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Chemical durability of iron-phosphate glass as the high level waste from pyrochemical reprocessing

Hirohide Kofuji [a]*, Tetsuji Yano[b], Munetaka Myochin[a],
Kanae Matsuyama[c], Takeshi Okita[c], Shinya Miyamoto[c]

[a]Japan Atomic Energy Agency, 4-33 Tokai-mura, Naka-gun, Ibaraki 319-1194, Japan
[b]Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan
[c]Toshiba corporation, 4-1 Ukishima-cho, Kawasaki-ku, Kawasaki 210-0862, Japan

Abstract

As a part of the research and development for the nuclear waste disposal concept suitable to the advanced fuel cycle systems and its performance evaluation, the iron-phosphate glass is examined as an alternative waste form for high level waste generated from pyrochemical reprocessing. In order to enhance the waste element content in the glass matrix and improve the durability of the waste form, optimization experiments of glass composition were carried out and the effect of additional other transition metal oxides was found out in this study.

Keywords: Iron phosphate glass; high level waste form; chemical durability; dissolution rate

1. Introduction

Metal electrorefining process is one of the pyrochemical reprocessing technologies and it has been developed as a candidate of the future reprocessing technique for fast breeder reactor (FBR) fuel cycle [1].

In the process, accumulated fission products (FP) elements in the electrorefiner are adsorbed to the zeolite and removed from molten salt. The FP containing zeolite is converted into glass bonded sodalite by HIP (Hot

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* Corresponding author. Tel.: +81-29-282-1111; fax: +81-29-282-9257.
E-mail address: kofuji.hirohide@jaea.go.jp.

Isostatic Pressing) method. The feasibility of such a method has been already confirmed well however the FP contents in the sodalite are relatively low (4 - 5 wt%) compared to the conventional borosilicate glass (>10 wt%) waste form which has been developed for the treatment of high activity waste generated from PUREX reprocessing [1]. Low content of FP elements in the sodalite leads to the increase of the high level waste volume therefore the reduction of waste volume has been recognized as one of the most important issues for the future development.

In order to reduce the volume of HLW, the phosphate conversion procedure has been examined as an alternative treatment method for spent electrolyte in Japan Atomic Energy Agency (JAEA) [2].

A phosphate glass is a suitable material for the solidification of the nuclear waste because rare earth FP chlorides can be easily converted into phosphate and removed from molten salt with phosphate glass filter. The phosphate glass essentially has low chemical durability due to the hydrophilic -P=O functional group existing in the glass network structure. However, according to the study of Day et al., chemical durability is largely increased by addition of Fe and formed iron phosphate glass can be used for the military nuclear waste which was difficult to be treated with borosilicate glass in US [3]. The waste elements can be contained more than 35 wt% in iron phosphate glass and chemical durability was not inferior to borosilicate glass in that study. Furthermore, it was shown that chemical durability was large at 30/70 - 40/60 in Fe/P molar ratio and the addition of multivalent metal oxide, i.e. Al_2O_3 strengthen the glass network structure and increases the durability of iron phosphate glass [4].

In the investigation for silicate glass [5], the ratio of non-bridging oxygen was reduced and dissolution rate of Si was decreased in the case of large hydration energy in the glass. Similarly for iron phosphate glass, dissolution of Fe is controlled in the case of higher ratio of bridged oxygen [6].

Referring to the preceding investigations, the adaptability of iron phosphate glass was evaluated as the high level waste form generating from pyrochemical reprocessing in this study. Basic mole ratio of Fe/P was set to 30/70 and several kinds of physical property and chemical durability were evaluated. In order to improve the glass properties, Co and Cr were added as a part of Fe as the element which have large hydration energies.

Some physical properties are measured for the glass sample in the viewpoint of applicability to the waste form.

2. Experimental

2.1. Preparation of glass sample

2.1.1. Glass composition

As the basic glass composition, molar ratio of Fe/P was adjusted to 30/70 and simulated fission product (FP) was added by outer percentage. The composition of added FP was determined according to that of spent electrolyte using for pyrochemical reprocessing [1]. Its composition is shown in table 1. The selected FP elements in the experiments had higher abundance in the spent electrolyte. In order to confirm the effect of additional transition metal, Cr, Co and Zn containing glass samples were prepared. Chromium(III) was expected as the crosslinkage element instead of Fe(III). Cobalt was added to control the generation of crystal in the glass and Zn was to decrease the glass melting temperature. The basic composition and parameters of all glass samples evaluated are shown in table 2.

Total simulated FP oxides added to the glass sample were from 5 to 35 wt%.

2.1.2. Glass preparation

The reagent grade chemicals (purities were 99% or more) were used for the experiments. As the resource of phosphorus, $NH_4H_2PO_4$ (99% purity) was used for the sample IP 1 - 6, H_3PO_4 (85% purity) was used for the sample IP 7 and 8. The prior prepared iron phosphate glass cullet was used as the basic composition for glass sample IP 1 - 3. Weighed raw materials were mixed in a high purity alumina crucible and heated up to the glass

melting temperature, 1200 - 1300°C and melted for 4 hours. After casted into carbon mold and cooled, glass samples were annealed between 500 and 550°C for 1 hour. After annealing, they were slowly cooled to the room temperature in the annealing furnace.

Formed glass samples were shaped in 10mm cube and their surfaces were polished with #800 - 1000 emery paper. After washing and drying, they were provided to the glass properties measurement and dissolution tests.

The homogeneity of the glass samples were estimated with XRD (X-ray Diffraction, RINT Ultima III, Rigaku Corp.) and SEM/EDS (Scanning Electron Microscopy – Energy Dispersive Spectroscopy, JSM-6360LA, JEOL Ltd.).

Table 1. Simulated FP composition

Element	Oxides	Content [mol% in oxide form]	
		IP 1 - 3, IP 8	IP 4 - 6
Cs	Cs_2O	1.70	1.92
Sr	SrO	6.73	6.97
Ba	BaO	15.7	16.2
Y	Y_2O_3	2.26	2.53
Sm	Sm_2O_3	-	6.13
Ce	CeO_2	39.6	32.9
Nd	Nd_2O_3	27.5	26.6
La	La_2O_3	6.6	6.79

Table 2. Composition and parameters of glass samples

ID	Basic composition [mol% ratio]	Simulated FP [outer wt%]	Source of phosphorus	Melting temperature [°C]
IP 1	$30Fe_2O_3$-$70P_2O_5$	5	$NH_4H_2PO_4$	1200
IP 2	$30Fe_2O_3$-$70P_2O_5$	15	$NH_4H_2PO_4$	1200
IP 3	$30Fe_2O_3$-$70P_2O_5$	35	$NH_4H_2PO_4$	1300
IP 4	$25Fe_2O_3$-$70P_2O_5$-$1Cr_2O_3$-$3(CoO)_2$-$1(ZnO)_2$	20	$NH_4H_2PO_4$	1200
IP 5	$25Fe_2O_3$-$70P_2O_5$-$1Cr_2O_3$-$3(CoO)_2$-$1(ZnO)_2$	25	$NH_4H_2PO_4$	1200
IP 6	$25Fe_2O_3$-$70P_2O_5$-$1Cr_2O_3$-$3(CoO)_2$-$1(ZnO)_2$	30	$NH_4H_2PO_4$	1200
IP 7	$30Fe_2O_3$-$70P_2O_5$	-	H_3PO_4	1250
IP 8	$25Fe_2O_3$-$70P_2O_5$-$1Cr_2O_3$-$3(CoO)_2$-$1(ZnO)_2$	30	H_3PO_4	1250

2.2. Glass properties measurements

As the major characteristics of the glass sample for the high level waste (HLW) form, density, coefficient of thermal expansion, glass transition temperature, softening temperature and thermal conductivity were measured. Viscosities of all samples were tried to be measured at around melting temperature but crystallizations avoided the measurements in some samples.

- <u>Density</u> of the glass sample was measured by the archimedian method at room temperature. A glass sample was suspended with thin string in water and the volume was calculated from the change of the weight. The density of the sample was obtained from its weight and volume.
- <u>Coefficient of thermal expansion</u> was evaluated with TMA (TMA8310, Rigaku Corp.) from 30 to 300 °C according to the standard method to measure the coefficient of linear expansion for the glass.
- <u>Glass transition temperature</u> was also measured with TMA (TMA8310, Rigaku Corp.). The temperature of cylindrical sample with 4 mm diameter and 20 mm length was raised 5 °C a minute.
- <u>Viscosity</u> was measured by the penetration, parallel plate and rotational viscometer (BRVM-313, OPT Corp.) sequentially and was approximated in the VFT (Vogel Fulcher Tamman) formula shown in equation (1).

$$log\eta = A + B/(T-C) \qquad\qquad (1)$$

where T is temperature, A, B and C are coefficients in approximation.

The viscosity at the melting temperature was obtained from VFT formula. Measured sample was 10 mm diameter and 5 - 7 mm height and programming rate was 5 °C/minute.

- <u>Softening temperature</u> was also evaluated from VFT formula. It was defined at the temperature where $log\eta = 7.6$.
- <u>Thermal conductivity</u> was derived by the following equation (2).

$$\lambda = \alpha \cdot Cp \cdot \rho \qquad\qquad (2)$$

where, λ is thermal conductivity [W/m·K], α is thermal diffusivity [m^2/s] and ρ is density [g/cm^3]

In equation (2), the specific heat capacity was measured with DSC (Differential Scanning Calorimetry, DSC-50, Shimadzu Corp.) at the room temperature and 300 °C, and the thermal diffusivity was measured with laser flash method thermal constant measuring apparatus (ULVAC-RICO Inc.).

2.3. Chemical durability

The chemical durability was evaluated by the MCC-1 (Materials Characterization Center -1) method [7]. And it is widely adopted for the measurement technique to estimate the dissolution rate of glass. It is defined by DR (normalized dissolution rate) of the glass constituent elements to the distilled water which is kept 90 °C during immersion time. DR is evaluated by the equation (3).

$$DR = (A_t/A_0) \times (W/S/d) \qquad\qquad (3)$$

Where, A_t is the leached mass of element from glass sample [g], A_0 is the initial content of the element [g], W is the initial weight of the sample [g], S is surface area of the sample and D is the immersion time [day].

The glass sample was provided to the normalized dissolution test after being ground, washing and drying. The concentrations of the leached elements in decoction were analyzed with ICP-AES (Inductively coupled plasma atomic emission spectrometry) and ICP-MS (Inductively coupled plasma mass spectrometry).

3. Results and discussion

3.1. Glass formation

The XRD patterns are shown in Fig. 1 for IP 1 - 6. Observed sharp peaks attributed to the crystals of $NdPO_4$ and $CePO_4$. The Standard diffraction patterns of $NdPO_4$ and $CePO_4$ are almost overlapped. For the other glass samples, only halo peaks were observed in the XRD patterns and all elements distributed homogeneously. They could be decided to be vitrified sufficiently.
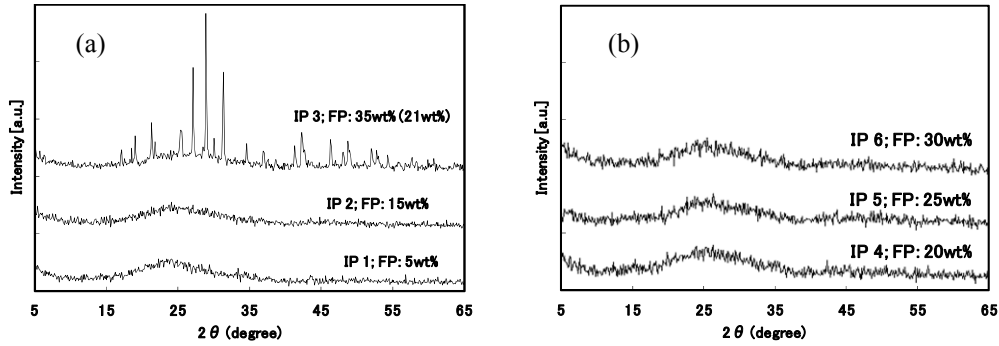
Fig. 1. XRD patterns of glass sample. (a): IP 1-3, (b): IP 4 – 6

As the results of SEM/EDS analyses, SEM images and element distributions of P, Fe and Nd are shown in Fig.2 for IP 2, IP 3 and IP 6.The crystal of rare earth phosphates ($NdPO_4$, same for other rare earth) was clearly identified among the glass matrix in IP 3. In order to promote the glass formation of IP 3, its glass melting temperature was raised to 1300 °C however a part of feed materials were remaining without melting. Therefore, the actual addition of simulated FP oxide was analyzed to be 20.8 % (outer percentage against glass basic composition).

Sample ID	SEM	P	Fe	Nd
IP 2 FP: 15 wt%				
IP 3 FP: 35(21) wt%				
IP 6 FP: 30 wt%				

Fig. 2. SEM and element distributions by EDS for the surface of typical glass samples

3.2. Glass properties as the waste form

The physical properties of iron phosphate glasses measured in this study are shown in table 3 compared with Japanese reference specifications of borosilicate glass (BSG) [8] which is used for the glass matrix of HLW in several nations. All of iron phosphate glass samples showed excellent properties compared to BSG in the test conditions of this study. Especially, large density, low viscosity at around glass melting temperature and short melting time are superior properties as the medium of high level waste form.

3.3. Chemical durability

During the dissolution test, cracking was generated in some samples of IP 1- 3 however it was largely reduced in IP 4-6. Glass network structure was strengthened by addition of transition metal, i.e. Cr and Co.

For the chemical durability, the results of normalized dissolution tests were shown in Fig. 3 for Fe, P, Cs, Sr, Ce and Nd as the representative elements that were components of iron phosphate glass samples. Difference tendency was shown in the transition of dissolution rate for Fe, P, Cs and Sr between IP 1 – 3 and IP 4 – 6. According to the recent study [1, 9], chemical durability of iron phosphate glass increases in the case that Fe(III)/Fe(II) is large. In this study, $NH_4H_2PO_4$ was used as the resource of phosphorous, thus the ratio of Fe(II) was thought to be increased due to NH_3 generated in the glass melting furnace.

The dissolution rate in IP 4 - 6 were once raised then changed to be constant or slightly decrease. This tendency was similar to the pH transition of decoction shown in Fig. 4. It was thought that elution of P raised the concentration of phosphoric acid in the decoction. However, as shown in Fig. 5, the extraction of P was limited in several μm from surface of glass sample. This shows the glass has large durability for long time.

These results suggests that it is important for improvement of chemical durability to maintain the glass network generated by the Fe(III) during the glass melting. Iron in the glass matrix is to be reduced to divalent in the condition of reducing atmosphere. Therefore, glass network formed by trivalent transition metal becomes to be kept by the replacement of a part of Fe to Cr. However, addition of Cr would be limited small amount because it is known that addition of large amount of Cr causes the generation of oxide deposition in the glass matrix. The similar effect for the increase of chemical durability is expected in addition of Al_2O_3 [4].

For the rare earth elements, every sample showed the low dissolution rate, and it suggests that they are kept in the glass network tightly and are difficult to be dissolved.

Table 3. Physical properties of the glass sample

Sample ID		IP 1	IP 2	IP 3	IP 4	IP 5	IP 6	ref. BSG[8]
Density [g/cm^3]		2.98	3.14	3.47	3.23	3.36	3.40	2.74
Coefficient of thermal expansion [10^{-6}/K]		6.73	6.74	7.38	7.78	7.99	7.93	8.8
Glass transition temperature Tg [°C]		520	522	506	490	488	500	~500
Viscosity [coefficient in VFT formula; logη=A+B/(T-C)]	A	-2.15	-0.297	n.a.	-9.51	-15.2	-12.8	η=4.0 Pa·s (at 1150°C)
	B	2684	1396		8000	12900	11200	
	C	619	702		124	20.1	53.1	
Softening Temperature [°C]		633	619	629*	591	586	601	~600
Thermal conductivity [W/m·K]	14.0°C	-	-	-	0.582	0.538	0.532	0.94 (at RT)
	18.0°C	0.778	0.656	0.888	-	-	-	
	300.0°C	0.858	0.772	0.812	0.852	0.855	0.837	

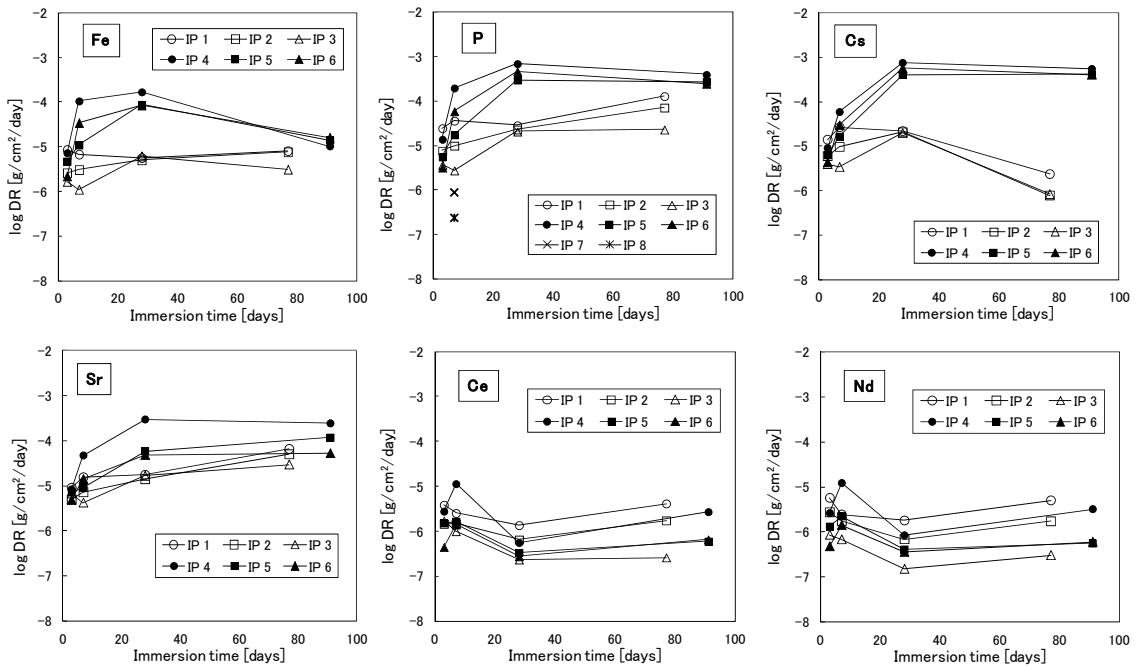*reliability is low due to crystallization

Fig. 3 Results of MCC-1 test, transition of the dissolution rates for some representative elements of the glass components
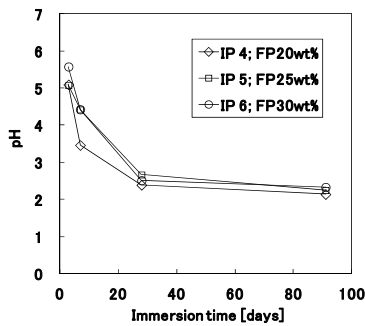

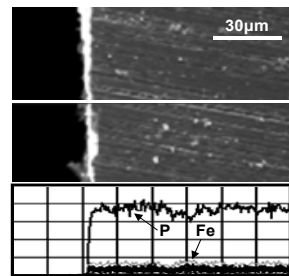Fig.4 Transitions of pH for decoction of IP 4, 5 and 6.

Fig. 5 Elements distribution for the cross section of IP 6 after 91 days of immersion

4. Conclusion

The adaptability of iron phosphate glass was evaluated as the high level waste form to treat with FP element generated from spent electrolyte of pyrochemical reprocessing in this study. According to the results of the glass properties evaluation and MCC-1 dissolution tests, iron phosphate glasses showed the excellent properties compared to other glasses, i.e. borosilicate glass. The durability of phosphate glass which has essentially large hydrophilicity are drastically improved by addition of Fe(III), furthermore, the possibility was indicated that replacement of a part of Fe to Cr suppresses the reduction of bridge forming transition metal. It is necessary to keep the valence of bridging transition metal into trivalent during glass melting.

On the other hand, generation of deposit in the glass does not cause the increase of dissolution rate, however it could be the cause of clacking formation in the actual high level waste form.

In this study, the potential of enough durable iron phosphate glass containing 30 wt% of FP was indicated under the condition that the ratio of Fe/P was 30/70 and a part of Fe were replaced to Cr and Co without oxide deposition in the glass matrix.

Acknowledgements

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