienna, D. K. Peeler, T. E. Day, and T. Neidt, “Iron phosphate glass for immobilization of Hanford LAW”, *Ceramic Transactions* 155 (2004) 309-318.
6. C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, “Iron phosphate glasses for vitrifying sodium bearing waste”, *Ceramic Transactions* 143 (2003) 329-336.
7. C. W. Kim, C. S. Ray, D. Zhu, D. E. Day, D. Gombert, A. Aloy, A. Moguš-Milanković, and M. Karabulut, “Chemically durable iron phosphate glasses for vitrifying sodium bearing waste (SBW) using conventional and cold crucible induction melting (CCIM) techniques”, *Journal of Nuclear Materials* 322 (2003) 152-164.
8. W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, “Solubility of high chrome nuclear wastes in iron phosphate glasses”, *Ceramic Transactions* 143 (2003) 347-354.
9. 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”, *Journal of Nuclear Materials* 327 (2004) 46-57.
10. www.specialmetals.com.
11. Personal Communication, D.F. Bickford, Westinghouse Savannah River Company (2003).

APPENDIX 1

Milestone Status Table

Task / Milestone Description	Planned Completion	Actual Completion	Comments
Identification of High Priority Candidate Wastes	6/15/02	6/15/02	
Evaluation of Candidate Refractories and Electrode Materials	6/15/03		Extended to 9/30/04
Evaluation of Raw Materials/Use of Industrial Wastes	6/15/03	6/15/03	
Evaluation of Melting Conditions/Techniques	6/15/03		Extended to 9/30/04
Wasteform Property and Characterization Measurements	6/15/03		Extended to 9/30/04
Preparation of Final Report	9/15/03		Extended to 9/30/04

APPENDIX 2

Budget Data

		Approved Spending Plan			Actual Spent to Date		
Budget Period		DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
From	To						
9/15/00	9/30/04	520,000	-	520,000	490,541*	-	490,541*

* As of May 31, 2004

Spending Plan for the Next Months

Month	Estimated Spending
June 04	10,500
July 04	10,500
August 04	4,200
September 04	4,259