Effect of B_2O_3 on the removal of phosphate ions from an aqueous solution in borosilicate glasses

Jin-su Nam, Cheol Y. Kim*

Department of Materials Science and Engineering, Inha University, 253 Yonghyun-dong, Nam-ku, Incheon, 402-751, South Korea

ARTICLE INFO

ABSTRACT

Recently, it was found by the authors of this study that glasses of a special composition have an ability to remove some hazardous ions from waste solutions. In the present study, a SiO_2–B_2O_3–CaO–Na_2O glass system has been chosen to remove phosphate ions from an aqueous solution. Several glasses with different amounts of B_2O_3 in the SiO_2–B_2O_3–CaO–Na_2O glass system have been prepared, and these glasses have been reacted with a solution containing 155 ppm of phosphate ions. A silica-rich layer is first formed on the glass surface by leaching Na^+ and Ca^{2+} ions from the glass, and then the Ca^{2+} and PO_4^{3-} ions in the solution have been uptaken on the silica-rich layer to precipitate hydroxyapatite crystals. In this manner, the phosphate ions could be removed from the solution. The efficiency of removing the phosphate ions was found to depend strongly on the B_2O_3 contents. With increase of B_2O_3 contents in the glass, more Ca^{2+} ions can be leach out of the glass, promotes the precipitation of hydroxyapatite. Therefore, the removal efficiency increases with increased B_2O_3 content. The phosphate ion removal efficiency was also sharply enhanced by increasing the surface area of the glasses and decreasing the pH of the solution.

1. Introduction

Phosphate is a very important element for many industries. The extensive industrial use of phosphates inevitably results in the discharging of large amounts of phosphate bearing wastes into municipal and industrial water effluent streams. Phosphate discharged into surface waters can disturb the balance of organisms present in the water and affect water quality, mainly through the depletion of the dissolved oxygen level. Depletion of the oxygen level in confined water bodies such as bays, lakes and ponds causes eutrophication [1,2].

Many studies have been carried out to develop procedures and technologies to remove phosphate ions from wastewater [3]. Conventional technologies for phosphate ion removal from wastewater are physical processes, biological processes and chemical precipitation processes using aluminum and calcium salt. Physical methods such as electrodialysis and reverse osmosis [4] have proved to be too expensive or inefficient [5]. Enhanced biological treatment offers high phosphate removal efficiency and low-cost. However, the variability in the chemical composition and temperature of wastewater would make the implementation of this process for wastewater treatment unfeasible [6]. Chemical methods are the most effective and well established methods. However,

the cost associated with the use of metal salts and the sludge production associated with the process may hinder the widespread application of such approaches [7]. Therefore, the application of low-cost and easily available materials such as fly ash, blast furnace slag, dolomite, hydroxides and mesoporous structural material in wastewater treatment has recently attracted great interest [8].

Recently, it has been reported that glasses of a particular composition have an ability to remove some hazardous ions from wastewater. When such glass is reacted in wastewater, the crystals containing hazardous ions precipitate on the glass surface. In this manner, hazardous ions can be removed from the wastewater. By controlling glass compositions, various hazardous ions can be removed from wastewater solutions, with relatively high efficiency [9–12].

In this study, SiO_2–B_2O_3–CaO–Na_2O glasses containing various amounts of B_2O_3 have been chosen to remove phosphate ions from an aqueous solution. The primary object of this study is to determine the effect of B_2O_3 in a glass on the efficiency of phosphate ion removal. The efficiency has been discussed in terms of a glass structure and reaction conditions.

2. Experimental

2.1. Preparation of borosilicate glasses

Table 1 shows the composition of the borosilicate glass used in this work. For these glass compositions, the ratio of SiO_2:Na_2O:CaO

---

* Corresponding author. Tel.: +82 32 860 7525; fax: +82 32 862 0129.
  E-mail address: cheolkim@inha.ac.kr (C.Y. Kim).

Table 1
Glass composition for this study (mole%).

Glass	SiO_2	B_2O_3	Na_2O	CaO
0B	60	0	20	20
10B	50	10	20	20
20B	40	20	20	20
30B	30	30	20	20
40B	20	40	20	20
50B	10	50	20	20

was kept constant at 60:20:20, and B_2O_3 was substituted for SiO_2 in the glass batch up to 50%. Appropriate amounts of raw materials, from the reagent grades of SiO_2, $CaCO_3$, Na_2CO_3 and B_2O_3, were weighed and mixed by gyroblender for 30 min. Then, the mixed glass batch was loaded in a Pt–Rh crucible and melted in an electrically heated furnace at temperatures ranging between 1100 and 1400 °C, depending on glass compositions, for 2 h. For better glass homogeneity, the glass melt was subsequently quenched, crushed, and then remelted under the same conditions. After the second melting, the glass melt was poured into a graphite mold to form a glass bar. To release any residual stress in the glass, the glass bar was annealed at 450 °C for 2 h and the furnace was shut off to cool the samples to room temperature before cutting.

The size of the prepared glass discs was $10 \times 10 \times 2$ mm. These discs were polished with 600-grit sandpaper and washed with acetone in an ultrasonic cleaner. Glass powder was also prepared by pulverizing the glass bar and sieving it, yielding a mean size of 80 μm and 500 μm. The prepared glass samples were kept in a desiccator until needed for use.

2.2. Preparation of the phosphate solution and reaction of the glass

The solution with phosphate ions was prepared by dissolving H_3PO_4 in distilled water. The solution contained 155 ppm of phosphate ions. The pH range of the solution was varied from 1.0 to 11.0 by adding appropriate amounts of HCl and NaOH.

One of the prepared bulk glass specimens ($10 \times 10 \times 2$ mm) was immersed in a polyethylene bottle containing 28 ml of the prepared solution with 155 ppm of phosphate ions, and reacted for various periods of time under dynamic conditions induced by using a shaker with a shaking speed of 120 rpm. The reaction temperature was kept at 30 °C. The ratio of the surface area of the sample (S) to the volume of the reacting solution (V) was set to 0.1 cm^{-1}.

After the glass sample was drawn out of the reacting solution, the glass specimens were treated with acetone for a few seconds to stop further reaction.

For the powder experiment, 1 g of the glass powder was reacted in 50 ml of prepared reacting solution, and the reaction was carried out under dynamic conditions by using a gyroblender.

2.3. Analysis of the reacted glass surface

The reacted surface of the glass was analyzed by using a Thin-film X-ray diffractometer (Philips PW3719 operated at 40 kV, 1.0° of incident beam angle, Cu target, scan speed: 0.05/s, 2θ:10–80°). A scanning electron microscope (SEM) (Hitachi X-4200, 20 kV) and a Fourier transform infrared (FT-IR) spectrometer (Bio-Rad FT-165) equipped with a diffused reflection unit were used to examine the reacted glass surfaces. The IR spectra were obtained in the range of 400–1600 cm^{-1} with a resolution of 2 cm^{-1}.

2.4. Measurement of ion concentration

After the glass powder was reacted in the solution containing phosphate ions, the concentration of the residual phosphate

ions was measured by the molybdenum blue method. Ammonuym molybdate and potassium antimonyl tartrate react with phosphate to form a phosphomolybdate that is reduced to intensely colored molybdenum blue by ascorbic acid [13]. The extinction at 885 nm caused by phosphomolybdate was measured by a UV–visible spectrometer (Shimadzu UV-260). All extinctions were compared to a standard calibration curve to calculate the ion concentrations.

The concentration of Si^{4+}, Ca^{2+} and Na^+ ions in the reacted solution that leached out of the glass were also measured. The concentration of Si^{4+} ions were measured by the molybdenum blue method similar to phosphate ion measurement [13]. Si^{4+} ion in a solution turns into silicomolybdate by adding molybdate, and the silicomolybdate produces a blue color by adding metol-sulfite and oxalic acid. The extinction at 810 nm was measured by a UV–visible spectrometer (Shimadzu UV-260). The concentration of Ca^{2+} and Na^+ ions was measured by an atomic absorption spectrometer (PerkinElmer Aanalyst 400) at a wavelength of 422.67 nm and 330.24 nm, respectively.

2.5. TEM and EDX analysis

Several broken pieces of precipitate obtained from the glass surface were collected and dispersed in alcohol, and a carbon-coated copper grid was dipped in the suspension to catch the precipitate. The copper grid with the obtained sample was examined using a transmission electron microscope (TEM) (Philips CM200, 120 kV, LaB6 filament) to investigate the crystallinity of the precipitate. Elemental analysis of the precipitate was also conducted using an energy-dispersive X-ray spectrometer (EDAX) attached to the TEM.

3. Results

3.1. Effect of B_2O_3 contents on phosphate removal

One gram of each glass powder (80 μm) with different B_2O_3 contents in the range of 0–50 mole% was reacted in a 50 ml solution containing 155 ppm of phosphate ions. The reaction was carried out under a dynamic condition in a gyroblender. The initial pH of the solution was 3.0. The phosphate ion concentrations left in the solution after reacting for 2, 5 and 10 min were measured, and the results are shown in Fig. 1.

The concentration of phosphate ions left in a reacting solution decreased linearly with B_2O_3 for all reaction times. This means that the removal capacity of phosphate ions increases with an increase of B_2O_3 in the glass composition. When glass containing 50 mole%
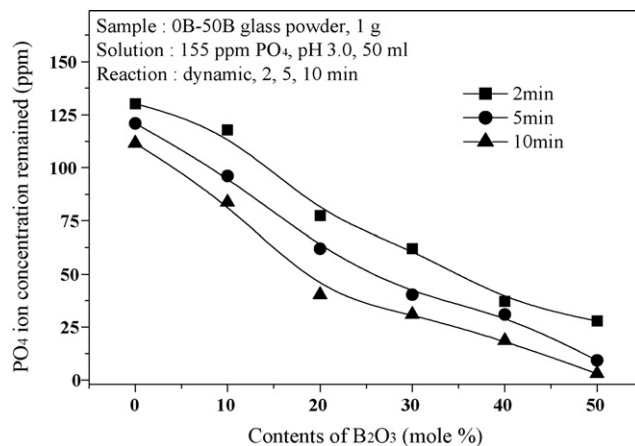

Fig. 1. Concentrations of phosphate ions remained in the solution after reaction times of 2, 5 and 10 min with 1 g of each glass powder with different B_2O_3 content in a range of 0–50 mole%.
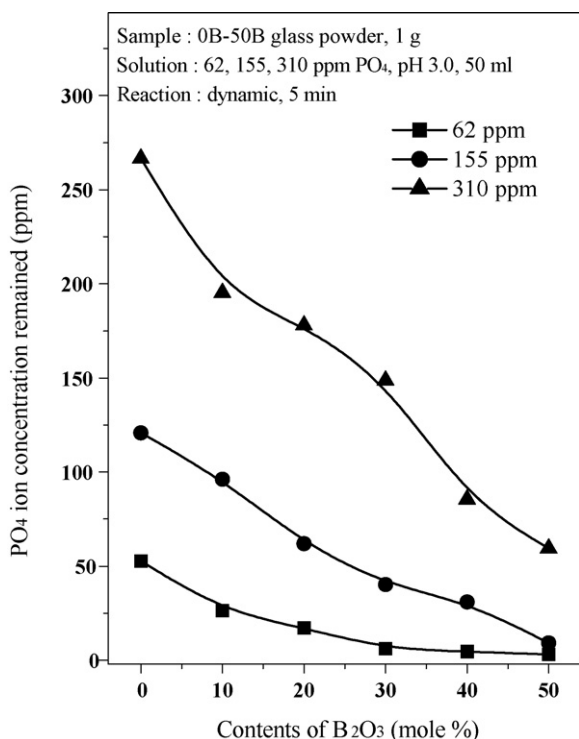
Fig. 2. Concentrations of phosphate ions remained in the solution after reaction with various initial phosphate concentrations of the reacting solution with 1 g of each glass powder for 5 min.

of B_2O_3 was reacted, most of the phosphate ions were removed within 10 min of reaction time.

The effect of the initial phosphate ion concentration of a solution on phosphate ion removal was examined for different glasses with various contents of B_2O_3. Initial phosphate ion concentration was varied from 62 ppm to 310 ppm. 1 g each of six different glass powders with a mean particle size of 80 μm was reacted for 5 min in phosphate solutions. After 5 min of reaction, the remaining phosphate ion concentration in the solution was measured. The results are presented in Fig. 2.

These results show the same linear dependency on B_2O_3 content for phosphate ion removal, regardless of initial phosphate concentration. Using 20B glass, it is possible to remove about 50% of phosphate ions from each solution in 5 min of reaction. However, using 40B glass it is possible to remove about 75% of phosphate ions under the same conditions.

3.2. Mechanism of phosphate ion removal

Pieces of each type of glass ($10 \times 10 \times 2$ mm), each with different B_2O_3 contents ranging from 0 to 50 mole%, were reacted in a 28 ml solution containing 155 ppm of phosphate ions for 12 h. The reaction was carried out under a dynamic condition in a shaker at 120 rpm. The pH of the solution was 3.0. After the reaction, the reacted glass surface was analyzed with thin film X-ray diffraction (XRD), and the results are presented in Fig. 3.

No crystalline phase was observed when the 0B glass was reacted with phosphate solution for 12 h. Only a typical X-ray amorphous bump was observed around 30° of 2θ, which originated from the silica phase in the glass [14,15]. The crystalline peak started to develop in the glass containing 10 mole% of B_2O_3, and the crystal peak intensity increased as B_2O_3 contents in the glass composition increased from 10 mole% to 30 mole%. The crystalline phase that deposited on the glass surface was identified as $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite). XRD results cannot be obtained for the samples
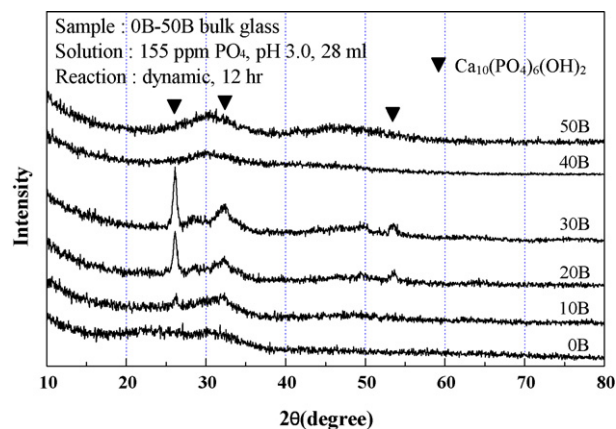

Fig. 3. Thin film XRD patterns of the surfaces of glasses with different B_2O_3 content in a range of 0–50 mole% reacted in a phosphate ion-containing solution with pH 3.0 for 12 h.

containing 40 mole% and 50 mole% of B_2O_3. Most of the deposited layers were peeled off in solution due to cracking of the thicker silica-rich layer.

Fig. 4 shows the results of the FT-IR study for each glass sample with different B_2O_3 contents after reaction in phosphate solution for 12 h. Typical PO_4 bending vibration can be seen in the range of wavenumbers of 550–600 cm^{-1}. The glass without B_2O_3(0B) showed only a bump in this range, which indicates the formation of Ca–P amorphous phase [16,17]. The peaks at 1250 cm^{-1} indicate the silica-rich layer. This indicates that an amorphous calcium phosphate film formed on the silica-rich layer when 0B glass was reacted with phosphate solution. As the B_2O_3 contents increased up
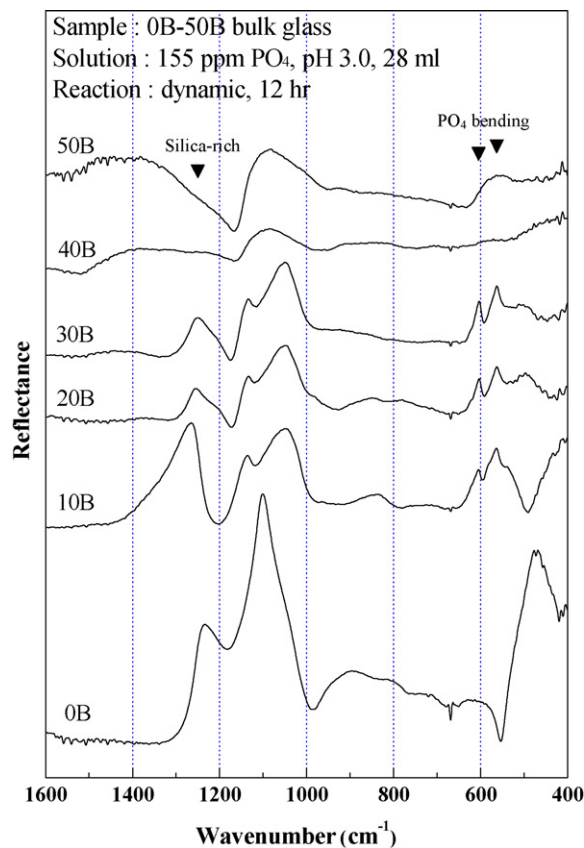

Fig. 4. FT-IR spectra of the surfaces of glasses with different B_2O_3 content in a range of 0–50 mole% reacted in a phosphate ion-containing solution with pH 3.0 for 12 h.
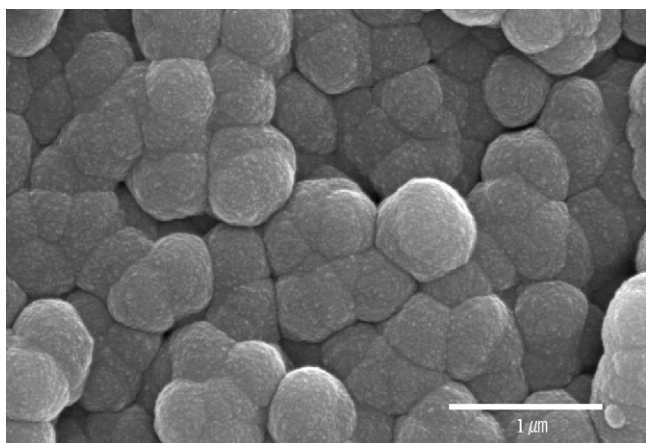
Fig. 5. SEM micrograph of 40B glass surface reacted with phosphate ion-containing solution with pH 3.0 for 12 h.

to 30 mole%, the P–O bending vibrations peak split into 610 cm^{-1} and 570 cm^{-1}, which are typical peaks for hydroxyapatite [18]. No crystalline phase was observed in the FT-IR spectra of the 40B and 50B glass, because most of the deposited layers had peeled off.

These results explain that the silica-rich layer was formed on the 0B glass surface first, but the hydroxyapatite crystals were not yet precipitated on this glass in 12 h of the reaction. However, in the reaction of the 10B, 20B and 30B glasses, P–O bending peak intensity increased with B_2O_3 contents. The hydroxyapatite crystal can precipitate on the glass in a short reaction time for glass compositions with higher B_2O_3 contents, indicating that the rate of crystal precipitation strongly depends on the B_2O_3 contents. In the present glass system, the molar ratio of SiO_2:Na_2O:CaO is 60:20:20 and B_2O_3 substituted for SiO_2 in the range from 0 mole% to 50 mole%. Therefore, the amount of SiO_2 in the glass composition decreased with B_2O_3.

It is known that B_2O_3 in glass weakens the structure of the glass, and the chemical reactivity of glass increases with B_2O_3 contents [19]; as a result, more Ca^{2+} ions leached out of the glass containing B_2O_3. This enhanced the hydroxyapatite crystal formation on the glass surface, and then a large amount of phosphate ions were eliminated from the solution.

One broken piece of the deposited layer from the 40B glass was examined using SEM, and its morphology is shown in Fig. 5. Many clusters were formed on the glass even if no XRD and FT-IR data were obtained because most of the deposits were lost. A transmission electron diffraction pattern for the cluster and the results of energy-dispersive X-ray spectroscopy (EDX) analyses has been given in Fig. 6. The diffraction pattern (Fig. 6(a)) indicates that the cluster has poor crystallinity and the EDX result (Fig. 6(b)) of the precipitated cluster shows a strong phosphate peak as well as a strong calcium peak. This indicates that a calcium phosphate cluster with low crystallinity was formed on the 40B glass surface.

These results show that phosphate ions can be removed from the solution by forming Ca–P crystalline phase on the glass surface.

3.3. Effect of particle size and amount of glass powder

The efficiency of removing phosphate ions from the solution can be improved by increasing the surface area of the glass used in the removal process. 20B and 40B glass powders with different particle sizes, such as 80 μm and 500 μm, were prepared. 1 g of each size of glass powders was reacted with 50 ml of solution containing 155 ppm of phosphate for various times, and the result is shown in Fig. 7.
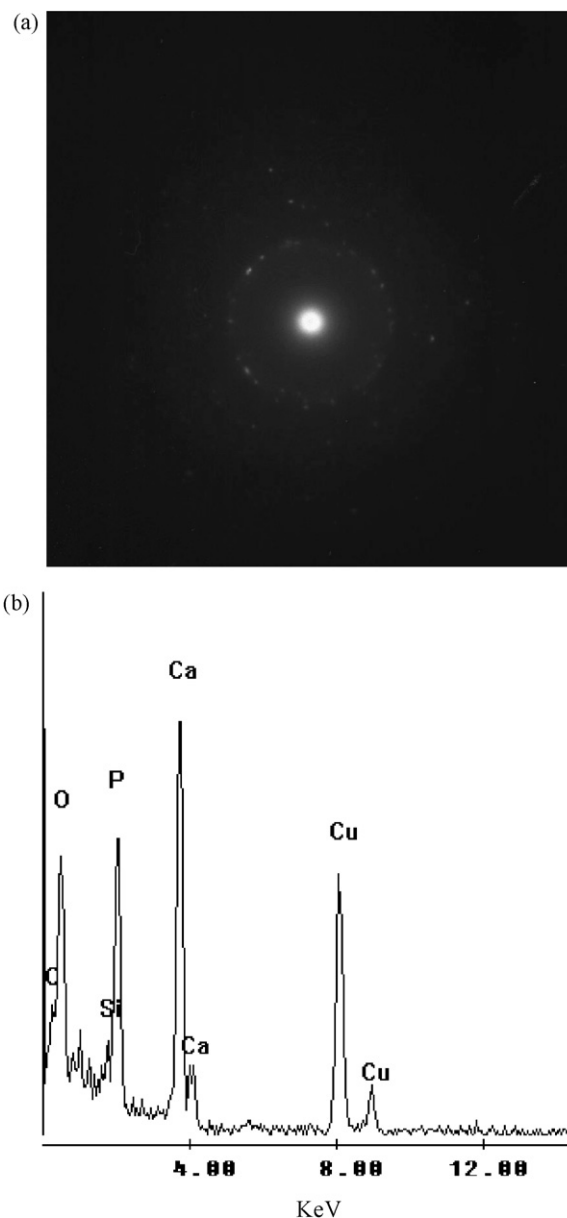

Fig. 6. Transmission electron diffraction pattern (a) and EDX result (b) of the clusters on the 40B glass after reaction with phosphate ion-containing solution with pH 3.0 for 12 h.
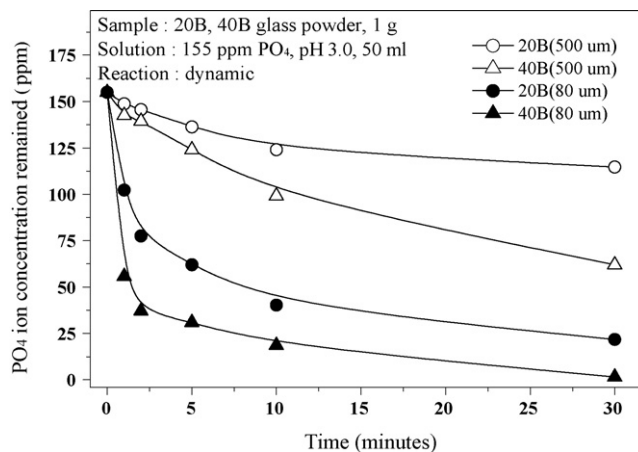

Fig. 7. Concentrations of phosphate ions remaining in the solution after reaction for various times with 1 g of 20B and 40B glass powders of different particle sizes.
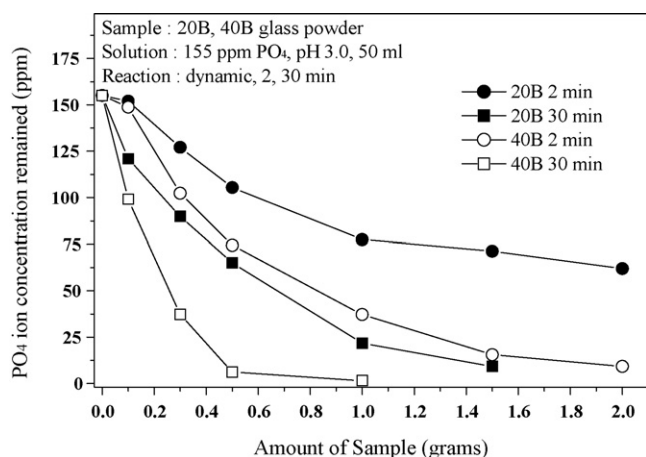
Fig. 8. Concentrations of phosphate ions remaining in the solution after reaction with different amounts of 20B and 40B glass powders for 2 and 30 min.

Fig. 9. Concentrations of phosphate ions removed from the solution after reaction in solutions with various initial pH levels for 5 min with 1 g of 20B and 40B glass powders.

If it assumed that the particles in the glass powder are spherical, the surface area of 1 g of 80 μm glass powder is 6.25 times larger than an equal amount of 500 μm glass powder.

In the reaction using 40B glass, 65% of phosphate ions were removed by 80 μm glass powder after 2 min of reaction, while it took 30 min to remove the same amount of phosphate ions when using 500 μm glass powder. The phosphate ion concentration remaining in solution decreased linearly with reaction time for glass with a particle size of 500 μm. For the glass powder with 80 μm particles, however, the phosphate ion concentration sharply decreased at the early stage of the reaction. For 40B glass powder, 80% of phosphate ions were removed in less than 5 min of reaction.

For the 20B and 40B glasses, various amounts of glass powder from 0.1 g to 2.0 g were reacted in 50 ml of solution with pH 3.0 for 2 min and 30 min. The results are shown in Fig. 8.

It can be seen that the phosphate removal efficiency increases as the amount of glass powder increases. The increase in the efficiency can also be explained by the increasing surface area where the reaction takes place.

Phosphate ion removal rate can be controlled by the amounts of glass added into solution as well as glass composition and reaction time. Using 40B glass, only 0.5 g of glass powder is needed to remove most phosphate ions in 30 min of reaction.

3.4. Effect of initial pH of the solution

1 g of 20B and 40B glass powder with a mean particle size of 80 μm was suspended in a bottle containing 50 ml solutions with pH ranging from 1.0 to 11.0. The solution originally contained 155 ppm of phosphate ions, and the bottle was rotated in a gyroblender. After 5 min of reaction, the concentration of phosphate ions removed from the solution was measured, and the result is shown in Fig. 9.

The highest phosphate ions removal efficiency was observed in the solution with pH 3.0 for both glass samples. In this acidic pH range, calcium ions easily leach out of the glass, promoting the formation of calcium phosphate crystals.

Phosphate ion removal efficiency decreases with as increase in the pH of the reaction solution. This is due to the retardment of Ca^{2+} ions leaching from the glass surface at higher pH. It is well known that the ion exchange between Ca^{2+} and H^+ ions under an acidic condition was more active [20].

However, when the glass was reacted in a solution with pH 1.0, the lowest phosphate ion removal efficiency was observed. Kim and Lee in a study of Bioglass, reported that hydroxyapatite crystal dissolves in a strong acid solution [21]. In a solution with pH 1.0,
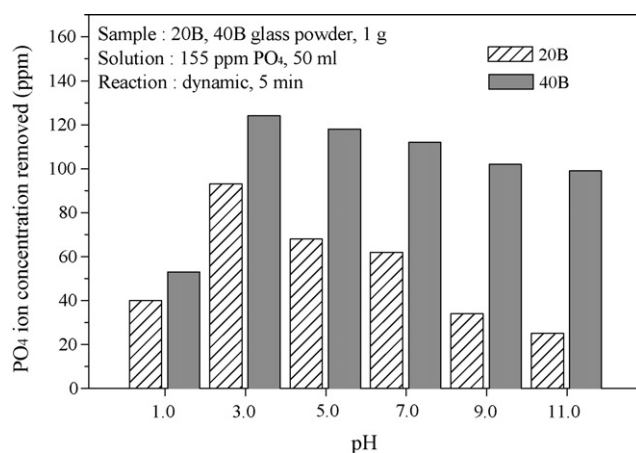
the pH is too low for the calcium phosphate crystals to be formed on the glass surface.

4. Discussion

Glass structure consists of network formers and network modifiers. Network formers, such as SiO_2 and B_2O_3, form a framework of glass structure, and modifiers, such as Na_2O and CaO, break the framework and produce non-bridging oxygen [20]. The bond between modifier cation and non-bridging oxygen shows ionic character with weak strength. When the glass is reacted in an acidic solution, the modifier cations can be exchanged with H^+ in a solution; that is, the modifier ions leach out of the glass surface. The ion leaching rate strongly depends on the glass composition.

It is generally known that B_2O_3 substituted for SiO_2 in network former sites in borosilicate glasses decreases the chemical durability of a glass, and increases the leaching tendency of modifier ions [19]. This phenomena was proved by many researchers with various methods such as ^{11}B MAS-NMR [22–24], FT-IR [25–27] and Raman spectroscopic [28] techniques. They have shown that the boron ions in the borosilicate glasses have two different coordination numbers such as three and four, and also shown that the fraction of three coordinated boron increased with an increase of B_2O_3 in the glass composition [23].

Fig. 10 shows the result of the FT-IR study for the obtained bulk glasses with different B_2O_3 contents. The peaks at 1100 cm^{-1}, 960 cm^{-1} and 500 cm^{-1} are due to the Si–O–Si stretching vibration, the Si–O$^-$ (non-bridging oxygen) stretching vibration, and Si–O–Si bending vibration, respectively. These three peaks related to Si–O vibration disappeared with B_2O_3 contents in glass [26]. The peaks at 1400 cm^{-1}, 1050 cm^{-1} and 700 cm^{-1} are due to the [BO_3] stretching vibration, the [BO_4] stretching vibration and B–O–B bending vibration, respectively [27]. These peaks related to B–O vibration increase with the amount of B_2O_3 in the glass composition.

These FT-IR results explain that [BO_3] and [BO_4] partially replace [SiO_4] site in glass structure. In addition, the amount of trigonal [BO_3] increase with B_2O_3 contents in the glass composition, which decreases the chemical durability of a glass, because [BO_3] units cannot form a 3-dimensional network structure [19]. This promotes the leaching of calcium ions from the glass surface and precipitating the hydroxyapatite crystals on the glass surface, as mentioned in Section 3.1.

To examine the B_2O_3 dependence on the glass chemical durability, 1 g of 20B and 40B glass powders (80 μm) was reacted with 50 ml of solution containing 155 ppm of phosphate ions for various
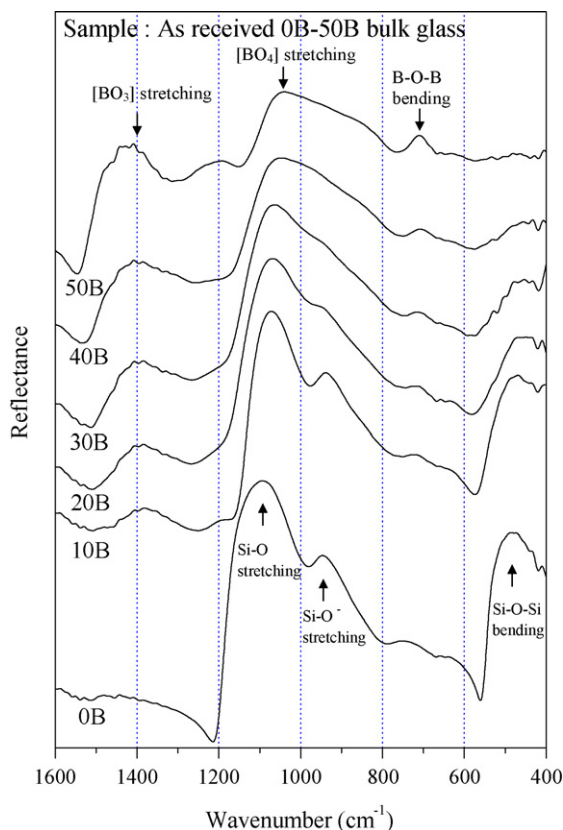
Fig. 10. FT-IR spectra of the obtained bulk glasses with different B_2O_3 contents in a range of 0–50 mole%.

Fig. 11. Concentrations of PO_4, Ca, Na and Si ions remaining in the solution after reaction for various times with 1 g of 20B (a) and 40B (b) glass powders.

times, and the concentrations of Na^+, Ca^{2+} and Si^{4+} ions remained in the solution after reaction are shown in Fig. 11.

For both samples, the concentration of Na^+ and Si^{4+} ions sharply increased at the early stage of reaction, and large amounts of phosphate ions were removed at this reaction time. The pH of the solution sharply increased from 3.0 to 9.5 because of the leaching of Na^+ ions from glass. In addition, the amounts of Na^+ and Si^{4+} ions leached out of the 40B glass are much higher than those of the 20B glass because the 40B glass is less chemically durable. About 70 ppm of Si^{4+} ions and 90 ppm of Na^+ ions leached out from the 20B glass for 5 min of reaction, while about 110 ppm of Si^{4+} ions and 190 ppm of Na^+ ions leached out from the 40B glass in the same reaction time. In both Fig. 11(a) and (b), low levels of Ca^{2+} ion concentration was observed in an early reaction time because the most of Ca^{2+} ions leached out of the glass were consumed to form hydroxyapatite with phosphate ions in the solution. After most of phosphate ions removed, Ca^{2+} ion concentration slowly increased. Because more amount of Ca^{2+} ions could be leached from the 40B glass than 20B glass, 40B glass showed higher phosphate ion removal efficiency than 20B glass did. When the 40B glass was reacted in a phosphate solution for 30 min, the concentration of Ca^{2+} ions increased to 31 ppm because all of phosphate ions already eliminated at this stage of reaction.

When the glass used in the present study was reacted with a solution containing phosphate ions, a large amount of Na^+ and Ca^{2+} ions leached out into the solution. This reaction leaves a silica-rich layer on the glass surface [8]. Leaching of glass modifier ions such as Na^+ and Ca^{2+} and the formation of a silica-rich layer on the glass surface was observed by XRD patterns and FT-IR spectra as shown in Figs. 3, 4 and 10.

This silica-rich layer may act as a seed to attract Ca^{2+} ions and PO_4^{3-} ions from the solution. At an early stage of the reaction,
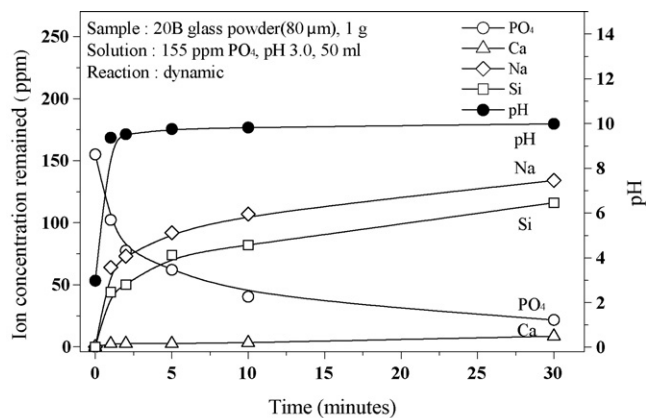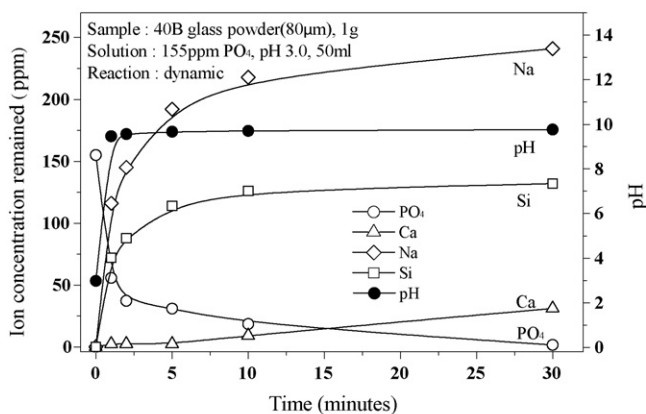
an amorphous calcium phosphate film was first formed on the silica-rich layer. As reaction time passed, the amorphous calcium phosphate film transformed into a hydroxyapatite crystalline phase [18,29].

In Fig. 4, a bump around 550–600 cm^{-1} is observed in the 0B sample, while the bump becomes separate peaks at 610 cm^{-1} and 570 cm^{-1} in the 10B sample. The split peaks in the 10B glass were a bump when the glass was reacted only 6 h. This indicates that a longer reaction time is required for the 10B sample to have a precipitated layer.

Phosphate ions from a solution are removed by precipitation of hydroxyapatite on the glass surface, as shown in Eq. (1). In this case, the Ca^{2+} ions are provided by leaching out of glass.

$$Ca^{2+}(glass) + PO_4^{3-}(solution) + OH^-(solution)$$
$$= Ca_{10}(PO_4)_6(OH)_2(hydroxyapatite) \qquad (1)$$
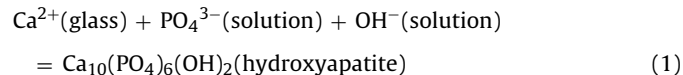
From the above results, the mechanism of phosphate ion removal by borosilicate glass can be illustrated in Fig. 12. When the glass was reacted with a solution containing phosphate ions, Ca^{2+} ions were leached from the glass, and a silica-rich layer was formed on the glass surface. In this reaction, the silica-rich layer provides nucleation sites to form crystal, and Ca^{2+} ions leached out of the glass, combining with phosphate ions in solution to form hydroxyapatite crystal on the silica-rich layer. In this manner, the phosphate ions can be removed from the solution. Therefore, Ca^{2+} ions must be supplied from the glass by ion leaching to facilitate the removal of phosphate ions from the solution.

As shown in Fig. 1, phosphate ion removal efficiency increased with increase in B_2O_3 contents. Glasses with low B_2O_3 content have
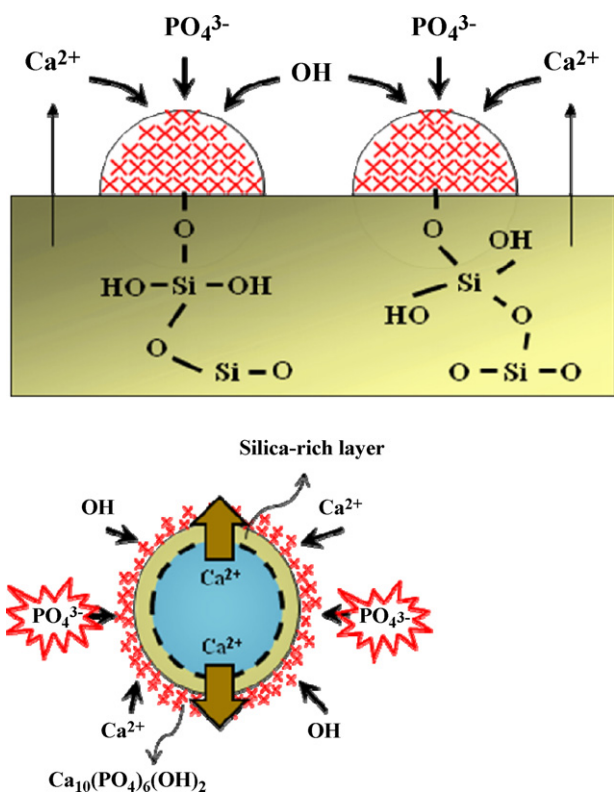
Fig. 12. Schematic diagram for the mechanism of phosphate ion removal by precipitation of hydroxyapatite crystals on borosilicate glass.

relatively high chemical durability, and this reduces the leaching rate of Ca^{2+} ions from the glass to prevent easy formation of hydroxyapatite crystals. The same result of the B_2O_3 dependence on the hydroxyapatite crystal deposition on the glass surface was also obtained in the study of bioactive glasses [30]. When the borosilicate bioactive glasses, derived from the silicate bioactive glass by partially replacing the SiO_2 with the B_2O_3, were immersed in a K_2HPO_4 solution, the hydroxyapatite layer formed more rapidly on the borosilicate glass than on the silicate glass.

Fig. 9 shows that the highest phosphate ion removal was observed in a solution with an initial pH of 3.0, and removal efficiency decreased with increase in pH. This is due to the leaching rate of Ca^{2+} ions, which strongly depends on the pH of the solution. However, at lower pH levels, such as pH 1.0, the solubility of the hydroxyapatite crystal is too high to be stable.

Phosphate ions can be removed from a solution more effectively when using glass with an increased surface area, by pulverizing the glass into finer powder or using a large amount of glass powder per unit volume, as shown in Figs. 7 and 8. This is because the increased glass surface provides more Ca^{2+} ions and nucleation sites for hydroxyapatite crystal precipitation.

5. Conclusions

When a borosilicate glass was reacted in a solution containing phosphate ions, the phosphate ions were eliminated by forming hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ crystals on the glass surface. Phosphate ion removal efficiency increased with increase in B_2O_3 content. The removal efficiency was the highest in the solution with pH 3.0, and removal efficiency decreased with increase in the pH of the reacting solution. Phosphate ions in a solution can be removed more effectively through maximizing the surface area of the glass by pulverizing the glass into powder or using a large amount of

glass powder per unit volume. For phosphate removal, Ca^{2+} ions must be supplied from glass through ion leaching. Accordingly, the condition with the highest Ca^{2+} ion leaching behavior shows the highest phosphate ion removal efficiency.

References

[1] B. Nowack, A.T. Stone, Competitive adsorption of phosphate and phosphonates onto goethite, Water Res. 40 (2006) 2201–2209.
[2] B.K. Ciswas, K. Inoue, K.N. Ghimire, H. Harada, K. Ohto, H. Kawakita, Removal and recovery of phosphorus from water by means of adsorption onto orange waste gel loaded with zirconium, Bioresour. Technol. 99 (18) (2008) 8685–8690.
[3] J. Driver, D. Lihmbach, I. Steen, Why recover phosphorus for recycling, and how? Environ. Technol. 20 (1999) 651–662.
[4] H.S. Altundogan, F. Tumen, Removal of phosphates from aqueous solutions by using bauxite. II. The activation study, J. Chem. Technol. Biotechnol. 78 (2003) 824–833.
[5] D. Mulkerrins, A.D.W. Dobson, E. Colleran, Parameters affecting biological phosphate removal from wastewaters, Environ. Int. 2 (30) (2004) 249–259.
[6] Y. Li, C. Liu, Z. Luan, X. Peng, C. Zhu, Z. Chen, Z. Zhang, J. Fan, Z. Jiaz, Phosphate removal from aqueous solutions using raw and activated red mud and fly ash, J. Hazard. Mater. B 137 (2006) 374–383.
[7] K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, J. Hazard. Mater. A 139 (2007) 447–452.
[8] J. Xiong, Z. He, Q. Mahmood, D. Liu, X. Yang, E. Islam, Phosphate removal from solution using steel slag through magnetic separation, J. Hazard. Mater. 152 (2007) 211–215.
[9] C.Y. Kim, M.S. Nam, SO_4^{2-} ion removal from solution by crystal precipitation on surface active glasses, J. Korean Ceram. Soc. 35 (12) (1998) 1286–1293.
[10] C.Y. Kim, M.S. Nam, Precipitation of carbonate crystal on surface active glasses, J. Mater. Sci. 35 (2000) 3245–3250.
[11] C.Y. Kim, H.J. Kim, J.S. Nam, Removal of lead ions from solution by phosphosilicate glass, J. Hazard. Mater. 153 (2008) 173–178.
[12] J.S. Nam, C.Y. Kim, Phosphate ion removal from a solution by soda-lime borosilicate glass, J. Non-Cryst. Solids 354 (45–46) (2008) 5009–5013.
[13] American Public Health Association, American Water Works Association, Water Environment Federation, Standard methods: for the examination of water and wastewater, American Public Health Association, New York, 1998.
[14] C. Ohtsuki, T. Kokubo, T. Takatsuka, T. Yamamuro, Compositional dependence of bioactivity of glass in the system CaO-SiO$_2$-P$_2$O$_5$:Its in vitro evaluation, J. Ceram. Soc. Jpn. 99 (1991) 1–6.
[15] C. Ohtsuki, T. Kokubo, T. Yamamuro, Mechanism of apatite formation on CaO–SiO$_2$–P$_2$O$_5$ glasses in a simulated body fluid, J. Non-Cryst. Solids 143 (1992) 84–92.
[16] K.C. Blakeslee, R.A. Condrate, Vibrational spectra of hydrothermally prepared hydroxyapatites, J. Am. Ceram. Soc. 54 (11) (1971) 559–563.
[17] C.Y. Kim, A.E. Clark, L.L. Hench, Compositional dependence of calcium phosphate layer formation in fluoride bioglasses®, J. Biomed. Mater. Res. 26 (9) (1992) 1147–1161.
[18] C.Y. Kim, A.E. Clark, L.L. Hench, Early stages of calcium-phosphate layer formation in bioglasses, J. Non-Cryst. Solids 113 (1989) 195–202.
[19] M.B. Volf, Chemical Approach to Glass, Elasevier, New York, 1984.
[20] A.K. Varshneya, Fundamentals of Inorganic Glasses, Academic Press, Inc., New York, 1994.
[21] C.Y. Kim, J.W. Lee, Surface bio-modification of titanium implants by an enamel process, J. Ceram. Process Res. 6 (4) (2005) 338–344.
[22] D.C. Bunker, G.W. Arnold, D.E. Day, P.J. Bray, The effect of molecular structure on borosilicate glass leaching, J. Non-Cryst. Solids 87 (1986) 226–253.
[23] R. Martens, W.M. Warmuth, Structural groups and their mixing in borosilicate glasses of various compositions–An NMR study, J. Non-Cryst. Solids 265 (2000) 165–175.
[24] L. Du, J.F. Stebbins, Nature of silicon-boron mixing in sodium borosilicate glasses: a high resolution ^{11}B and ^{17}O NMR study, J. phys Chem. B 107 (2003) 10063–10076.
[25] P. Pernice, S. Esposito, A. Aronne, V.N. Sigaev, Structure and crystallization behavior of glasses in the BaO–B$_2$O$_3$–Al$_2$O$_3$ system, J. Non-Cryst. Solids 258 (1999) 1–10.
[26] A. Yao, D. Wang, W. Huang, Q. Fu, M.N. Rahaman, D.E. Day, In vitro bioactive characteristics of borate based glasses with controllable degradation behavior, J. Am. Ceram. Soc. 90 (1) (2007) 303–306.
[27] E.I. Kamitsos, Infrared studies of borate glasses, Phys. Chem. Glasses 44 (2) (2003) 79–87.

[28] W.L. Konijnendijk, J.M. Stevels, The structure of borosilicate glasses studied by Raman scattering, J. Non-Cryst. Solids 20 (1976) 193–224.

[29] A. Tilocca, Structure models of bioactive glasses from molecular dynamics simulations, Proc. R. Soc. A 465 (2009) 1003–1027.

[30] W. Huang, D.E. Day, K. Kittiratanapiboon, M.N. Rahaman, Kinetics and mechanisms of the conversion of silicate(45S5), borate, and borosilicate glasses to hydroxyapatite in dilute phosphate solutions, J. Mater. Sci.: Mater. Med. 17 (2006) 583–596.