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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

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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

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

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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 × 10 × 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 × 10 × 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 $0.1\ \mathrm{cm}^{-1}$.

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 $400–1600\ \mathrm{cm}^{-1}$ with a resolution of $2\ \mathrm{cm}^{-1}$.

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%

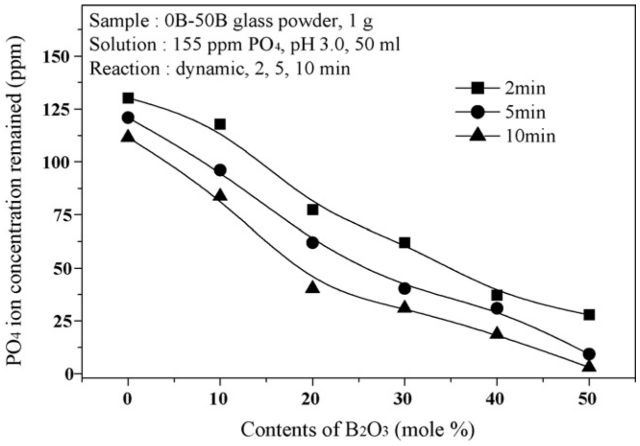

Fig. 1. Concentrations of phosphate ions remained in the solution after reaction times of 2, 5 and 10 min with 1 g of each glass powder with different B_2O_3 content in a range of 0–50 mole%.