Structural study of chemically durable BaO–FeO_x–P₂O₅ glasses by Mössbauer spectroscopy and high performance liquid chromatography

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Abstract

The relationships between the structure and corrosion resistance of glasses with the nominal compositions $x\text{BaO}-(100-x)[y\text{Fe}_2\text{O}_3-(1-y)\text{P}_2\text{O}_5]$, where $x = 0, 10, 20$, and $y = 30, 35, 40$, are discussed. High performance liquid chromatography was used to characterize the phosphate anions that constitute the glass structure, and Mössbauer spectrometry was used to characterize the fractions and coordination environments of Fe^{2+} and Fe^{3+} ions in the glasses. Weight loss measurements in water were recorded and the most durable glasses were those with the smallest average phosphate anion sizes, independent of the relative BaO and Fe_2O_3 contents.

1. Introduction

Iron phosphate glasses can be produced with a wide range of compositions at relatively low temperatures, while retaining excellent chemical durability, and so have been developed as alternative hosts for the nuclear waste [1, 2]. Ternary barium iron phosphate ($\text{BaO-FeO}_x\text{-P}_2\text{O}_5$) glasses have been considered to be suitable hosts to encapsulate the radioactive Sr-ions in the sludge created as a secondary waste from the BaSO_4 -treatment of contaminated water generated at the Fukushima Dai-ichi nuclear power plant [3]. In that study, the MCC-2 static leaching method (120°C for 72 hours) was used to characterize the corrosion resistance of those $\text{BaO-FeO}_x\text{-P}_2\text{O}_5$ glasses, and the most durable glasses were found to have O/P molar ratios ~ 3.4 , close to the pyrophosphate stoichiometry (O/P = 3.5), where the O/P ratio considered the glass composition after waste loading [4].

Structural parameters, like the Q^i terms, describe the compositional dependence of the phosphate tetrahedra which constitute the glass structure. Here, 'i' represents the number of bridging oxygens on a tetrahedron. Thus, a Q^2 tetrahedron links two neighboring tetrahedra in a polyphosphate anion that is terminated by two Q^1 tetrahedra, and Q^0 tetrahedra are isolated from other phosphate units by bonds through other cations in the glass composition [5]. **These anions can be described in a general formula as $(\text{PO}_3\text{O}_{1/2})^{2-}-(\text{PO}_2\text{O}_{2/2})_x-(\text{PO}_3\text{O}_{1/2})^{2-}$, where O is a bridging oxygen that links neighboring tetrahedra.** Increasing the O/P ratio of a nominally metaphosphate composition (O/P = 3) reduces the average size of the phosphate anions as Q^1 tetrahedra replace Q^2 tetrahedra.

The effects of composition on the dissolution rates of $\text{Na}_2\text{O-FeO}_x\text{-P}_2\text{O}_5$ glasses are complex. Some glasses preferentially release alkali ions and others dissolve congruently, and depending on the experimental conditions, both linear and parabolic dissolution kinetics can be observed [6]. Using structural information obtained by High Performance Liquid Chromatography (HPLC) [7], Mössbauer spectrometry, and micro-Raman spectroscopy [8], it was found that the most durable glasses have structures based on small phosphate anions (e.g., pyrophosphates, $Q^1\text{-}Q^1$, and triphosphates, $Q^1\text{-}Q^2\text{-}Q^1$) that are linked through metal polyhedra [6].

Much less is known about the dissolution behavior of the $\text{BaO-FeO}_x\text{-P}_2\text{O}_5$ glasses [9]. Such information will be important for the design of an optimal composition to host the radioactive Sr/Ba sludge created in the clean-up of the Fukushima Dai-ichi accident. The aim of the present study was to investigate the property-structure relationships in barium-doped iron phosphate glasses designed to immobilize (Ba, Sr) SO_4 sludge [10]. In particular, the focus in the present work was on the relationship between water durability and glass structure, defined by both the phosphate anions and the iron polyhedra.

2. Experimental Procedures

Binary iron phosphate (IP) glasses were prepared from mixtures of reagent grade Fe_2O_3 and

H₃PO₄ that were melted in a Pt crucible in air at 1150–1250°C [3] to produce glasses with the nominal molar compositions of $x\text{Fe}_2\text{O}_3-(100-x)\text{P}_2\text{O}_5$, where $x = 30, 35, 40$. IP glass particles (< 300 µm in diameter) were then mixed with reagent grade BaSO₄ powder, used as a sludge simulant, and the mixtures were melted at 1150°C for 1 h in air using a Pt crucible. The resulting melt was poured into a graphite mold and then subsequently annealed at the glass transition temperature for 1 h and cooled to room temperature at a rate of ~1 °C/min. The compositions of the quenched glasses were determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 2000 DV, Norwalk, USA). Iron phosphate glasses were digested in 3–7 M H₂SO₄ aqueous solution for several days at 80–90°C in capped Teflon containers. The digestion time and temperature depended on the chemical durability of the glasses. In general, glasses with high Fe contents and low O/P ratios dissolved more slowly. Solutions for ICP were diluted with deionized H₂O, with dilution factors of 1: 9 or 1: 99, depending on the expected ion concentration of the solution. Chemical analyses by x-ray fluorescence (XRF) indicated that less than 0.1 mole% SO₃ was retained in all BaSO₄-loaded IP glasses.

The Fe²⁺/Fe_{tot} fraction in each glass was determined by a titration method using ~0.002 mol/L of KMnO₄ aqueous solution. Samples were ground into a powder (< 100 µm) under a N₂ atmosphere, and the powder was then dissolved in 5 mol/L of hydrochloric acid under an Ar atmosphere. The solution included Zimmermann-Reinhardt reagent which was dissolved in solutions of phosphoric acid (85 %) and concentrated sulfuric acid (95 %).

High performance liquid chromatography (HPLC, Dionex ion chromatography system) was used to study the phosphate anion distributions [11] in the barium iron phosphate glasses. Glass powders (75–150 µm, 50 mg) were partially dissolved for 24 hours in an aqueous solution (50 ml) with 0.22 M NaCl + 5 mM EDTA and a pH of 10.1 ± 0.1. Phosphate anions are stable against hydrolysis under these conditions [11, 12]. The concentration of EDTA is about three times the total concentration of iron and barium leached from glasses at the time of experiments. The HPLC system and experimental procedures are described in more detail in reference [5]. HPLC experiments were run in triplicate and the average phosphate chain-lengths from these experiments were determined with relative uncertainties of ±5%.

⁵⁷Fe Mössbauer spectra were collected to determine the valence states of iron ions as well as their coordination environments in the glass network. The spectra were obtained in a transmission setup at room temperature using a conventional constant acceleration spectrometer with a 25 mCi ⁵⁷Co gamma-ray source embedded in rhodium matrix. The velocity scale of the spectrometer was first calibrated using a spectrum of α-Fe foil at room temperature. All Mössbauer spectra were analyzed by Lorentzian line fitting into three doublet sites using the Recoil software [13]. Details about these experiments and the spectral analyses are given in reference [7, 8].

Two corrosion experiments were performed. In the first experiment, polished glass plates were

exposed to water in sealed vessels at 120°C for 72 hours, and then the changes in sample weight were measured, **normalized to the original geometric surface area of the sample ($\Delta W/S$)**. These experiments are described in [3]. In the second set of corrosion experiments, glass powders (~200 mg, 300–425 μm , triplicates) were first ultrasonically rinsed in absolute ethanol to remove dust particles, and then were placed into polypropylene containers (Evergreen Scientific, 50 ml centrifuge tubes) with 50 ml of deionized H_2O . The initial **S/V** ratio (ratio of powder surface area to leachate volume) was fixed at $\sim 24 \pm 1 \text{ m}^{-1}$. Samples were held for different times at 70°C ($\pm 2^\circ\text{C}$), and then the solutions were analyzed for Ba, Fe, and P using ICP-OES.

3. Results

Table 1 summarizes the compositions of barium iron phosphate glasses prepared for this study. In general, the analyzed phosphate contents are 2–4% lower than the batched concentrations, indicating some P_2O_5 -loss during glass processing. The IP30 glass had a greater discrepancy between the batched (70 mole%) and analyzed (62.7 mole%) P_2O_5 -contents. Titration analyses indicate that the average $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio for all glasses is about 10–14 %, although the ferrous ratio for the IP30 ($x = 30$) glass was about 25%.

Table 1 Batched and analyzed compositions of the barium iron phosphate glasses. Analyzed compositions are averaged for three measurements. **The reproducibility of the analyzed compositions and ion ratios are ± 0.1 and ± 0.05 , respectively.**

Abbreviation	Batched composition (mol%)			Analyzed composition (mol%)				Ion ratio in glasses by ICP-OES		
	BaO	Fe_2O_3	P_2O_5	BaO	FeO	Fe_2O_3	P_2O_5	$\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ (%)	O/P	Fe/P
IP30	0	30	70	0	14.8	22.5	62.7	24.8	3.16	0.48
10BaIP30	10	27	63	9.8	5.6	24.8	59.8	10.1	3.25	0.46
20BaIP30	20	24	56	19.6	5.8	21.6	53.1	11.8	3.35	0.46
IP35	0	35	65	0	8.0	29.9	62.1	11.8	3.29	0.55
10BaIP35	10	31.5	58.5	9.6	7.3	26.9	56.2	11.9	3.37	0.54
20BaIP35	20	28	52	19.2	7.4	23.4	49.9	13.6	3.47	0.54
IP40	0	40	60	0	10.5	32.8	56.7	13.8	3.46	0.67
10BaIP40	10	36	54	9.6	8.0	30.7	51.8	11.5	3.56	0.67

Fig. 1. Chromatographs from barium iron phosphate glasses for (a) $y = 30$, (b) $y = 35$, and (c) $y = 40$.

Figure 1 shows the HPLC chromatographs for the three series of glasses ($y = 30, 35$, and 40) with increasing BaO contents. Each peak in the chromatograph, from short times to longer times, represents a phosphate anion with an increasing number of PO_4 tetrahedra. The first peak, near the retention time of three minutes, is due to orthophosphate (P_1) anions, the second peak, near seven minutes, is due to pyrophosphate (P_2) anions, the third to triphosphate anions (P_3), etc. Individual peaks out to about the P_{10} anion could be resolved. The broad hump centered near 20 minutes in the chromatograph from the IP30 glass is due to the presence of larger P-anions that cannot be resolved

by the HPLC system [5].

Fig. 2. A comparison of O/P ratio (solid symbols, left axis) and average phosphate chain-length, $\bar{n}$, (open symbols, right axis) determined from the HPLC chromatographs with those predicted from the glass compositions by ICP-OES. Circles are the IP30 data, triangles are IP35 data, and squares are IP40 data. The reproducibilities for analyzed O/P ratios by HPLC and by ICP are ± 0.03 and ± 0.05 , respectively, and the uncertainty for the average phosphate chain-length is ± 0.2 . The solid line is a 1:1 comparison of the O/P ratios, and the dashed line is the predicted relationship for $\bar{n}$, from Eq. 1.

Increasing the O/P ratio in a glass composition, whether by increasing the baseline Fe_2O_3 content (IP30 < IP35 < IP40) or by adding BaO to one of the baseline IP glasses, causes a decrease in the average P-anion size, as indicated, for example by the increases in the relative intensities of peaks due to P_1 and P_2 anions in the respective chromatographs in Figure 1. Figure 2 compares the O/P ratios calculated from the anion distributions determined by HPLC with those determined from the analyzed glass compositions by ICP-OES, after accounting for the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio determined by titration.

Also shown in Figure 2 is the average P-anion size ($\bar{n}$, number of P-tetrahedra per anion) as a function of O/P ratio. The dashed line represents the expected relationship, assuming that all oxygens in the glass structure are associated with the P-anions:

$$\bar{n} = \frac{1}{[\text{O/P}] - 3} \quad (1)$$

For the phosphate-rich glasses ($\text{O/P} < 3.3$), HPLC predicts slightly greater O/P ratios and shorter average P-anions than those calculated from the analyzed (ICP) glass compositions, most likely because of difficulties in accounting for the larger P-anions in the chromatographs from these glasses. There is excellent agreement between the predicted and measured phosphate species for glasses with $\text{O/P} > 3.3$.

Fig. 3. Mössbauer spectra from the barium iron phosphate glasses for $y = 30$ (left), $y = 35$ (middle), and $y = 40$ (right), and increasing BaO-contents (top-to-bottom). Each spectrum (black line) is fitted with deconvolution curves for the three iron sites indicated; the red line is the best-fit summation of the curves for these three sites, summarized in Table 2.

Figure 3 shows the Mössbauer spectra collected for many of the samples. Each Mössbauer spectrum has been decomposed into three sets of doublets using Lorentzian line shapes. These doublets represent Fe^{2+} in an octahedral site, and Fe^{3+} in both tetrahedral and octahedral sites [8]. Table 2 summarizes the isomer shift (IS in mm/s), quadrupole splitting (QS in mm/s), FWHM (full width at half maximum) of the Lorentzian contribution to each peak (w in mm/s), along with the relative fractions of ferrous sites ($\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$), as well as the fitting uncertainties (χ^2). Regarding the two Fe^{3+} sites, the octahedral sites correspond to the greater IS value [14].

Table 2 Fitting results of the Mössbauer spectra from the barium iron phosphate glasses with estimated errors in parentheses. The estimated errors for the values of IS, QS and w are each $< 5\%$. The fitting uncertainties (χ^2) are also listed.

	Fe ²⁺ /Fe total (%) by titration	Fe ²⁺ (octahedral)			Fe ³⁺ (octahedral)			Fe ³⁺ (tetrahedral)			Fraction of site (%)			χ^2
		IS (mm/s)	QS (mm/s)	w (mm/s)	IS (mm/s)	QS (mm/s)	w (mm/s)	IS (mm/s)	QS (mm/s)	w (mm/s)	Fe ²⁺ (oct)	Fe ³⁺ (oct)	Fe ³⁺ (tet)	
IP30	24	1.29(2)	2.07(3)	0.58(2)	0.51(1)	0.81(1)	0.42(2)	0.28(2)	0.84(3)	0.36(3)	28.2(7)	39.3(6)	32.5(9)	1.2(2)
10BaIP30	10	1.27(2)	2.07(2)	0.50(3)	0.55(2)	0.86(3)	0.44(3)	0.29(3)	0.87(2)	0.44(4)	14.0(9)	35.0(1)	51.0(1)	0.6(4)
IP35	12	1.27(2)	2.04(1)	0.53(2)	0.50(2)	0.86(2)	0.45(2)	0.25(2)	0.86(3)	0.40(3)	13.7(8)	50.0(9)	37.0(9)	0.7(2)
10BaIP35	12	1.24(3)	2.09(4)	0.60(3)	0.50(2)	0.85(3)	0.44(3)	0.24(3)	0.94(3)	0.43(4)	19.5(9)	43.0(1)	38.0(1)	0.5(3)
20BaIP35	14	1.29(10)	2.06(9)	0.48(9)	0.45(9)	0.90(8)	0.56(9)	0.20(9)	1.10(8)	0.26(9)	16.5(2)	74.0(1)	9.7(2)	0.5(3)
IP40	14	1.26(1)	2.11(2)	0.50(2)	0.44(2)	0.90(3)	0.50(2)	0.18(2)	0.93(3)	0.31(3)	18.2(8)	63.3(9)	18.5(1)	0.6(2)
10BaIP40	12	1.22(3)	2.10(4)	0.38(5)	0.47(2)	0.91(3)	0.51(4)	0.19(4)	0.89(5)	0.30(5)	12.1(9)	64.0(1)	24.0(1)	0.5(3)

The overall fraction of Fe²⁺ species determined by the titration method (Table 1) was consistently lower by about 1-4% in absolute values, than what was determined by Mössbauer spectrometry, but the compositional trends in Fe²⁺/Fe_{tot} determined by these two methods are in agreement (Table 2 and Figure 4a). It is worth noting that for the Mössbauer spectral analysis, similar recoil-free fractions were used for both Fe²⁺ and Fe³⁺ in different coordinations and this can introduce an estimated error up to $\pm 3\%$ as calculated previously on similar iron-phosphate glass compositions [4]. The Mössbauer hyperfine parameters given in Table 2 are similar to those reported in the literature for similar glasses [1, 14, 15]. Differences found in the fraction of Fe²⁺ in similar glass compositions arise from the differences in the synthesis conditions, especially the temperature, as is well-demonstrated in the literature [16]. There appears to be an increase in the fraction of octahedral ferric ions with increasing O/P ratio for the present glasses (Figure 4b).

Fig. 4. The relationship between (a) O/P ratio by ICP-OES, relative ratios of Fe²⁺ (octahedral site) and Fe³⁺ analyzed from Mössbauer spectra (respective open and solid circles with solid lines) and by titration techniques (open and solid squares with dashed lines) for $y = 30$ (black), $y = 35$ (red), and $y = 40$ (blue) series, and relative ratios of Fe³⁺ (octahedral, triangles with solid lines), and (b) Fe³⁺ (tetrahedral, squares with dotted lines) sites analyzed from the Mössbauer spectra. The reproducibility for the Fe²⁺ and Fe³⁺ proportions by titration was $< 1\%$ relative, and the reproducibility for the analyzed O/P ratios is ± 0.05 . Each line is a guide for the eye.

Fig. 5. Normalized weight loss in distilled water after 72 hours at 120°C, from reference [3], versus the analyzed O/P ratio. The reproducibility for the analyzed O/P ratio is ± 0.05 . The dashed line is a guide for the eye.

Figure 5 shows the weight losses from the barium iron phosphate glasses after immersion in 120°C water for 72 hours [3]. In general, glasses with O/P ratios more than ~ 3.3 exhibit much lower weight losses, independent of the BaO concentrations. The pH of the solution at the conclusion of these tests depended, in general, on the P_2O_5 -content of the original glass, increasing from 3.5 for IP30 glass to 5.3 for the IP40 glass.

Table 3 Analyzed atom ratios in bulk glasses and in solution after 144 hours in 70°C deionized water, along with the absolute P-contents in the respective solutions. The uncertainties of the atomic ratios for the analyzed glass and for the solution were $< 5\%$ and $< 40\%$, respectively. The reproducibility of the P-contents was $< 8\%$.

Glass	Analyzed glass atomic ratio		Solution analyses atomic ratio		P-content (ppm)
	Ba/P	Fe/P	Ba/P	Fe/P	
20BaIP30	0.18	0.46	0.19	0.00	0.8
IP35	0.00	0.55	0.00	0.03	1.3
10BaIP35	0.09	0.54	0.09	0.01	0.5
20BaIP35	0.19	0.54	0.19	0.01	0.5

Table 3 compares the ion ratios analyzed in four Ba-Fe-phosphate glasses (from Table 1) with those released into 70°C water after 144 hours. The Ba/P ratios in solution are virtually identical to

those in the respective base glasses, whereas much less iron was released into solution. Also shown in Table 3 are the absolute P-contents measured in each solution after 144 hours on test. These values correlate well with the respective weight losses reported for these glasses after 72 hours in water at 120°C, as shown in Figure 5 [3].

4. Discussion

1. Glass structure

The addition of BaSO₄ to the iron phosphate melts affects the types of phosphate anions that constitute the glass structure, and the corrosion rates of the glasses, without incorporating detectable sulfate species into the glass. This is consistent with the work of Bingham *et al.* [1] who added up to 50 mole% BaSO₄ to glasses similar to IP40 and found that almost all of the SO₃ was volatilized from the melts. For example, for a glass similar to the 10BaIP40 in the present study, they detected 0.023 mole% SO₃ remaining from a batched composition with 9.10 mole% SO₃. Given this, the structures and properties of the present glasses are discussed in terms of their equivalent concentrations of BaO, not BaSO₄.

The HPLC data in Figure 1 indicate that a variety of phosphate anions constitute the structures of the Ba-Fe-phosphate glasses, and increasing the nominal BaO and Fe₂O₃ contents decreases the average sizes of these anions in a way that can be predicted from the glass composition (Figure 2). However, the chromatographs from glasses with similar O/P ratios but different relative concentrations of BaO and Fe₂O₃ (e.g., 10BaIP 30 and IP35, 20BaIP30 and 10BaIP35, 20BaIP35 and IP40) indicate some small but consistent differences in the distributions of phosphate anions that may be related to the relative field strengths of barium and ferric ions. Consider the melt disproportionation reaction

Here, two pyrophosphate anions combine in the melt to form an orthophosphate anion and a triphosphate anion. If this reaction can be treated as an equilibrium chemical reaction, then an equilibrium constant (K_2) can be calculated using the relative concentrations of these three anions determined from the respective peaks in the chromatographs. For each of the three pairs of glasses with similar O/P ratios, the glass with the greater analyzed Ba/Fe ratio had a lower K_2 (Table 4). The K_2 is determined from the relative area of the peaks denoted as A(P₁), A(P₂), and A(P₃) in the chromatograph [7], as indicated in Figure 1.

$$K_2 = \frac{[A(P_1)][\frac{A(P_3)}{3}]}{[\frac{A(P_2)}{2}]^2} \quad (3)$$

This is consistent with many studies of phosphate glasses which show that increasing the field strength of a modifying cation creates more complex phosphate structures through melt disproportionation reactions like reaction (2) [11, 17]. A recent chromatographic study of Na-Fe-phosphate glasses revealed a greater value for K_2 for compositions with lower O/P ratios [5], consistent with the trend noted for the Ba-Fe-phosphate glasses indicated in Table 4.

Table 4 Pyrophosphate reaction equilibrium constants (K_2) for glasses with similar O/P ratios but different Ba/Fe ratios. The reproducibilities for the analyzed Ba/Fe ratio by ICP and the O/P ratios by HPLC are ± 0.10 and ± 0.03 , respectively.

Glass	Analyzed glass atomic ratio		
	Ba/Fe	O/P	K_2
IP35	0.0	3.29	0.51
10BaIP30	0.18	3.25	0.50
10BaIP35	0.46	3.37	0.24
20BaIP30	1.19	3.35	0.19
IP40	0.0	3.46	0.29
20BaIP35	1.01	3.47	0.22

The phosphate anions are linked through their nonbridging oxygens in bonds to the iron and barium polyhedra. The Mössbauer data (Figures 3 and 4) reveal that about 12% of the iron incorporated in these glasses are ferrous ions that occupy octahedral sites, and that the rest are ferric ions that occupy two different sites. In general, the spectra indicate that more octahedral ferric species are present in glasses with greater O/P ratios. Overall, the iron ions occupy sites with an average coordination number between 5 and 6, an observation that is consistent with the study of Bingham *et al.* [1].

Fig. 6. A schematic model of the structure of a barium iron phosphate glasses with $x = 20$, $y = 35$. Close correlation with Ba^{2+} ions and Q^0 units are depicted.

Figure 6 shows a schematic model of the Ba-Fe-phosphate glass structure, based in part on the reported structure of $\text{Ba}_3\text{Fe}_4\text{P}_6\text{O}_{24}$ ($3\text{BaO} \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$) [15], a crystal that possesses Q^0 phosphate units that share corners with octahedral Fe^{3+} sites. Barium ions occupy sites with nine and twelve oxygens with various Ba-O bond-lengths. Similar structural moieties are expected in the glasses prepared for this study, although other species including longer phosphate anions and different ferrous and ferric sites are also incorporated into the glasses, as indicated in Figure 6.

2. Chemical Durability

For conventional phosphate glasses in pH neutral solutions, corrosion occurs by the hydration of metal-O-P bonds that then release **metal ions** along with the phosphate anions [18]. Under such conditions, the phosphate anions themselves remain intact because of their slow hydrolysis rates. This is why chromatographic analyses of the solutions of dissolved phosphate glasses can provide accurate descriptions of the anion distributions in the original glasses.

Chromatography indicates that the IP30 glasses have the longest average P-anions of the glasses tested here, and that the average anion size decreases with the addition of BaO (Figure 2). Corrosion rates also decrease in the same order, implying that the hydration resistance of an Fe-O-P or Ba-O-P bond is greater when those nonbridging oxygens are associated with a Q^1 tetrahedron than with a Q^2 tetrahedron. For the glasses in the present study, there is an inverse dependence of corrosion rate on the fraction of Q^2 tetrahedra determined from the respective chromatography data, independent of the relative Ba- and Fe-concentrations. Dickinson used *ab initio* calculations to show that the stability of a metal-O-P bond against protonation decreased with an increase in the partial charge on

that oxygen [19], consistent with the slower corrosion rates of phosphate glasses with lower Q^2 concentrations.

The effect of iron on the corrosion resistance of the Ba-Fe-phosphate glasses is complicated. If the aqueous durability depends on limiting the numbers of Q^2 species, then, ion for ion, glasses with greater relative numbers of ferric ions instead of ferrous ions should have lower corrosion rates because of the resulting higher O/P ratio for the former species. The 20BaIP35 glass has a similar O/P ratio (~ 3.46) and similar fraction of Q^2 -sites ($\sim 19\%$) compared to the IP40 glass, and both glasses have similar dissolution rates, despite the former having much less Fe_2O_3 in its composition (28 vs. 40 mole%, as batched). Similar comparisons can be made between the 10BaIP30 and IP35 glasses, and the 20BaIP30 and 10BaIP35 glasses; the glasses in each set have similar structures and similar chemical durabilities despite having very different BaO and Fe_2O_3 contents. Thus it seems that the nature of the phosphate network is more critical when predicting the chemical durability of these glasses than the relative fractions of BaO and Fe_2O_3 . This simple model for dissolution, based on the hydration of metal-O-P bonds, does not account for the preferential release of P and Ba to the dissolution solutions (Table 3). Because the solubility product of $Fe(OH)_3$ is significantly lower (2.79×10^{-39}) in room temperature water than is $Ba(OH)_2 \cdot 8H_2O$ (2.55×10^{-4}) [20], it is conceivable that these glasses dissolve by the metal-O-P hydration process described above, but then the iron species precipitate on the glass surface or somewhere else in the reaction vessel, as has been reported for Na-Fe-phosphate glasses reacted in water [6]. Behavior of surface reaction and a corrosion mechanism relevant to the microstructure in the present Ba-Fe-phosphate glasses will be reported elsewhere.

5. Conclusion

The corrosion resistance of glasses in the $xBaO-(100-x)[yFe_2O_3-(1-y)P_2O_5]$ system depends on their composition and structure. Increasing the BaO and Fe_2O_3 contents decreases the average length of the P-anions that constitute the glass structure, as shown using High Performance Liquid Chromatograph (HPLC), and Mössbauer spectrometry shows that iron is incorporated principally as Fe^{3+} ions in both tetrahedral and octahedral sites. The chemical stability against hydration of Fe-O-P bonds to Q^1 and Q^0 tetrahedra appears to be responsible for the lower corrosion rates of glasses with greater O/P ratios, including those greater BaO concentrations. Such glasses, then, appear to be the best candidates for waste remediation applications.

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Table 1

Abbreviation	Batched composition (mol%)			Analyzed composition (mol%)				Ion ratio in glasses by ICP-OES		
	BaO	Fe ₂ O ₃	P ₂ O ₅	BaO	FeO	Fe ₂ O ₃	P ₂ O ₅	Fe ²⁺ /Fe total (%)	O/P	Fe/P
IP30	0	30	70	0	14.8	22.5	62.7	24.8	3.16	0.48
10BaIP30	10	27	63	9.8	5.6	24.8	59.8	10.1	3.25	0.46
20BaIP30	20	24	56	19.6	5.8	21.6	53.1	11.8	3.35	0.46
IP35	0	35	65	0	8.0	29.9	62.1	11.8	3.29	0.55
10BaIP35	10	31.5	58.5	9.6	7.3	26.9	56.2	11.9	3.37	0.54
20BaIP35	20	28	52	19.2	7.4	23.4	49.9	13.6	3.47	0.54
IP40	0	40	60	0	10.5	32.8	56.7	13.8	3.46	0.67
10BaIP40	10	36	54	9.6	8.0	30.7	51.8	11.5	3.56	0.67

Table 2

		Fe2+/Fe total (%) by titration	Fe2+ (octahedral)			Fe3+ (octahedral)			Fe3+ (tetrahedral)			Fraction of site (%)			χ^2
			IS (mm/s)	QS (mm/s)	w (mm/s)	IS (mm/s)	QS (mm/s)	w (mm/s)	IS (mm/s)	QS (mm/s)	w (mm/s)	Fe2+ (oct)	Fe3+ (oct)	Fe3+ (tet)	
IP30	24		1.29(2)	2.07(3)	0.58(2)	0.51(1)	0.81(1)	0.42(2)	0.28(2)	0.84(3)	0.36(3)	28.2(7)	39.3(6)	32.5(9)	1.2(2)
10BaIP30	10		1.27(2)	2.07(2)	0.50(3)	0.55(2)	0.86(3)	0.44(3)	0.29(3)	0.87(2)	0.44(4)	14.0(9)	35.0(8)	51.0(9)	0.6(4)
IP35	12		1.27(2)	2.04(1)	0.53(2)	0.50(2)	0.86(2)	0.45(2)	0.25(2)	0.86(3)	0.40(3)	13.7(8)	50.0(9)	37.0(9)	0.7(2)
10BaIP35	12		1.24(3)	2.09(4)	0.60(3)	0.50(2)	0.85(3)	0.44(3)	0.24(3)	0.94(3)	0.43(4)	19.5(9)	43.0(8)	38.0(8)	0.5(3)
20BaIP35	14		1.29(10)	2.06(9)	0.48(9)	0.45(9)	0.90(8)	0.56(9)	0.20(9)	1.10(8)	0.26(9)	16.5(9)	74.0(9)	9.7(9)	0.5(3)
IP40	14		1.26(1)	2.11(2)	0.50(2)	0.44(2)	0.90(3)	0.50(2)	0.18(2)	0.93(3)	0.31(3)	18.2(8)	63.3(9)	18.5(8)	0.6(2)
10BaIP40	12		1.22(3)	2.10(4)	0.38(5)	0.47(2)	0.91(3)	0.51(4)	0.19(4)	0.89(5)	0.30(5)	12.1(9)	64.0(8)	24.0(9)	0.5(3)

Table 3

Glass	Analyzed glass atomic ratio		Solution analyses atomic ratio		P-content (ppm)
	Ba/P	Fe/P	Ba/P	Fe/P	
20BaIP30	0.18	0.46	0.19	0.00	0.8
IP35	0.00	0.55	0.00	0.03	1.3
10BaIP35	0.09	0.54	0.09	0.01	0.5
20BaIP35	0.19	0.54	0.19	0.01	0.5

Table 4

Glass	Analyzed glass atomic ratio		
	Ba/Fe	O/P	K_2
IP35	0.0	3.29	0.51
10BaIP30	0.18	3.25	0.50
10BaIP35	0.46	3.37	0.24
20BaIP30	1.19	3.35	0.19
IP40	0.0	3.46	0.29
20BaIP35	1.01	3.47	0.22

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6