IRON PHOSPHATE GLASS AS POTENTIAL WASTE MATRIX FOR HIGH-LEVEL RADIOACTIVE WASTE

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ABSTRACT

Recently, Iron Phosphate Glass (IPG) is investigated as the alternative final waste form for High-Level Radioactive Waste (HLW) in U.S. This study is aimed to investigate feasibility of IPG to HLW arising from commercial reprocessing in Japan. In order to evaluate favorable preparation conditions, maximum waste loading and property of IPG, the melting tests were carried. From the results of melting tests, the favorable preparation conditions was with matrix of Fe / P 0.43 (mole ratio in products) and melting at 1200□ for 4h. The products of 10-20mass% waste loading of simulated HLW were glassy and had no crystal peaks, however the product of 30mass% waste loading showed some crystal peaks by XRD analysis. IPG and Borosilicate glass (BG) had about the same thermal properties. As a result, IPG had enough potential for high waste loading and the extremely good chemical durability for consideration as a waste form for Japanese HLW.

INTRODUCTION

BG is to be applied as the final waste matrix for HLW in Japan where the commercial vitrification facility is under construction in Rokkasho Village in Aomori Prefecture. Considering, that the chemical composition of HLW may change in the future resulting from the use of MOX fuels and high burn-up fuels, there is a possibility to extend spent fuel storage period, and it is definitely important to reduce total final waste volume, development of potential waste matrix which is flexible to compositional change and high waste loading of HLW is worth to study.

Recently, The investigation on IPG is recommended for consideration as an alternative final waste form for HLW in U.S. IPG has the feature of flexibility in dealing with chemical compositional changes, high waste loading and has a generally good chemical stability [1-3]. In addition, IPG seems to have different and independent glass property with respect to it's response to chemical waste components and different and perhaps better chemical stabilities, as compared to conventional borosilicate glass [4,5].

This study is aimed at investigating the feasibility of using IPG for vitrification of HLW arising from commercial reprocessing in Japan. Because the elemental and chemical composition of Japanese HLW is significantly different from US HLW, in part due to commercial reprocessing of the spent nuclear fuel, especially with respect to DOE defense wastes. Followings were studied in order to evaluate several characteristic of IPG.

- -Effect of melting operations (Crucible material, Temperature, Melting time)
- -Effect of matrix compositions (Fe/P: Mole ratio in IPG)
- -Waste loading (HLW, Na_2O)

EXPERIMENTAL METHODS

Preparation of products

The desired amount of HLW surrogate, which was prepared from reagent grade chemicals, were mixed with batch glass materials in a crucible (150 cc), and vitrified products were prepared by heating the crucible in an electric furnace. Cooling method of products was selected in accord with the purpose of the test and included [a] natural cooling, [b] forced cooling and [c] controlled annealing.

The chemical composition of Simulated HLW in Japan is shown in **Table 1**. Nd was used as surrogate for the actinide elements and the minor elements (smaller than 1 mol%) were eliminated from Simulated HLW, as is traditional with simulant testing. The chemical components of simulated HLW were added as oxides, but Na and Cs were used in their carbonate forms.

Test parameters were selected to study [a] A variety of crucible materials, [b] melting temperatures & melt time, [c] Fe/P matrix ratio and to [d] investigate maximum waste loading with diverse glass formations. Test parameters are described in **Table 2**.

Table1. Chemical composition of Simulated HLW

Oxides		mass%
Fission products	SrO	2.15
	ZrO_2	16.66
	MoO_3	10.65
	RuO_2	5.82
	PdO	3.29
	TeO_2	1.25
	Cs_2O	5.81
	BaO	3.84
	La_2O_3	3. 06
	CeO_2	6.24
	Nd_2O_3	16.12 *
	Gd_2O_3	7.51
Corrosion products	Fe_2O_3	13.44
	Cr_2O_3	2.29
	NiO	1.90
Total		100.00

* 5.38% of Actinides was replaced by Nd_2O_3

Table 2. Test Parameters

Item		Parameters
Effect of melting operations	Crucible material	Metal (SUS316, Ni), Silicon Carbide, Carbon, and various Ceramics (Alumina, Zirconia, etc.)
	Temperature (°C)	1000 - 1300 (heated for 2 hours)
	Time (Hours)	1 - 8 (Both at 1000 and 1200 °C)
Effect of matrix composition	Fe/P molar ratio	0.25, 0.43 and 0.67
Waste loading (mass%)		HLW : 10 - 40 mass% Na_2O : 0 - 10 mass%

Analysis of products

The products were analyzed by X-ray diffractometry (XRD) and Scanning electron microscopy / Energy dispersive X-ray spectroscopy (SEM/EDX) on crystallization. Crystallinity of product can be given by **equation (1)** from XRD data. The reason to use this value is to find some relationship with testing parameters for the products.

$$\text{Crystallinity X [\%]} = Icr / (Icr + Ia) \times 100 \qquad (\textbf{Eq.1})$$

Icr Integral calculus strength of a crystalline structure
Ia Integral calculus strength of a non-crystalline structure

The dissolution of crucible material in the products and the solubility of HLW components were evaluated by XRF analysis. The chemical durability of the products was measured by Production consistency test (PCT) [6] in order to understand basic leaching property.

TEST RESULTS AND DISCUSSION

Effect of melting operations

First of all, the melting tests in various crucible materials were carried out in order to select appropriate crucible material for melting. Because IPG melts has relatively corrosive feature than BG melts for crucible materials and appropriate material is important to eliminate vitrified products contaminated and adversely effected. Alumina (Al_2O_3>97 mass%), Silicon carbide (SiC >98%), Spinel (Al_2O_3: 71 mass%, MgO: 28 mass%) and Magnesia (MgO >99.7mass%) had no appearance corrosion or erosion. But, Zirconia (ZrO_2: 93 mass%, CaO: 5 mass%) cracked by thermal shock. Carbon crucibles burned (oxidized) and metal crucibles were heavily corroded. From XRF results, the dissolution of crucible materials into products are shown in **Table 3.** The dissolution of Silicon carbide, spinel and magnesia was greater than that of alumina. Since IPG is an acidic material, an acidic or amphoteric compatible material is considered to be suitable material. As a result, Alumina was selected as crucible material. D. E. Day et al. reported that Zircon, Alumina and Chrome were suitable for IPG melting, results of this work are in good agreement with the report [7]

In order to evaluate the dissolution of crucible material during melting, the relationship with melting temperature or time and dissolution of Al_2O_3 analyzed by XRF analysis. As shown in **Figure 1**, dissolution of Al_2O_3 increased with the increase of melting temperature, melting time, waste loading and Fe/P ratio.

Table 3. Dissolution of crucible materials into glass

		Acidic oxide	Amphoteric	Basic oxide		SiC[b]
		Zirconia[a]	Alumina	Spinel	Magnesia	
Chemical composition		ZrO_2: 93% CaO: 5%	Al_2O_3 >97%	Al_2O_3: 71% MgO: 28%	MgO >99.7%	SiC >98%
Dissolution Ratio [%]	Fe/P:0.43	NA	1.2	3.8	5.3	1.3
	Fe/P:0.67	6	1.1	2.2	3.7	1.4

a Mostly dissolution of CaO was estimated

b Mostly dissolution of SiO_2 was estimated.

NA: Not available

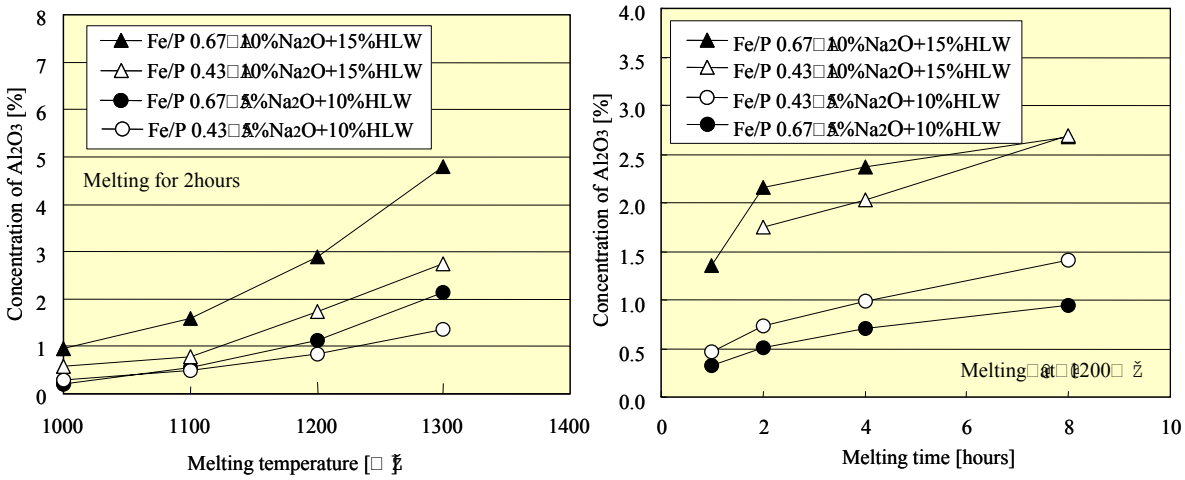


Figure1. Relationship with melting temperature or time and dissolution of Al_2O_3

In order to investigate influence of melting operations to Crystallinity, the relationship with melting temperature or time and Crystallinity was analyzed by XRD. Comparing with visual observation and XRD results, Crystallinity value below 30% seemed to represent glassy product. Products of Fe/P matrix ratio with 0.43 or at high melting temperature tended to be more glassy. But, products of high waste loading tended to be crystalline. As a result, it was found that favorable preparation conditions for glassy ,low dissolution of Alumina and high waste loading was with matrix of Fe / P ratio 0.43 and melting at 1200□ for 4h. (**Table 4.**)

Table 4. Setting Basic Melting Conditions

Fe/P	0.43			0.67		
Waste loading	10mass%Na_2O + 15mass%HLW					
Melting temperature [°C]	1200		1300	1200		1300
Melting time [hours]	4	8	2	4	8	2
Crystallinity [%]	23.2	27.7	27.9	68.0	46.3	69.1
. Dissolution of Al_2O_3 [%]	2.03	2.69	2.83	2.37	2.68	4.80

Effect of matrix composition and Waste loading

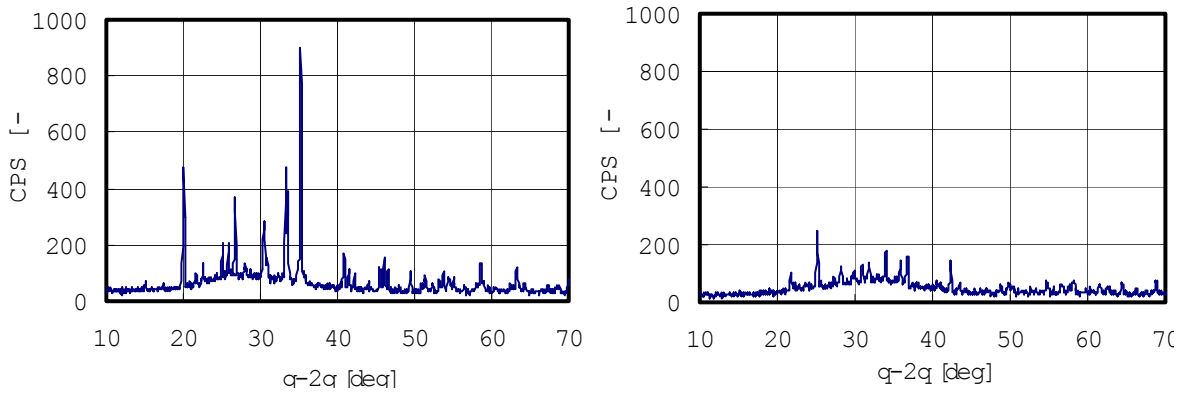
In order to compare capability of IPG with borosilicate glass, we studied the relationship with waste loading and crystallinity of products. There are some issues to be considered when deciding maximum waste loading such as physical properties, chemical stabilities, thermal transformation and so on. From previous studies in Japan, acceptable waste loading for BG is about 20 to 30 mass%.

The IPG products of 10-20 mass% waste loading of simulated HLW were glassy and have no crystal peaks. The product of 30 mass% waste loading showed some crystal peaks by XRD analysis, the peaks were identified as zirconium phosphate by SEM/EDX analysis. The product of 40 mass% waste loading was almost crystalline. As a result, the waste loading of IPG was almost comparative to BG. A table with such information would be nice.]

From results of XRD analysis, crystallinity increased with waste loading and Fe/P ratio. Especially, the crystallinity of the product with Fe/P ratio of 0.67 increased greatly. Crystallinities below 30 mass% is almost glassy. In order to prepare product of high waste loading (>30 mass%) and glassy form, low Fe/P ratios are preferred [e.g., 0.43 to 0.25].

XRD on crystallized products are shown in **Figure 2.** Product of natural cooling (Fe/P 0.43, 5 mass% Na_2O + 30 mass% HLW) observed crystal peak of iron sodium phosphate ($NaFeP_2O_7$). On the other hand, product of high waste loading (Fe/P 0.43, 5% Na_2O + 30% HLW) observed crystal peak of Zirconium phosphate (ZrP_2O_7). Therefore waste loading condition and cooling condition can influence to kind of crystals in the products.

Also, we observed some influences of cooling conditions on the crystal associated peaks even ~~in~~ for the same waste loading. From viewpoint of distinguishing whether the product is actually a good and stable waste form, it is necessary to know the relationship between crystal species identification and those effects to chemical durability.



(Fe/P Ratio 0.43, 5%Na_2O+10% HLW, natural cooling) (Fe/P Ratio 0.43, 5% Na_2O+30% HLW, forced cooling)

Figure 2. XRD crystal peaks influenced by waste loading and/or cooling method

<u>The Solubility of HRLW Components in IPG Glass Products</u>

In order to consider homogeneous solubility of HLW elemental components in product, existence state of HLW components was observed by SEM/EDX analysis. BSE pattern and EDX pattern of product at Fe/P ratio 0.43 and 5 mass% Na_2O + 30 mass% HLW are shown in **Figure 3**. Na, Cs, Ni and Al were in the glass phase. Nd and Ce formed phosphate and Pd, Ru and Te were metallic.

The numbers of element species identified in product increased with HLW loading. Five element species (Group) in product were identified in the case of HLW 30 mass%.

- Group 1 is glassy and consists of glass matrix and Na.
- Group 2 is glassy and partially crystal, it consists of elemental lanthanides and P.
- Group 3 is glassy and partially crystal, it consists of glass matrix, Zr and Na.
- Group 4 is a metal deposit and consists of Pd and Te.
- Group 5 is a metal deposit, it consists of Ru.

From this result, the solubility of chemical components was summarized in **Table 5**. The elements of valence +1,+2 and +4 have high solubility. Mo has low solubility in BG and tend to form yellow phase, however it has high solubility (>50%) in IPG. From results of EDS analysis, Platinum group (Pd, Rh, Ru) formed the alloy. Especially, the concentration of Pd in the alloy was high. For this reason, we suspect that Pd has a high generation free energy as an oxide.

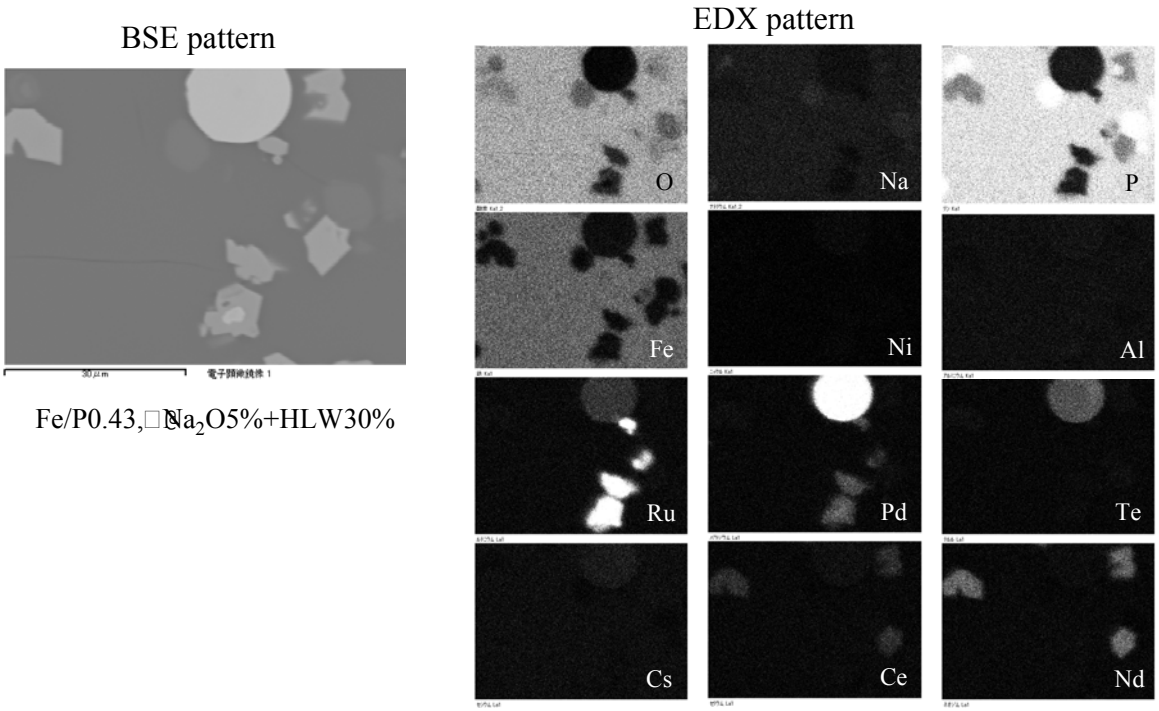


Figure 3. Elemental dispersion in the products

Table 5. Solubility of Chemical Components

Valence	Group	Element	Behavior
+1	Alkaline metal	Na, Cs	Na : Soluble in glass Cs : Soluble in glass and volatilization
+2	Alkaline earth metal	Ca, Sr, Ba	Soluble in glass (High solubility)
		Ni	Soluble in glass
	Platinum group	Pd	Metal deposit [ΔG of oxide□Pd□Cu□Pb□Ni]
+3	Amphoteric element	Al	Soluble in glass
	Glass matrix	Fe	□
	Lanthanide	La, Nd, Gd	Soluble in glass and Crystal of phosphate
+4		Zr	Soluble in glass and Crystal of phosphate
	Platinum group	Ru	Soluble in glass, Metal deposit and volatilization
		Te	Soluble in glass, Metal deposit and volatilization
	Lanthanide	Ce	Soluble in glass and Crystal of phosphate
+5	Glass matrix	P	□
+6		Mo	Soluble in glass (High solubility) and volatilization

Physical and Chemical Properties of the Glass Products

Physical properties of products and measurement method are shown in **Table 6**. The density is higher than BG (about 2.7g/cm^3) and increases with Fe/P ratio and waste loading. IPG and BG have about the same thermal expansion and thermal conductivity. Altogether, the property of the products depends on Fe/P ratio, which ratio is an important factor to IPG.

Results of PCT for 7 days showed that IPG had extremely good chemical durability. The leaching rate of Fe/P ratio 0.25 was greater than that of Fe/P ratio 0.67 (**Figure 4**.). In order to prepare product of low leaching rate, high Fe/P ratio is preferred such as 0.43 or 0.67. The chemical compositions of Group1 (Na, Cs, Ba and Mo) showed higher normalized leaching rate than the other compositions of products. The chemical compositions of Group 2 and 3 (Zr, lanthanide element), which have partial crystalline in it, had smaller normalized leaching rates than the other compositions. For this reason, we consider that phosphate of Zr and lanthanide elements have low solubility in leaching solution.

In order to increase waste loading, it is important to know the relation between crystallization and chemical durability of the products. Additional screening studies should be further performed on crystalline IPG. to know its potential features.

Table 6. Properties of the Glass Products

Property	Method	Obtained value
Density	Archimedes' method	2.90-3.45 [g/cm^3]
Thermal expansion	Differential expansion meter	7.3-14.9 [10^{-6}/□] (between 20 and 500□)
Thermal conductivity	Laser flush method	1.2-1.45[W/m□K] (at 100□) 1.05-1.30 [W/m□K] (at 300□)
Specific heat		0.96-1.28 [J/g□K] (at 300□)
Chemical durability	PCT	About 10^{-9}[g/cm^2/min] (at 90□,7days)

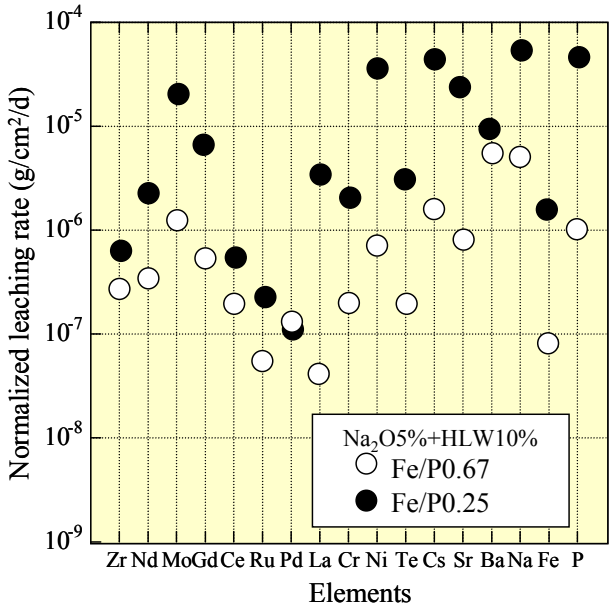


Figure 4. Relationship Between Chemical Durability and the Fe/P Ratio (PCT Test Results)

CONCLUSIONS

This study indicates that IPG have enough potential for high waste loading and the extremely good chemical durability for Japanese HLW. However, the waste loading of glassy IPG is comparative to BG. In order to increase waste loading, further study on crystalline IPG is expected in the near future.

ACKNOWLEDGEMENTS

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