DISSOLUTION BEHAVIOR OF Na₂O–FeO–Fe₂O₃–P₂O₅ GLASSES

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ABSTRACT

The dissolution behavior of five series of Na₂O–FeO–Fe₂O₃–P₂O₅ glasses with ranges of O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios were investigated in deionized water (DI H₂O) using static and semi-dynamic tests. Glass composition, which determines the average phosphate chain length, determines the dissolution mechanism and kinetics. The initial dissolution kinetics are parabolic and are described by a 3D diffusion model (DM), whereas a linear contracting volume model (CVM) describes the later-stage dissolution kinetics. Temperature dependent rate parameters, k_{DM} and k_{CVM} , decrease by several orders of magnitude with increasing Fe/P ratio, but are less dependent on the O/P ratio. The surface morphology and composition of the corroded glasses are characterized by analytical electron microscopy, which provides information related to the change from DM to CVM kinetics. Three types of dissolution behavior were identified for these Na-Fe-phosphate glasses, and were associated with either selective leaching or congruent dissolution. Type I behavior involves selective leaching of ions for both the DM and the CVM stages. Type II behavior involves congruent dissolution for both dissolution stages. Type III behavior involves congruent dissolution during the DM stage and then selective leaching in the CVM stage.

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1. Introduction

Information about the dissolution processes and ion release rates of phosphate glasses in aqueous environments is important for a wide range of engineering applications, from biomaterial design to nuclear waste remediation. Through compositional control, the solubility of phosphate glasses can be tailored to obtain ion release rates that vary by many orders of magnitude [1,2]. The chemical durability of phosphate glass has been related to the composition and structure. Studies have shown that the addition of alkali oxides to phosphate glasses increases their dissolution rates in aqueous environments, whereas the addition of alkaline earth and high field strength cations (e.g., CaO, MgO, CuO, Al₂O₃ and Fe₂O₃) generally decreases dissolution rates [3,4,5].

Because they possess excellent chemical durability, often superior to silicate and borosilicate glasses, iron phosphate glasses with Fe/P ratios between 1:3 and 2:3 have been developed for the vitrification of high level nuclear waste (HLW) [6,7,8,9]. In addition, high concentrations of alkali oxides (up to 20 wt%) can be incorporated into the iron phosphate glasses without deterioration of their good chemical durability [7]. The chemical durability of iron phosphate glasses with simulated sodium bearing waste (SBW) and HLW meets all current US Department of Energy (DOE) requirements for waste remediating materials [6,10,11,12].

The degradation rates of Na₂O–CaO–P₂O₅ glasses used as bio-active and bio-resorbable materials can also be tailored by adding Fe₂O₃ to suit various end applications [13]. The good chemical durability of iron phosphate glasses has been attributed to their chemical structure. The hydration rates of phosphate chains decrease with increasing iron oxide content because of the greater chemical stability of P–O–Fe bonds [14]. For Na₂O–CaO–P₂O₅ glasses doped with increasing amounts of Fe₂O₃, the contact angle of polar liquids increases, indicating a decrease in

the total surface energy of the glasses and this has also been related to improved chemical durability [15]. For phosphate glasses that contain both Fe^{2+} and Fe^{3+} , the chemical durability is independent of the relative Fe^{2+} content [14].

The dissolution behavior of glass is determined by the reactions of the glass network and the release of different ions to the solution. Surface conditions and layer formation, saturation effects and solution chemistry must also be taken into account when describing the dissolution processes [16]. Often, the initial stage of corrosion is controlled by an ion exchange process or by the diffusion of water into the glass network, followed then by the dissolution of the glass matrix with increasing depth of alkali depletion in the outer glass surface [1,12,16]. The hydration reactions between glass and water are based on the hydrolytic cleavage of bonds in the glass network that are related to different energies of hydration. The least stable bonds between metal ions and nonbridging oxygens (NBO) from the glass network, $\text{M}-\text{O}_{\text{nb}}$, are generally the first to be hydrated. The fraction of NBO and the concentration of mobile ions (e.g., Na^+) determine the initial glass hydration rates [17]. The rate of ion exchange across the hydration layer as well as the penetration of water into the bulk glass is determined by the surface concentration of the interdiffusing ions, the multi-component interdiffusion coefficient, and the exchange potential of the interdiffusing species at the exchange site [17].

One treatment of glass/water reactions is based on transition state theory in combination with reversible and irreversible thermodynamics. Two main approaches, geochemical and thermodynamic, have been used to study the glass dissolution processes. Models derived from these two approaches have been applied successfully to many corrosion studies of nuclear waste glasses [16,18,19,20,21]. Both the geochemical and thermodynamic approach to glass corrosion depend on a quantitative determination of the equilibrium, which is described by a complex

solubility product changing with the amount of glass dissolved into solution [20,22]. The hydration and hydrolysis processes associated with glasses in aqueous solutions have been related to the free energy changes for reactions that occur between the glass constituents and the absorbed water molecules, and the overall free energies of hydration for different compositions have been estimated [16]. The relationships between the calculated thermodynamic stability and glass dissolution rates can then be used to estimate the relative glass durability in aqueous solutions [18].

In the present study, the dissolution behavior of sodium iron phosphate glasses, with constant nominal O/P ratios (3.0~3.5) and different Fe/P (0~0.67) ratios, is systematically investigated by two types of dissolution tests. Leachate solution analysis shows that the congruence and leaching kinetics of each constituent are compositionally dependent. The kinetics that control glass dissolution are discussed with respect to the structure and composition of the glass.

2. Experimental Procedures

2.1. Glass preparation

The procedures for preparing and analyzing the structures of the sodium iron phosphate glasses used in the present study have been described in previous papers [23,24]. Briefly, glasses were made from batches of raw materials including Na_2CO_3 (Alfa Aesar, $\geq 98\%$), Fe_2O_3 (Alfa Aesar, $\geq 99\%$) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, $\geq 98\%$) that were melted in fused SiO_2 crucibles (Leco #728-701) between 1000 °C and 1250 °C in air for two hours. Iron phosphate glasses were digested in 3–7 M H_2SO_4 aqueous solution for 7 to 14 days at 80–90 °C in closed Teflon containers, and cation concentrations, including small amounts of silica from the crucibles, were

determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 2000 DV, Norwalk, USA). The fraction of iron present as Fe^{2+} was determined by a wet chemical technique [25]; on average, the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio for these glasses was 0.19 [23,24]. Compositional series with similar O/P ratios are labeled from A to E according to their iron contents. Glasses in series A have average analyzed O/P ratios of 3.04 and analyzed Fe/P ratios between 0.00 and 0.37; series B glasses have average analyzed O/P ratios of 3.12 and analyzed Fe/P ratios between 0.00 and 0.42; series C glasses have average analyzed O/P ratios of 3.27 and analyzed Fe/P ratios between 0.00 and 0.49; series D glasses have average analyzed O/P ratios of 3.40 and analyzed Fe/P ratios between 0.00 and 0.58; series E glasses have average analyzed O/P ratios of 3.49 and analyzed Fe/P ratios between 0.00 and 0.66. Glass E-0.66, for example, is a sample in the E-series with a batched O/P ratio of 3.5 and an analyzed Fe/P ratio of 0.66.

2.2. *Dissolution studies*

Glass powders were ultrasonically prewashed in absolute ethanol to remove dust particles, and two types of corrosion tests with different experimental conditions were conducted:

Test 1 (static): Glass powders (200 ± 2 mg, 300–425 μm , triplicates) were placed into polypropylene tubes (Evergreen Scientific, 50 ml centrifuge tubes) with 50 ml of deionized H_2O . The initial SA/V ratio (ratio of powder surface area to leachate volume) was $24 \pm 1 \text{ m}^{-1}$. These experiments were done at different temperatures (21, 40, 60 and 80 $^\circ\text{C} \pm 2$ $^\circ\text{C}$).

Test 2 (semi-dynamic): Glass powders (450 ± 2 mg, 150–355 μm , triplicates) were sealed into small bags (2 cm $\times$ 2 cm) made from Nylon mesh (Blick Art Materials, 284 TPI mesh, opening size of 51 microns). Samples were put into 50 ml deionized H_2O at 60 ± 2 $^\circ\text{C}$ with an

initial SA/V ratio of $77 \pm 2 \text{ m}^{-1}$, and solutions were replenished with 50 ml of fresh deionized H₂O for every indicated time interval (2, 6, 12, 23, 50, 79, 107 and 132 hours).

For both tests, after specific time intervals, glass particles were dried at 90 °C for 8 hours and placed in desiccator, weight losses from dried particles were measured and ion concentrations (ppm levels) in leachate solutions were analyzed using ICP-OES. Solutions for ICP were filtered to remove solid particles and diluted with 1wt% HNO₃. Dilution factors were 1:9 or 1:99, depending on the predicted ion concentrations of the solution. The pH values of leachate solutions were measured using a pH electrode (Fisher Scientific Accumet Research AR25).

The surface morphologies and compositions of corroded glasses were characterized by scanning electron microscopy (SEM) (FEI Helios NanoLab 600 DualBeam FIB/SEM) with energy-dispersive X-ray spectrometry (EDS). Samples were coated with carbon prior to these analyses.

3. Results

3.1. Static Dissolution

The concentrations of ions released into solution were normalized to the initial glass composition. The normalized elemental mass release, NL(i) (mg/cm²), was calculated by Eq. (1),

$$NL(i) = \frac{C_i}{(f_i) \cdot (SA(t)/V)} \quad (1)$$

where C_i is the measured concentration (ppm) of element i in solution, f_i is the mass fraction (wt%) of element i in the initial glass, $SA(t)/V$ is the time-dependent ratio of glass surface area (cm²) to leachate volume (L) [6]. Instantaneous release rates for each element can be determined from the slope, $\partial[NL(i)]/\partial t$, at any given time in the plot of NL(i) versus time [16]. If all glass

constituents are released into solution in the same proportion as they are present in the solid, congruent dissolution is observed and $\partial[NL(i)]/\partial t$ is the same for all elements. The average release rate is equal to the instantaneous release rates only if $NL(i)$ is linear with time.

Fig. 1 (a) shows that for the static dissolution Test 1, the amount of P released into water from the D-series glasses ($O/P = 3.40 \pm 0.03$) decreases by nearly four orders of magnitude with an increase in the Fe/P ratio from 0.23 to 0.58. Fig. 1 (b) shows the normalized mass release (mg/cm^2) data for sodium, phosphorus and iron from the same series of experiments. Congruent dissolution is observed for glasses with low iron contents ($\text{Fe}/\text{P} = 0.23$ and 0.32), and preferential release of sodium is observed from glasses with greater iron content ($\text{Fe}/\text{P} = 0.39$ and 0.49); the glass with $\text{Fe}/\text{P} = 0.58$ is Na-free. Fig. 1 (c) shows how the pH of the leachate solutions changes with time for the D-series glasses. In general, glasses with greater Na-contents (lower Fe/P ratios) create more basic leachate solutions. Static dissolution tests on the E-series glasses ($O/P = 3.49 \pm 0.01$) showed similar results for the ion release data and leachate solution pH, with the latter increasing to 8.3–8.7 for glass E-0.23.

Fig. 2 shows some results from static dissolution (Test 1) experiments for the B-series of glasses. These glasses have lower O/P ratios (3.12 ± 0.02) than the D-series, and so have longer average phosphate chains [23]. Fig. 2 (a) shows the normalized mass release (mg/cm^2) data for sodium, phosphorus and iron. Once again, glasses with lower Fe/P ratios dissolve congruently, especially initially, whereas glasses with greater Fe/P ratios preferentially release elements in the order $\text{Na} > \text{P} > \text{Fe}$. In contrast to the glasses with greater O/P ratios, the pH values of the leachate solutions of the B-series glasses decrease with time, with the more acidic solutions associated with glasses with the lowest iron content, and so the greatest P_2O_5 contents (Fig. 2 (b)). Static dissolution tests on A-series glasses ($O/P = 3.04 \pm 0.01$) showed similar compositional

dependences of leach rates and leachate solution pH, with the latter decreasing to 2.9–3.1 for glass A-0.13.

An average of 3 mole% SiO_2 was incorporated into the Na–Fe–phosphate melts from the crucible [23,24]. Fig. 3 shows the Si/P ratios in leachate solutions for the A-series glasses ($\text{O/P} = 3.04 \pm 0.01$). The glasses with greater iron contents ($\text{Fe/P} = 0.23$ and 0.37) released substantially more Si than did the glass with $\text{Fe/P} = 0.13$. The latter glass dissolved congruently. Similar results were observed for other glass series; glasses with greater iron contents released Si into DI H_2O at relatively greater rates than other constituents (Na, Fe and P).

3.2. *Semi-dynamic dissolution*

Fig. 4 (a) compares the normalized mass release (mg/cm^2) data for sodium, phosphorus and iron from the C-series of glasses, ($\text{O/P} = 3.27 \pm 0.02$), obtained in the static dissolution Test 1, with those obtained from the semi-dynamic dissolution Test 2. The glass with $\text{Fe/P} = 0.23$ dissolves congruently at a much greater rate when the solution is refreshed (Test 2) than in static conditions (Test 1). For the more durable glasses with greater Fe/P ratios, there is less difference in the release rates for the two tests. Similar compositionally-dependent results were observed for other glass series tested by these two techniques.

Fig. 4 (b) compares the ion release rates in the two dissolution tests for two glasses with similar normalized mass release rates, but much different compositions. Glass A-0.23 has an O/P of 3.04 and glass E-0.33 has an O/P of 3.50. Glass A-0.23 exhibits congruent dissolution behavior in the semi-dynamic Test 2 for the entire 130 hours of the test, whereas preferential release of ions ($\text{Na} > \text{P} > \text{Fe}$) is evident after about 24 hours in static Test 1. For glass E-0.33,

both tests reveal congruent dissolution behavior for the entire 130 hours. Changes in solution pH and the Si release behavior were similar for the two tests.

4. Discussion

4.1. Dissolution kinetics

Two shrinking-core models [26] are applied to the glass dissolution data. Glass particles are assumed to have spherical geometries and reactions between the aqueous solution and the glass particles are three dimensional (3D), occurring at the outer surface of the particles. The reaction interface moves into the particle and the unreacted glass core shrinks uniformly so that the reacting area decreases with reaction time.

If a diffusion process controls the rate of reaction for spherical particles, a 3D diffusion model (DM) with parabolic time dependence could be used to describe that reaction [27,28]:

$$1 - (1 - \alpha)^{1/3} = k_{DM} t^{1/2} \quad (2)$$

where α is the mass fraction of a particle that has reacted in time t , and k_{DM} is the temperature-dependent reaction rate parameter.

A contracting volume model (CVM) would describe linear reaction kinetics, with a reaction rate parameter of k_{CVM} , for spherical particles [27,28,29]:

$$1 - (1 - \alpha)^{1/3} = k_{CVM} t \quad (3)$$

The P-release data for all static dissolution (Test 1) experiments were analyzed to determine the time-dependence of $\alpha(P)$ and then were fit by the DM and CVM rate equations. An example of the model-fitting is shown for glass B-0.12 in Fig. 5. Initially, there is a rapid release of phosphorus to solution and the parabolic release kinetics are consistent with the

Diffusion Model (Eq. 2). After about fifteen hours, the release kinetics slow down compared to the original DM predictions, and are instead well-fit by the Contracting Volume Model (Eq. 3).

Fig. 6 shows the two-model fit applied to glasses from the B-series ($O/P = 3.12 \pm 0.02$) and the D-series ($O/P = 3.40 \pm 0.03$). In every case, the initial P-release data fit the Diffusion Model and later data fit the Contracting Volume Model, although the reaction time where the transition from one model to the other differed for glasses with different compositions (Table 1). For glasses with longer phosphate chains (e.g., series B, $O/P \sim 3.12$), the transition time from DM to CVM does not change significantly with greater Fe/P ratio, whereas for glass series with shorter phosphate chains (e.g., series D, $O/P \sim 3.40$), the first stage controlled by the 3D diffusion mechanism is generally prolonged as the Fe/P ratio increases.

Fig. 7 (a) shows the dependence of k_{DM} on the Fe/P ratio and Fig. 8 (a) shows a similar dependence of k_{CVM} . Clearly, glasses with greater iron contents react more slowly in both reaction regimes. Fig. 7 (b) and Fig. 8 (b) summarize the compositional dependences of k_{DM} and k_{CVM} , respectively, for all glasses reacted in DI water using Test 1. Here, it is apparent that the Fe/P ratio has a greater effect on the dissolution kinetics of the Na–Fe–phosphate glasses than does the O/P ratio. The slowest reacting glasses studied here are Na-free and have O/P ratios near 3.4. The superior chemical durability of glasses around this composition is attributed to the low rate of glass surface hydration. Bunker et al. [1] related surface hydration to inter-chain hydrogen bonding in the hydrated glass surface; two phosphate chain ends are linked by hydrogen bonds leading to longer effective chain lengths and slower dissolution rates. On the other hand, the existence of SiO_2 in phosphate glass network may deleteriously affect chemical durability, since Si is selectively released from the network of glasses with greater iron contents (Fig. 3). The greater silica content may explain why the lowest k_{DM} and k_{CVM} values were

observed for the Na-free glass with O/P ~3.4 ($\text{SiO}_2 = 0.95 \text{ mol\%}$ [24]) instead of the Na-free glass with O/P ~3.5 ($\text{SiO}_2 = 2.84 \text{ mol\%}$ [24]).

The dissolution kinetics of Series D ($\text{O/P} = 3.40 \pm 0.03$) glasses were determined at different temperatures using the static dissolution Test 1, and activation energies (Q) were calculated assuming an Arrhenius dependence of the reaction rate constants on absolute temperature (T):

$$k_{DM} = k_0 \exp(-Q/RT) \quad (4)$$

where k_0 is a pre-exponential factor and R is the gas constant.

Fig. 9 (a) shows the Arrhenius analyses of the different ion release data sets for glass D-0.23, which exhibits congruent dissolution behavior. Also shown is an analysis of the reacted volume (α) based on the total ion release concentrations and on the weight loss data. Fig. 9 (b) shows that minima in the activation energies for the glasses from series D ($\text{O/P} \sim 3.40$) occurs at $\text{Fe}/(\text{Na}+\text{Fe}) \sim 0.39$.

4.2. Dissolution mechanism

Bunker et al. [1] developed the general description for the dissolution reactions between phosphate glasses and water. The first stage of dissolution is controlled by diffusion, including penetration of H_2O into the glass network and diffusion of ions through the developing hydrated layer back into solution. Water hydrates the phosphate anions by reacting with the metal (Na,Fe) –O–P bonds that link neighboring P-anions:

At longer times, according to Bunker, linear reaction kinetics dominate as the hydrated metals and phosphate anions are released into solution. Under neutral pH conditions, the P-anions released from the glass hydrolyze slowly and so are (initially) representative of the P-anions in the original glass structure, making it possible to use solution techniques like chromatography to characterize phosphate glass structures [23,30].

The reaction rate constants for both the diffusion and the contracting volume models clearly show that increasing the relative iron concentration of a Na-Fe-phosphate glass reduces the dissolution rates of the glasses (Fig. 7 and Fig. 8). From Bunker's model, smaller values of k_{DM} might be interpreted as slower diffusion of water into a Fe-rich glass and/or slower diffusion of reaction products through the hydrated layer, and the smaller values of k_{CVM} may indicate slower hydration rates for Fe-O-P bonds compared to Na-O-P bonds.

Besides glass composition, solution chemistry also affects the dissolution mechanism. Fig. 10 (a) compares $\alpha(P)$ obtained in the static dissolution Test 1 with those from the semi-dynamic dissolution Test 2 for the C-series of glasses (O/P ratio ~ 3.27). The pH values of the respective leachate solutions are shown in Fig. 10 (b). The pH reaches a constant value because the species released from the glasses form buffered solutions [1]. Replenishing the solution decreases the buffering effects of the leachate solution (Fig. 10 (b)), and shortens the time duration of the first dissolution stage with the greater rate parameter k_{DM} ; the dissolution kinetics quickly enter the second stage with the smaller rate parameter k_{CVM} (Fig. 10 (a)), which causes the initial $\alpha(P)$ to be smaller in the semi-dynamic Test 2 than in the static Test 1. However, replenishing the solution increases the k_{CVM} for the second stage, causing the $\alpha(P)$ in Test 2 to eventually exceed that in Test 1 (Fig. 10 (a)). Glasses with high iron contents (e.g., C-0.49) have longer first stages

(DM controlled) than glasses with low iron contents (e.g., C-0.23), so the former glasses require longer times for the $\alpha(P)$ in Test 2 to exceed $\alpha(P)$ in Test 1.

4.3. *Dissolution and glass composition*

For the sodium iron phosphate glasses in the present study, the dissolution behavior can be categorized into three types, based on whether congruent dissolution or selective dissolution describes the diffusion-controlled stage and the reaction-controlled stage; these types of dissolution behavior are summarized in the compositional map in Fig. 11.

Type I behavior involves selective release of Na- and P-species (relative to Fe) for both dissolution stages. Two examples of the corrosion surface morphology associated with Na-containing glasses that exhibit Type I behavior are shown in Fig. 12, where (12a) is for glass C-0.38 and (12b) is for glass E-0.48. After the second dissolution stage, a thin alteration layer is observed for glass C-0.38. EDS analyses (Table 2) indicate that the surface composition of corroded Na-containing glasses are Na and Fe rich, especially after the second dissolution stage. For Na-free iron phosphate glasses, the mass release rates of glass constituents become quite low after entering the second stage of dissolution, and increasing the O/P ratio of the glass leads to decreasing k_{DM} and k_{CVM} (Fig. 7 (b) and Fig. 8 (b)). For this kind of dissolution process, ion concentrations in the leachate are below the respective solubility limits, and saturation is not involved in the decrease in the mass release rates. No clear precipitation phases or alteration layers were observed on glass surfaces by SEM. EDS analyses (Table 2) indicate that the surface composition of the corroded Na-free glasses are similar to the initial, unreacted glass. This is inconsistent with the observation from the solution analyses for the preferential release of

phosphate species. It is possible that a resulting Fe-rich surface layer is too thin to be detected by EDS.

Type II behavior involves congruent dissolution for both stages. The first stage controlled by diffusion is often too short to be observed, and glass dissolution quickly enters the second stage, where phosphate anions are released from the glass network, along with the metal ions, by hydration reactions at the glass surface [1]. An example of the surface morphology that develops for a glass that exhibits Type II behavior is shown in Fig. 13. The glass surface is covered by etch pits that increase in size with corrosion time. Similar observations were made in a corrosion study of Na–Ca–phosphate glasses and were explained by a surface reaction-limited corrosion mechanism [31]. EDS analyses (Table 2) show that the surface compositions of glasses that exhibit Type II corrosion behavior are also similar to those of the original glasses.

Type III corrosion behavior involves congruent dissolution for the first stage, then selective ion release for the second stage. Glass A-0.13 is a representative example. Fig. 14 (a) shows that uniformly distributed etch pits (0.3–0.8 μm) form on glass surfaces during the first stage (DM) of dissolution, and Table 2 shows that the Fe/P and Na/P cation ratios of these surfaces, determined by EDS, are similar to those in the original glass. During the second stage (CVM), the mass release of glass constituents is continuous and linear in the acidic ($\text{pH} = 2.9\text{--}3.1$) leachate solution. Electron microscopy reveals that precipitates or alteration layers are present (Fig. 14 (b1)), and EDS (Table 2) indicates that these phases are Na-deficient ($\text{Na/P} \sim 0.03$) and iron-rich ($\text{Fe/P} \sim 0.57$) compared with the initial glass, consistent with selective leaching behavior shown by normalized mass release in Fig. 2 (a). More extensive surface precipitates, associated with the etch pits, are shown in Fig. 14 (b2).

For glasses that show selective leaching behavior (Type I and Type III), alteration layers were observed by SEM except for Na-free glasses. Based on the ion concentration measurements, the formation of alteration layers could be attributed to the Fe left behind after the first dissolution stage (Type I), and the precipitation of Fe from the leachate solutions during the second dissolution stage (Type I and Type III). Such reactions could explain the decreases in Fe concentrations of the leachates at the end of the second dissolution stage (e.g., Fig. 1 and Fig. 2). For glasses that follow Type I behavior, Na is also enriched on the corroded glass surfaces, leading to a greater Na/P ratio than is found in the base glass, but the net concentration of Na in solution still increases with dissolution time. The transition between the two dissolution stages could be related to the nature of the alteration layer and the start of Fe precipitation from solution.

The activation energies calculated from the dissolution kinetics for the D series glasses (O/P~3.40) exhibit a minimum near $\text{Fe}/(\text{Na}+\text{Fe}) = 0.39$ (Fig. 9b), and this may be related to a change in the dissolution mechanism. In this series, glasses with $\text{Fe}/(\text{Na}+\text{Fe}) \geq 0.39$ exhibit Type I dissolution behavior (selective leaching), whereas glasses with $\text{Fe}/(\text{Na}+\text{Fe}) < 0.39$ exhibit Type II (congruent) dissolution behavior. The activation energies measured in the dissolution studies of these glasses (20-60 kJ/mole) are somewhat lower than what has been reported in dissolution studies of longer-chained phosphate glasses (e.g., 54-67 kJ/mole [1], 79 kJ/mole [32], 63-103 kJ/mole [33]), but are similar to the activation energies for the dissolution of phosphate minerals, like β -TCP (42 kJ/mole [34]), monazite (43 kJ/mole [35]), thorium phosphate–diphosphate (TPD) (42 kJ/mol [36]) and OCP (48 kJ/mole [37]). The activation energy for proton conductivity in hydrated phosphate glasses is 10-25 kJ/mole [38,39], and so the lower activation energy for the dissolution rates of the D-series glasses might indicate a diffusion-limited process. Sales and

4.4. Leachate pH prediction

There are three types of sites on phosphate anions, each with a different acid dissociation constant (pK_a), that can be protonated in an aqueous solution at an appropriate pH value: middle site 1, terminal site 2 and terminal site 3 [1,41],

Middle site 1 has a pK_a value between pH 1–2. Terminal site 3 has a pK_a value around pH 12. The pK_a values for terminal site 2 are sensitive to the presence of cations in solutions and vary between pH 3–11 [1,41]. Therefore, for phosphate anions in the leachate solutions for this study, with final pH values from 3 to 9 (Fig. 1 (c) and Fig. 2 (b)), the middle sites (1) are all in anionic form and should be charge-balanced by Na^+ , Fe^{2+} or Fe^{3+} ions in solution, and every terminal site 3 will be protonated. The other terminal sites (2) are likely partially protonated and so can have a buffering effect on the solution pH. The greater the number of middle sites (1), the more negative

the surface charge of the anion will be. However, according to Bunker et al. [1], there seems to be no correlation between the surface charge and the rate of glass dissolution.

To predict the pH value of a leachate, the following assumptions are made: (1) There is no hydrolysis of phosphate chains released to solution over the course of the dissolution experiments; this is consistent with reports of hydrolysis rates in the literature [42]; (2) The phosphate anion distributions in solution are the same as those in the original glasses; this is consistent with the high-pressure liquid chromatography (HPLC) data reported in a previous study [23]; (3) In a leachate solution, phosphate anions with chain lengths $n > 2$ have both anionic terminal site 2 and protonated terminal site 3 and can be described by the formula $(H_2P_nO_{3n+1})^{-n}$; (4) The iron redox in solution is the same as that in the original glass.

The pH values of the leachates in the static dissolution Test 1 reached a constant value in the first 24 hours of glass dissolution (e.g., Fig. 2 (b)). Since the phosphate anions are the major anions in solution, the total number of terminal phosphates in chains released to the leachate solution can be determined from the total phosphorus released and the phosphate chain length distributions in the original glasses [23], and these can then be related to the solution pH value.

For a better prediction of solution pH, the charged species in a leachate, especially for phosphate anions PO_4^{3-} and $P_2O_7^{4-}$, need to be determined for different pH ranges according to their pK_a values. Table 3 lists the pK_a values of all the possible species in an aqueous solution containing Na, P, Fe, and Si ions. From these values, the major species and buffer reactions in the leachate solutions of Na–Fe–phosphate glasses with pH range 2–7 and 7–10 can be determined, and these are listed in Table 4. Because of their high field strength, hydrated iron cations in aqueous solution attract electron density between the O and the H atoms, making weaker O–H bonds and easier dissociation of the H^+ ions from coordinated H_2O [43].

According to the principle of charge balance in solution, the total positive charge (A) must equal the total negative charge (B), and this can be expressed by the following equations,

$$A = [H^+] + [Na^+] + 2\{[Fe(H_2O)_5(OH)]^{2+}\} + 2\{[Fe(H_2O)_6]^{2+}\} + \{[Fe(H_2O)_5(OH)]^+\} = [H^+] + C \quad (7)$$

$$B = [OH^-] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [H_2P_2O_7^{2-}] + [HP_2O_7^{3-}] + [P_2O_7^{4-}] + \sum_{i=3}^n \{n [(H_2P_nO_{3n+1})^{-n}]\} + [(H_3SiO_4)^-] + [(HCO_3)^-] + 2[(CO_3)^{2-}] = [OH^-] + D \quad (8)$$

At 25 °C,

$$K_w = [H^+][OH^-] = 1.01 \times 10^{-14} \quad (9)$$

Combining equations leads to,

$$(C - D) = [OH^-] - [H^+] = \frac{1.01 \times 10^{-14}}{[H^+]} - [H^+] \quad (10)$$

The concentration (mol/L) of hydrogen ions required to balance this charge is then calculated from,

$$[H^+] = \frac{-(C-D) + \sqrt{(C-D)^2 + 4.04 \times 10^{-14}}}{2} \quad (11)$$

The starting pH value of DI H₂O used in this study is 6.11 ± 0.23 at room temperature.

According to acid-base equilibria and mass balance of H₂CO₃ in DI H₂O, the amount of CO₂ in

solution can be calculated as $\sim 10^{-7}$ mol for any leachate solution [45]. The concentrations of other ions in solution were measured by ICP-OES. The major species in a leachate are chosen for different pH ranges from Table 4, and then the pH values were calculated from equations 7–11. Fig. 15 shows the comparison of measured and predicted pH values of the leachate solutions. For the glass series with longer phosphate chains (e.g., O/P ~ 3.12 , Fig. 15 (a)) and glasses with greater iron contents (e.g., Na-free iron phosphate glasses, Fig. 15 (b)), the predicted pH values from the ion concentrations in leachate solutions are quite close to the measured pH values. For glasses with short phosphate chains that release greater concentrations of orthophosphate and pyrophosphate anions into solution, the predicted pH is somewhat lower than the measured pH, perhaps because the model does not sufficiently account for the buffering effects of these small anions.

5. Summary

The dissolution behavior of five series of $\text{Na}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses with a range of O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios was investigated by static and semi-dynamic dissolution tests in water. Two kinetic stages are observed for the dissolution processes. The first stage follows a 3D diffusion model (DM) and the second stage follows a linear contracting volume model (CVM). The transition time from DM to CVM depends on composition; for glasses with longer phosphate chains, the transition time does not change significantly with greater Fe/P ratio, whereas for glasses with shorter phosphate chains, the first stage (diffusion controlled) is generally prolonged as the Fe/P ratio increases. For glasses with greater O/P ratios (O/P > 3.3) and lower iron contents (Fe/P < 0.32), the first stage is ≤ 6 hours.

The rate parameters for two dissolution stages, k_{DM} and k_{CVM} , decrease by several orders of magnitudes with an increase in Fe/P ratio, and they are much more dependent on iron content than the O/P ratio (average phosphate chain length). The slowest reacting glasses studied here are Na-free and have O/P ratios near 3.4, taking into consideration possible effects of silica contamination on glass durability. Replenishing the solution during a dissolution test decreases the buffering effects of the leachate solution, and shortens the time duration of the first dissolution stage and increasing the k_{CVM} for the second stage.

There are three types of dissolution behavior for these Na-Fe-phosphate glasses. Type I behavior involves selective leaching of ions for both stages. Type II behavior involves congruent dissolution for both stages. Type III behavior involves congruent dissolution during the first stage and then selective leaching in the second stage. These different types of corrosion processes produce different surface morphologies and compositions that are consistent with the normalized ion release information obtained by ICP. The leachate pH depends on the relative concentrations of ions released to solution, including the types of phosphate anions, and pH predictions made from the leachate compositions are in good agreement with the measured pH values.

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Table 1 Transition time from DM to CVM kinetics in static dissolution Test 1.

Glass series	Analyzed		Transition time (hour)
	O/P	Fe/P	
A	3.04	0.37	18 ± 2
	3.04	0.23	21 ± 3
	3.03	0.13	18 ± 2
B	3.15	0.42	18 ± 2
	3.10	0.32	21 ± 3
	3.12	0.22	21 ± 3
	3.13	0.12	12 ± 1
C	3.28	0.49	19 ± 3
	3.25	0.38	18 ± 3
	3.24	0.32	24 ± 5
	3.27	0.23	18 ± 2
D	3.36	0.58	27 ± 3
	3.38	0.49	26 ± 2
	3.40	0.39	18 ± 1
	3.42	0.32	15 ± 3
	3.43	0.23	6 ± 1
E	3.48	0.66	24 ± 5
	3.48	0.58	24 ± 4
	3.48	0.48	36 ± 1
	3.50	0.39	27 ± 3
	3.50	0.34	6 ± 1
	3.51	0.23	<6

Table 2 Compositional differences between as-made and corroded glass surfaces.

Dissolution behavior	Glass examples	Unreacted		Corroded glass surfaces		
		ICP-OES		EDS		Surface condition
		Fe/P	Na/P	Fe/P	Na/P	
Type I	A-0.37	0.37	–	0.34 (3)	–	No precipitation phases or alteration layers were observed.
	B-0.42	0.42	–	0.40 (1)	–	
	C-0.49	0.49	–	0.49 (1)	–	
	E-0.66	0.66	–	0.64 (3)	–	
	C-0.38	0.38	0.26	0.46 (1)	0.36 (2)	Fig. 12 (a1)
				0.44 (1)	0.37 (1)	Fig. 12 (a2)
	E-0.48	0.48	0.50	0.50 (5)	0.63 (3)	Fig. 12 (b1)
				0.55 (2)	0.62 (5)	Fig. 12 (b2)
Type II	E-0.23	0.23	1.28	0.26 (1)	1.29 (3)	Fig. 13
Type III	A-0.13	0.13	0.61	0.13 (1)	0.59 (1)	Fig. 14 (a)
				0.57 (1)	0.03 (1)	Fig. 14 (b)

Table 3 Acid dissociation constants (pK_a) of possible species in an aqueous solution containing Na, P, Fe, Si ions [44,45].

Aqueous acid-base equilibria	Step	pK_a	T (°C)
$[Fe(H_2O)_6]^{3+} \leftrightarrow [Fe(H_2O)_5(OH)]^{2+} + H^+$		2.17	25
$[Fe(H_2O)_6]^{2+} \leftrightarrow [Fe(H_2O)_5(OH)]^+ + H^+$		8.30	25
$H_4SiO_4 \leftrightarrow (H_3SiO_4)^- + H^+$	1	9.9	30
$(H_3SiO_4)^- \leftrightarrow (H_2SiO_4)^{2-} + H^+$	2	11.8	30
$(H_2SiO_4)^{2-} \leftrightarrow (HSiO_4)^{3-} + H^+$	3	12	30
$(HSiO_4)^{3-} \leftrightarrow (SiO_4)^{4-} + H^+$	4	12	30
$H_3PO_4 \leftrightarrow (H_2PO_4)^- + H^+$	1	2.15	25
$(H_2PO_4)^- \leftrightarrow (HPO_4)^{2-} + H^+$	2	7.20	25
$(HPO_4)^{2-} \leftrightarrow (PO_4)^{3-} + H^+$	3	12.35	25
$H_4P_2O_7 \leftrightarrow (H_3P_2O_7)^- + H^+$	1	0.83	25
$(H_3P_2O_7)^- \leftrightarrow (H_2P_2O_7)^{2-} + H^+$	2	2.26	25
$(H_2P_2O_7)^{2-} \leftrightarrow (HP_2O_7)^{3-} + H^+$	3	6.72	25
$(HP_2O_7)^{3-} \leftrightarrow (P_2O_7)^{4-} + H^+$	4	9.46	25
$H_3PO_3 \leftrightarrow (H_2PO_3)^- + H^+$	1	1.3	20
$(H_2PO_3)^- \leftrightarrow (HPO_3)^{2-} + H^+$	2	6.70	20
$H_2CO_3 \leftrightarrow (HCO_3)^- + H^+$	1	6.35	25
$(HCO_3)^- \leftrightarrow (CO_3)^{2-} + H^+$	2	10.33	25

Table 4 Major species and buffer reactions in leachate solutions of Na–Fe–phosphate glasses with pH ranges 2–7 and 7–10.

pH 2–7	pH 7–10
$(H_2PO_4)^- \leftrightarrow (HPO_4)^{2-} + H^+$	$(HPO_4)^{2-} \leftrightarrow (PO_4)^{3-} + H^+$
$(H_2P_2O_7)^{2-} \leftrightarrow (HP_2O_7)^{3-} + H^+$	$(HP_2O_7)^{3-} \leftrightarrow (P_2O_7)^{4-} + H^+$
$(H_2PO_3)^- \leftrightarrow (HPO_3)^{2-} + H^+$	$(HPO_3)^{2-}$
$H_2CO_3 \leftrightarrow (HCO_3)^- + H^+$	$(HCO_3)^- \leftrightarrow (CO_3)^{2-} + H^+$
$H_4SiO_4 \leftrightarrow (H_3SiO_4)^- + H^+$	
$[Fe(H_2O)_5(OH)]^{2+}$	
$[Fe(H_2O)_6]^{2+} \leftrightarrow [Fe(H_2O)_5(OH)]^+ + H^+$

Fig. 1. Glass series D ($\text{O/P} = 3.40 \pm 0.03$) dissolved in DI H₂O at 60 ± 2 °C by static dissolution Test 1. (a) Logarithm of normalized phosphorus mass release (mg/cm^2). (b) Normalized mass release (mg/cm^2) of sodium, phosphorus and iron. (c) pH values of leachate solutions.

Fig. 1. Glass series D ($O/P = 3.40 \pm 0.03$) dissolved in DI H_2O at 60 ± 2 °C by static dissolution Test 1. (a) Logarithm of normalized phosphorus mass release (mg/cm^2). (b) Normalized mass release (mg/cm^2) of sodium, phosphorus and iron. (c) pH values of leachate solutions. (cont.)

Fig. 2. Glass series B ($O/P = 3.12 \pm 0.02$) dissolved in DI H₂O at 60 ± 2 °C by static dissolution Test 1. (a) Normalized mass release (mg/cm²) of sodium, phosphorus and iron. (b) pH values of the leachate solutions.

Fig. 3. Si/P ratios in leachate solutions for glass series A (O/P ratio = 3.04 ± 0.01). The average Si/P ratio in these glasses 0.02 ± 0.01 , indicated by the gray band.

Fig. 4. Comparison of normalized mass release (mg/cm^2) of sodium, phosphorus and iron between static dissolution Test 1 and semi-dynamic dissolution Test 2 at 60 ± 2 °C. (a) Glass series C ($\text{O}/\text{P} = 3.27 \pm 0.02$). (b) Glasses with similar ranges of normalized mass release (mg/cm^2) rates.

Fig. 5. Static dissolution Test 1 at 60 ± 2 °C: Mass fraction of phosphorus leached from glass B-0.12, $\alpha(P)$, changed with dissolution time (hour), fitted by the 3D diffusion model (DM, dashed line) and contracting volume model (CVM, solid line). Temperature-dependent rate parameters are given.

Fig. 6. Static dissolution Test 1 at 60 ± 2 °C: $\alpha(P)$ fitted by the 3D diffusion model (DM, dashed line) and contracting volume model (CVM, solid line); (a) Glass series B ($O/P = 3.12 \pm 0.02$). (b) Glass series D ($O/P = 3.40 \pm 0.03$).

Fig. 7. Static dissolution Test 1 at 60 ± 2 °C: (a) The effect of Fe/P ratio on the rate parameter for the 3D diffusion model, k_{DM} . (b) Compositional dependence of k_{DM} in room temperature DI water.

Fig. 8. Static dissolution Test 1 at 60 ± 2 °C: (a) The effect of Fe/P ratio on the rate parameters for the contracting volume model, k_{CVM} . (b) Compositional dependence of k_{CVM} in room temperature DI water.

Fig. 9. Static dissolution Test 1: (a) Arrhenius analyses of k_{DM} for glass D-0.23; (b) Compositional dependence of activation energies for glass series D ($O/P = 3.40 \pm 0.03$), based on individual ion release rates, total ion concentrations (α , Λ) and weight loss measurement (WL, M).

Fig. 10. Comparison of mass fraction of phosphorus, $\alpha(P)$, released from glasses and changes in leachate pH, for glass series C ($O/P = 3.27 \pm 0.02$) for static dissolution Test 1 and semi-dynamic dissolution Test 2 at 60 ± 2 °C. The lines are guides for the eyes.

Fig. 11. Compositional map for dissolution stage 1 (Diffusion Model), congruent dissolution behavior (gray) and selective leaching behavior (yellow). Compositional map for dissolution stage 2 (Contracting Volume Model), congruent dissolution behavior (angled lines) and selective leaching behavior (vertical lines) (60 ± 2 °C, DI H_2O).

Fig. 12 Surface morphology of Type I glass (Na-containing) after static dissolution Test 1 at 60 ± 2 °C. For glass C-0.38 (a): (a1) 16 hours, pH value ~4.8. (a2) 123 hours, pH value ~5.1. For glass E-0.48 (b): (b1) 30 hours, pH value ~5.8. (b2) 100 hours, pH value ~6.1.

Fig. 13. Surface morphology of glass E-0.23 (Type II) after a static dissolution Test 1 at 60 ± 2 °C for 10 hours; solution pH was ~8.6.

Fig. 14. Surface morphology of glass A-0.13 (Type III) in static dissolution Test 1 at 60 ± 2 °C. (a) 18 hours, pH value ~ 3.1 . Greater magnification of specific area of (a1) is shown in (a2). (b) 84 hours, pH value ~ 3.0 , two types of surface morphology are observed (b1 and b2).

Fig. 15. Comparison of measured (symbols) and predicted (solid lines) pH values of leachate solutions. (a) Glass series B (O/P ~3.12); (b) Na-free iron phosphate glasses.

References

- [1] B.C. Bunker, G.W. Arnold, and J.A. Wilder. "Phosphate glass dissolution in aqueous solutions." *Journal of Non-Crystalline Solids* 64, no. 3 (1984): 291-316.
- [2] B.C. Sales, and L.A. Boatner. "Lead-iron phosphate glass: a stable storage medium for high-level nuclear waste." *Science* 226, no. 4670 (1984): 45-48.
- [3] X. Yu, D.E. Day, G.J. Long, and R.K. Brow. "Properties and structure of sodium-iron phosphate glasses." *Journal of Non-Crystalline Solids* 215, no. 1 (1997): 21-31.
- [4] Y.B. Peng, and D.E. Day. "High thermal expansion phosphate glasses. PT.1." *Glass Technology* 32, no. 5 (1991): 166-173.
- [5] I. Ahmed, M. Lewis, I. Olsen, and J.C. Knowles. "Phosphate glasses for tissue engineering: Part 2. Processing and characterisation of a ternary-based P_2O_5 -CaO- Na_2O glass fibre system." *Biomaterials* 25, no. 3 (2004): 501-507.
- [6] D.E. Day, Z. Wu, C.S. Ray, and P. Hrma. "Chemically durable iron phosphate glass wasteforms." *Journal of Non-Crystalline Solids* 241, no. 1 (1998): 1-12.
- [7] W. Huang, D.E. Day, C.S. Ray, C.W. Kim, and A. Mogus-Milankovic. "Vitrification of high chrome oxide nuclear waste in iron phosphate glasses." *Journal of Nuclear Materials* 327, no. 1 (2004): 46-57.
- [8] C.W. Kim, and D.E. Day. "Immobilization of Hanford LAW in iron phosphate glasses." *Journal of Non-Crystalline Solids* 331, no. 1 (2003): 20-31.
- [9] L. Zhang, L. Ghussn, M.L. Schmitt, E.D. Zanotto, R.K. Brow, and M.E. Schlesinger. "Thermal stability of glasses from the $Fe_4(P_2O_7)_3$ - $Fe(PO_3)_3$ system." *Journal of Non-Crystalline Solids* 356, no. 52 (2010): 2965-2968.
- [10] 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, no. 2 (2003): 152-164.
- [11] American Society for Testing and Materials (ASTM), *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)*, C 1285-97, 1998.
- [12] A. Jiříčka, J.D. Vienna, P. Hrma, and D.M. Strachan. "The effect of experimental conditions and evaluation techniques on the alteration of low activity glasses by vapor hydration." *Journal of Non-Crystalline Solids* 292, no. 1 (2001): 25-43.

- [13] I. Ahmed, C.A. Collins, M.P. Lewis, I. Olsen, and J.C. Knowles. "Processing, characterisation and biocompatibility of iron-phosphate glass fibres for tissue engineering." *Biomaterials* 25, no. 16 (2004): 3223-3232.
- [14] Karabulut, Mevlüt, G. K. Marasinghe, Chandra S. Ray, D. E. Day, G. D. Waddill, C. H. Booth, P. G. Allen, J. J. Bucher, D. L. Caulder, and D. K. Shuh. "An investigation of the local iron environment in iron phosphate glasses having different Fe (II) concentrations." *Journal of Non-Crystalline Solids* 306, no. 2 (2002): 182-192.
- [15] Abou Neel, E. A., I. Ahmed, J. J. Blaker, A. Bismarck, A. R. Boccaccini, M. P. Lewis, S. N. Nazhat, and J. C. Knowles. "Effect of iron on the surface, degradation and ion release properties of phosphate-based glass fibres." *Acta Biomaterialia* 1, no. 5 (2005): 553-563.
- [16] D.E. Clark, and B.K. Zaitos. "Corrosion of glass, ceramics and ceramic superconductors: Principles, testing, characterization and applications." Noyes Publications, Park Ridge, NJ (1992).
- [17] T.A. Abrajano, J.K. Bates, and C.D. Byers. "Aqueous corrosion of natural and nuclear waste glasses I. Comparative rates of hydration in liquid and vapor environments at elevated temperatures." *Journal of Non-Crystalline Solids* 84, no. 1 (1986): 251-257.
- [18] D. Perret, J.L. Crovisier, P. Stille, G. Shields, U. Mäder, T. Advocat, K. Schenk, and M. Chardonens. "Thermodynamic stability of waste glasses compared to leaching behaviour." *Applied Geochemistry* 18, no. 8 (2003): 1165-1184.
- [19] R. Conradt, and P. Geasee. "An improved thermodynamic approach to the stability of multi-component silicate glasses in aqueous solutions." *Berichte der Bunsengesellschaft für physikalische Chemie* 100, no. 9 (1996): 1408-1410.
- [20] R. Conradt. "Chemical durability of oxide glasses in aqueous solutions: A review." *Journal of the American Ceramic Society* 91, no. 3 (2008): 728-735.
- [21] B. Grambow. "Geochemical approach to glass dissolution." *Corrosion of Glass, Ceramics and Ceramic Superconductors* (1992): 124-152.
- [22] R. Conradt. "A proposition for an improved theoretical treatment of the corrosion of multi-component glasses." *Journal of Nuclear Materials* 298, no. 1 (2001): 19-26.
- [23] L. Ma, R.K. Brow. "Structural study of Na₂O-FeO-Fe₂O₃-P₂O₅ glasses by high-pressure liquid chromatography." *Journal of Non-Crystalline Solids* 387 (2014): 16-20.
- [24] L. Ma, R.K. Brow, A. Choudhury. "Structural study of Na₂O-FeO-Fe₂O₃-P₂O₅ glasses by Raman and Mössbauer spectroscopy." *Journal of Non-Crystalline Solids* 402 (2014): 64-73.
- [25] S.I. Grishin, J.M. Bigam, and O.H. Tuovinen. "Characterization of jarosite formed upon bacterial oxidation of ferrous sulfate in a packed-bed reactor." *Applied and Environmental Microbiology* 54, no. 12 (1988): 3101-3106.

- [26] O. Levenspiel. Chemical Reaction Engineering. John Wiley, New York, 1972.
- [27] M.N. Rahaman. Ceramic Processing. CRC Press, 2006.
- [28] Y. Gu, W. Xiao, L. Lu, W. Huang, M.N. Rahaman, and D. Wang. "Kinetics and mechanisms of converting bioactive borate glasses to hydroxyapatite in aqueous phosphate solution." *Journal of Materials Science* 46, no. 1 (2011): 47-54.
- [29] S.B. Jung, and D.E. Day. "Conversion kinetics of silicate, borosilicate, and borate bioactive glasses to hydroxyapatite." *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B* 50, no. 2 (2009): 85-88.
- [30] B.C. Sales, L.A. Boatner, and J.O. Ramey. "Chromatographic studies of the structures of amorphous phosphates: a review." *Journal of Non-Crystalline Solids* 263 (2000): 155-166.
- [31] F. Delahaye, L. Montagne, G. Palavit, J. Claude Touray, and P. Baillif. "Acid dissolution of sodium–calcium metaphosphate glasses." *Journal of Non-Crystalline Solids* 242, no. 1 (1998): 25-32.
- [32] H. Gao, T. Tan, and D. Wang. "Dissolution mechanism and release kinetics of phosphate controlled release glasses in aqueous medium." *Journal of Controlled Release* 96, no. 1 (2004): 29-36.
- [33] A. El Hadrami, M. Mesnaoui, M. Maazaz, and J.-J. Videau. "Kinetic dissolution of phosphate glasses containing toxic heavy metals." *Journal of Non-Crystalline Solids* 331, no. 1 (2003): 228-239.
- [34] S. Ni, and J. Chang. "*In vitro* degradation, bioactivity, and cytocompatibility of calcium silicate, dimagnesium silicate, and tricalcium phosphate bioceramics." *Journal of Biomaterials Applications* 24, no. 2 (2009): 139-158.
- [35] E.H. Oelkers, and F. Poitrasson. "An experimental study of the dissolution stoichiometry and rates of a natural monazite as a function of temperature from 50 to 230 °C and pH from 1.5 to 10." *Chemical Geology* 191, no. 1-3 (2002): 73-87.
- [36] A.C. Thomas, N. Dacheux, P. Le Coustumer, V. Brandel, and M. Genet. "Kinetic and thermodynamic study of the thorium phosphate–diphosphate dissolution." *Journal of Nuclear Materials* 281, no. 2-3 (2000): 91-105.
- [37] J. Zhang, and G.H. Nancollas. "Kinetics and mechanisms of octacalcium phosphate dissolution at 37 °C." *The Journal of Physical Chemistry* 96, no. 13 (1992): 5478-5483.
- [38] T. Akamatsu, T. Kasuga, and M. Nogami. "Formation of metaphosphate hydrogels and their proton conductivities." *Journal of Non-Crystalline Solids* 351, no. 8-9 (2005): 691-696.
- [39] Y. Abe, M. Hayashi, T. Iwamoto, H. Sumi, and L.L. Hench. "Superprotonic conducting

phosphate glasses containing water." *Journal of Non-Crystalline Solids* 351, no. 24-26 (2005): 2138-2141.

[40] Sales, B. C., and L. A. Boatner. "Physical and chemical characteristics of lead-iron phosphate nuclear waste glasses." *Journal of Non-Crystalline Solids* 79, no. 1-2 (1986): 83-116.

[41] J.R. Van Wazer, and K.A. Holst. "Structure and properties of the condensed phosphates. I. some general considerations about phosphoric acids." *Journal of the American Chemical Society* 72, no. 2 (1950): 639-644.

[42] J.R. Van Wazer. *Phosphorus and Its Compounds, Volume 1: Chemistry*. Interscience Publishers (1958): 717-800.

[43] B. Averill, and P. Eldredge. *Chemistry: Principles, Patterns, and Applications*. Pearson Education, Inc. (2007): 721-774.

[44] W.B. Jensen. *The Lewis Acid-Base Concepts: An Overview*. Wiley-Interscience, New York, 1980.

[45] W.M. Haynes, ed. *CRC Handbook of Chemistry and Physics*. CRC press, 2012.