

Removal of lead ions from solution by phosphosilicate glass

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Received 1 February 2007; received in revised form 13 August 2007; accepted 13 August 2007

Available online 22 August 2007

Abstract

A new technique to remove Pb^{2+} ions from a solution by using a phosphosilicate glass was introduced. When the phosphosilicate glass with an invert glass composition [mol%: 44.9% SiO_2 –5.2% P_2O_5 –23.7% Na_2O –26.2% CaO] was reacted with the solution containing Pb^{2+} ions. The glass surface turned into silica-rich layer by leaching of glass modifiers, such as Na^+ and Ca^{2+} ions, and the $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals developed on the silica-rich layer. The Pb^{2+} ions were removed from the solution by precipitating this crystal on the glass surface. The Pb^{2+} ion removal rate depended strongly on the pH of the solution and was the highest at pH 2.0. In the solution of pH 1, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ was not formed due to its high solubility in such a strong acid.

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Keywords: Pb^{2+} ions; Precipitation; Phosphosilicate glass; $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals; Silica-rich layer

1. Introduction

Industrial wastewater is one of the major sources of aquatic pollution. Among the aquatic pollutants, heavy metals have gained relatively more significance in view of their persistence, bio-magnification and toxicity [1]. Conventional methods for removing heavy metals include chemical precipitation and ion exchange. These become inefficient or expensive especially when the concentration of the heavy metal ion is less than 200 ppm [2].

Suzuki et al. [3–5] used hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] to remove Pb^{2+} or Cd^{2+} ions from a solution by immersing the hydroxyapatite in the solution containing Pb^{2+} and Cd^{2+} ions. In these reports, the Pb^{2+} and Cd^{2+} ions were exchanged with the Ca^{2+} ions in the hydroxyapatite. The hydroxyapatite has been widely used for artificial bone substitution and the ions comprising that crystal can be easily replaced by other ions. That is, Pb^{2+} , Cd^{2+} and Sr^{2+} ions can be substituted for Ca^{2+} ion and Cl^- and F^- ions for OH^- in the hydroxyapatite crystal. However, there is a limitation to the amount of exchangeable cations.

In Bioglass[®], which is also used as a bone substitute, studies, it is well documented that hydroxyapatite crystals form on glass

surfaces when the Bioglass[®] is reacted in the solution, such as tris-buffer solution and simulated body fluids. It is believed that a silica-rich layer, which is formed by the preferential leaching of Na^+ and Ca^{2+} ions from the glass surface when the Bioglass[®] is immersed in the solution, can attract Ca^{2+} and P^{5+} ions from the solution to form hydroxyapatite [6–8].

Recently, it has been reported that CO_3^{2-} and SO_4^{2-} ions, which cause serious scale problems in drainage pipes and vessels, can be removed from wastewater with the glass [9,10]. This glass contains alkaline earth metal ions, such as Ca^{2+} , Sr^{2+} , and Ba^{2+} . When the glass is immersed in CO_3^{2-} and SO_4^{2-} ion-containing wastewater, the carbonate and sulfate crystals form on the silica-rich layer of the glass. In this way, the anions in the solution can be removed.

The primary objective of this study was to remove Pb^{2+} ions from a solution by using a phosphosilicate glass. The formation of the crystalline phase containing the Pb^{2+} ions and Pb^{2+} ion removal capacity were examined in terms of the pH of the solution and the reaction time.

2. Materials and methods

2.1. Preparation of phosphosilicate glass

The composition of the phosphosilicate glass for this work was chosen as 44.9% SiO_2 –5.2% P_2O_5 –23.7% Na_2

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O–26.2%CaO (mol%: named 5.2P glass). Most of commercial glasses have less than 25 mol% of glass modifiers, such as alkali and alkaline earth oxides. The glass for this study, however, contained about 50 mol% of glass modifiers to improve its chemical reactivity in the solution. This glass is called an invert glass.

Appropriate amounts of raw materials, from the reagent grades of SiO₂, CaCO₃, Na₂CO₃ and H₃PO₄, were weighed and mixed in a gyroblender for 30 min. Then, the mixed glass batch was loaded in a Pt–Rh crucible, and melted in an electrically heated furnace at the temperature of 1430 °C for 2 h. For a better glass homogeneity, the glass melt was quenched and crushed, and then remelted in the same conditions. The glass melt was cast into a graphite mold to make a bar and then the glass bar was annealed at 570 °C to release any residual stress.

The obtained glass bar was cut into rectangular specimens of 10 mm × 10 mm × 2 mm. These glasses were polished with 600-grit sandpaper and washed with acetone in an ultrasonic cleaner. The prepared glass sample was kept in a desiccator until needed for use.

2.2. Preparation of the solution and reaction of the glass

The solution containing Pb²⁺ ions was prepared by dissolving 255.8 mg of Pb(NO₃)₂ in 1 L of distilled water. This solution contained 160 ppm of Pb²⁺ ions. The pH of the solution varied in a range from 1 to 4 by adding an appropriate amount of HCl.

The glass specimen was immersed in a polyethylene bottle with 28 mL of the prepared solution and reacted for various periods of time. The ratio of the surface area of the glass to the volume of the solution was set at 0.1 cm⁻¹ and the reaction temperature was kept at 37 °C throughout the experiment. After the reaction, the glass specimens were removed from the solution and washed with acetone to prevent further reaction.

2.3. Analysis of the reacted glass surface and measurement of ion concentration

The reacted surface of the glass was analyzed with a thin film X-ray diffractometer (PW3719, Philips, Netherlands). The incident beam angle was set at 1.5°. The morphology of the reacted glass surface was also examined with a scanning electron microscope (X-650, Hitachi, Japan). Fourier Transformed-Infrared Spectrometer (Bio-Rad, FT-165) attached to a diffused reflection unit was also applied to examine the glass surfaces as well as the reacted sample surfaces. The IR spectra were obtained in the range of 400–1200 cm⁻¹ with a resolution of 2 cm⁻¹.

After the glass was reacted in the Pb²⁺ ion-containing solution, the concentration of Pb²⁺ ions remaining in the reacted solution was measured with an atomic absorption spectroscope (AA-Scan 1, Thermo Jarrel Ash, USA). The concentration of P⁵⁺ ions that leached out of the glass was also analyzed with an UV-Visible spectroscope (UV-260, Shimadzu, Japan). The absorption at 885 nm wavelength was compared to the standard curve obtained by the Murphy and Riley method [11].

3. Results

3.1. pH dependence of crystal precipitation on glass surfaces

The prepared glasses were reacted in the solution containing Pb²⁺ ions with various pH ranging from 1 to 4 for 20 h. After the reaction, the surfaces of the glasses were analyzed with a thin film XRD as shown in Fig. 1.

No crystalline phase was observed when the glass was reacted in the solution with pH 1. Only a typical X-ray amorphous bump was observed on this sample. The bump, around $2\theta = 30^\circ$ for the original glass, shifted to $2\theta = 25^\circ$ after reaction, indicating that a silica-rich layer had formed on the glass surface [12,13].

When the glass reacted with the solution containing Pb²⁺ ions with pH 2, Pb₁₀(PO₄)₆(OH)₂ and Ca(PO₃)₂ crystals precipitated on the glass surface. At pH 3 and 4, only Pb₁₀(PO₄)₆(OH)₂ crystals formed on the glass. Sharper XRD peaks were observed in the stronger acid solutions. In the solution with pH 4, however, somewhat broader peaks of Pb₁₀(PO₄)₆(OH)₂ crystals were observed.

The glass surfaces, after reaction in the Pb²⁺ ion-containing solution with pH of 1 through 4 for 20 h, were also examined under SEM and the results are presented in Fig. 2. The glass surface reacted with pH 1 showed only a cracked-silica-rich gel layer. The crack developed when the silica gel layer dried out after reaction. At pH 2, well-developed Pb₁₀(PO₄)₆(OH)₂ crystals with needle-shape were observed, but scarce-scattered crystals were obtained at pH 3. Although Pb₁₀(PO₄)₆(OH)₂ crystals were shown in the XRD results, only crystal clusters were observed in SEM at pH 4.

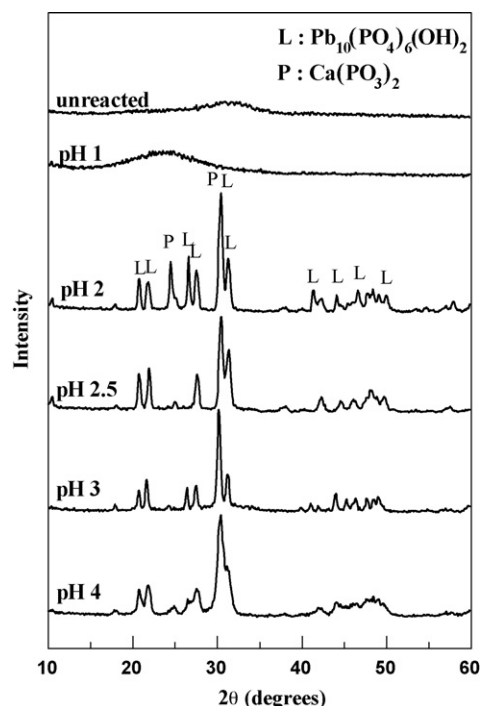


Fig. 1. Thin film XRD patterns of 5.2P glass surface reacted with Pb²⁺ ion-containing solution with various pHs for 20 h.

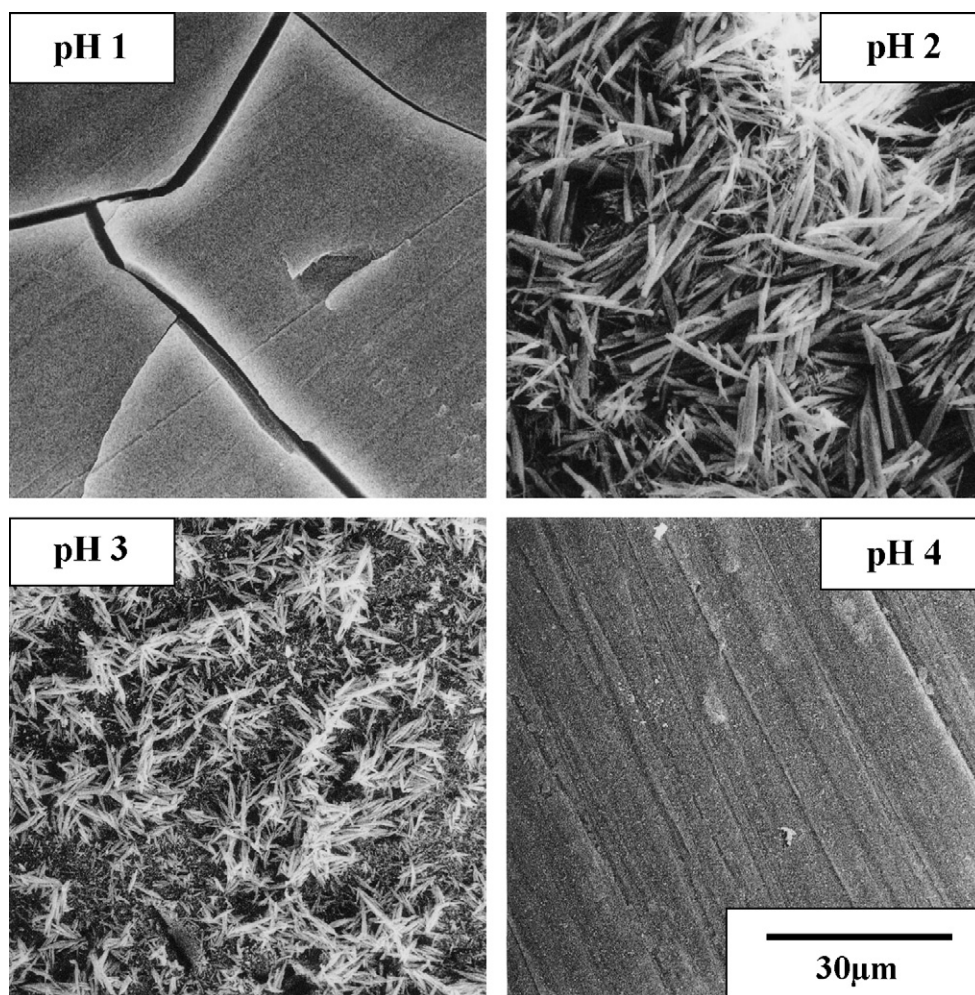


Fig. 2. SEM micrographs of 5.2P glass surface reacted with Pb^{2+} ion-containing solutions with various pHs for 20 h.

The reason for the absence of crystal formation at pH 1 is that the crystal dissolves at this pH level. To confirm this, the $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals obtained after reaction at pH 2 for 20 h were treated in the solution of pH 1. The sample surface was examined by FT-IR and the results are shown in Fig. 3. The characteristic peaks of apatite [14,15] at 569 cm^{-1} and 602 cm^{-1} , which is assigned as P–O bending vibration, disappeared slowly with treatment time. Those peaks disappeared completely after 10 s of reaction, indicating that all crystals dissolved in 10 s.

3.2. pH dependence of Pb-ion removal

The Pb^{2+} ion concentration of the solution after reaction was measured as shown in Fig. 4. Before the reaction, the original solution contained 160 ppm of Pb^{2+} ions. As discussed earlier, the glass that forms $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals can accomplish the uptake of the Pb^{2+} ions. When the glass was treated in the solution with pH 1 for 20 h, no removal of Pb^{2+} ions was observed. This matched well the results that were obtained in the experiments with XRD and SEM. No crystals formed at this level of pH of the solution. When the glass was reacted in the solution with pH 2 and 2.5, however, most of the Pb^{2+} ions were removed from the solution after 20 h of reaction time. Pb^{2+} ion

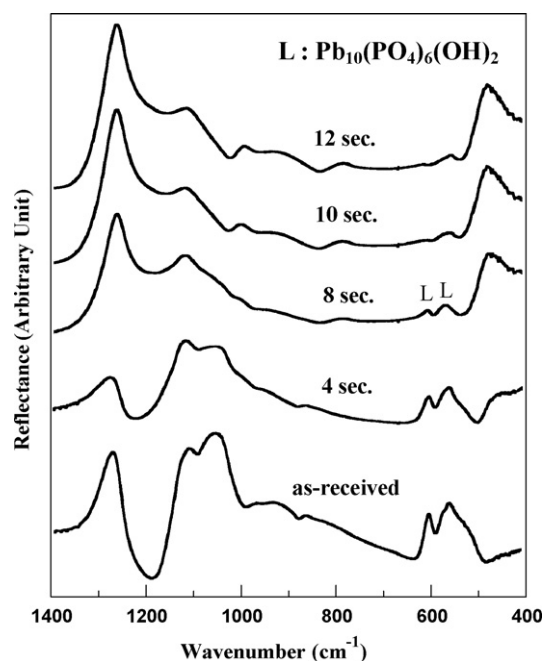


Fig. 3. FT-IRRS spectra of dissolution of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ in acidic solution with pH 1.

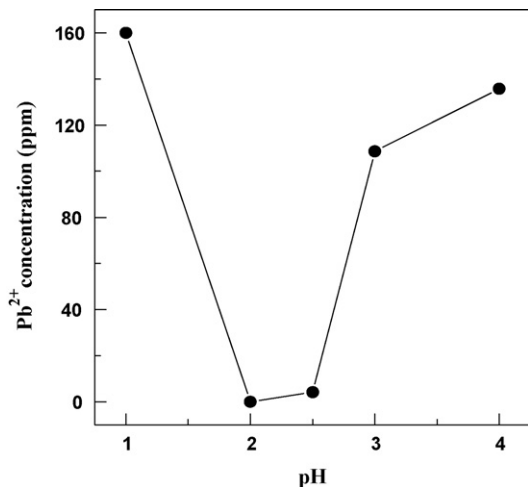


Fig. 4. Concentrations of Pb²⁺ ions left in the solution reacted with 5.2P glass for 20 h.

removal capacity decreased sharply with a further increase in the pH of the reacting solution.

From these results, it can be conclusively stated that this phosphosilicate glass can effectively remove Pb²⁺ ions from the solution.

3.3. Time dependence of crystal precipitation on glass surfaces

The crystal build-up phenomena were examined by varying reaction times from 30 s to 40 h. In this experiment, the glass was reacted with the Pb²⁺ ion-containing pH 2 solution, where well-developed Pb₁₀(PO₄)₆(OH)₂ crystals precipitated on the glass surface. The thin film XRD results are shown in Fig. 5.

Pb₁₀(PO₄)₆(OH)₂ crystals started to develop after 40 min of reaction and the intensities of the XRD peaks increased with reaction time, indicating the increase in thickness of the crystal layer. After 10 h of reaction, the XRD peak for the Ca(PO₃)₂ crystals ($2\theta = 26^\circ$) increased sharply. Compared with Fig. 7, which will be discussed later, most of the Pb²⁺ ions in the solution were removed from the solution at this time of reaction. Ca²⁺ and P⁵⁺ ions, which were leached out of the glass, combined together to form the second crystal Ca(PO₃)₂.

Fig. 6 shows the SEM micrographs of the glass surfaces after reaction for various periods of time. The glass surface after 10 min of reaction showed that needle-shaped scattered crystals covered the glass surface. The cracked surface is the silica-rich layer and the crack developed during the drying process of the gel layer due to dehydration. More crystals built up constantly with reaction time on the silica-rich layer and finally the crystals completely covered the glass surface. Larger cracks appeared at 40 min of reaction and were due to the thicker silica gel layer.

3.4. Time dependence of Pb-ion removal

The concentrations of Pb²⁺ ions left in the solutions after reactions for various periods of time were measured and the results are shown in Fig. 7. In this experiment, once again, the

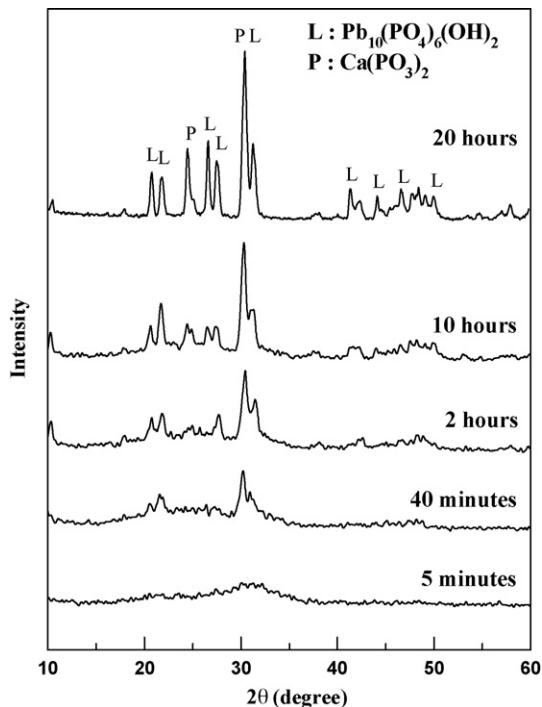


Fig. 5. Thin film XRD patterns of 5.2P glass surfaces reacted with Pb²⁺ ion-containing solution with pH 2 for various times.

surface area of the glass sample to volume of solution was set at 0.1 cm^{-1} . 160 ppm of Pb²⁺ ions in the unreacted solution decreased to 150 ppm in the first 20 min of reaction and the uptake rate of the Pb²⁺ ions increased sharply with reaction time. After 120 min of reaction, only 28 ppm of Pb²⁺ ions were left in the solution. After that, the Pb²⁺ ion removal rate slowed down a little and the uptake of most of the Pb²⁺ ions was achieved after 6 h of reaction time.

Fig. 8 shows the concentrations of P⁵⁺ ions left in the solutions after reaction for various periods of time. Because no P⁵⁺ ions were present in the original solution, P⁵⁺ ions had to be supplied from the glass to form the Pb₁₀(PO₄)₆(OH)₂ crystals. The low concentration of P⁵⁺ ions in the early stage of reaction is one of reasons for the low rate of Pb²⁺ ion removal from the solution up to 20 min of reaction. There is a possibility that the newly formed crystals have a tendency to block the further leaching of P⁵⁺ ions. This is probably another reason that the P⁵⁺ ion concentration stayed nearly constant after 10 h of reaction. At this stage, most of the Pb²⁺ ions in the solution had been removed and some of P⁵⁺ ions were consumed for the formation of Ca(PO₃)₂ crystals.

4. Discussion

When glass reacts to an acidic solution, the ions in the glass leach out of the surface. In the SiO₂–P₂O₅–CaO–Na₂O glass system, glass modifier ions, such as Na⁺ and Ca²⁺, dissolve more easily from the glass surface than any other glass-forming ions, such as Si⁴⁺ and P⁵⁺. Due to this difference in ion-leaching rates, the silica-rich layer forms on the glass surface. The leaching of these glass modifiers takes place with the ion exchange between

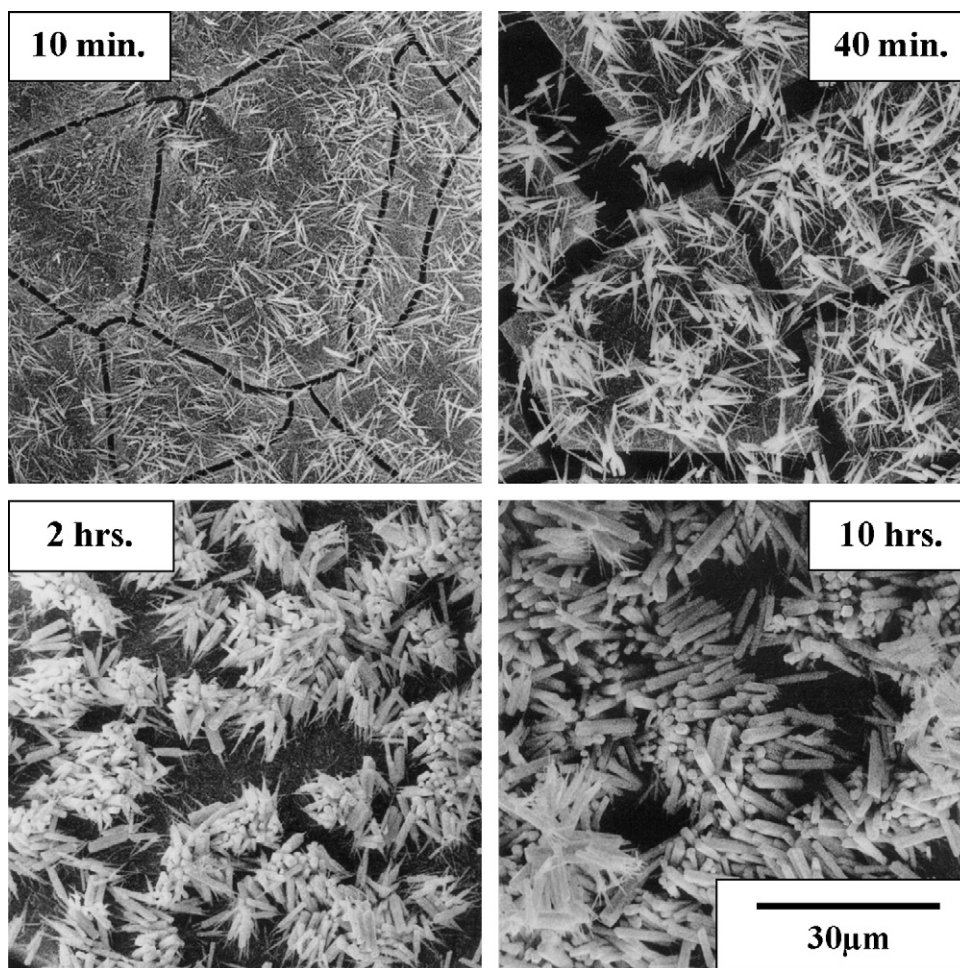


Fig. 6. SEM micrographs of 5.2P glass surfaces reacted with Pb²⁺ ion-containing solution with pH 2 for various times.

the cations in the glass and the H⁺ ions from the solution. And, therefore, many silanol groups are expected to be present in the silica-rich layer. The X-ray bump around $2\theta = 25^\circ$ in Fig. 1 (at pH of 1) is due to this silanol groups.

The XRD patterns in Fig. 1 showed sharper peaks when the glasses reacted in a solution with pH of 2 and 3. In the solution with pH 4, however, somewhat broader peaks of Pb₁₀(PO₄)₆(OH)₂ crystals were observed. Probably, this can be

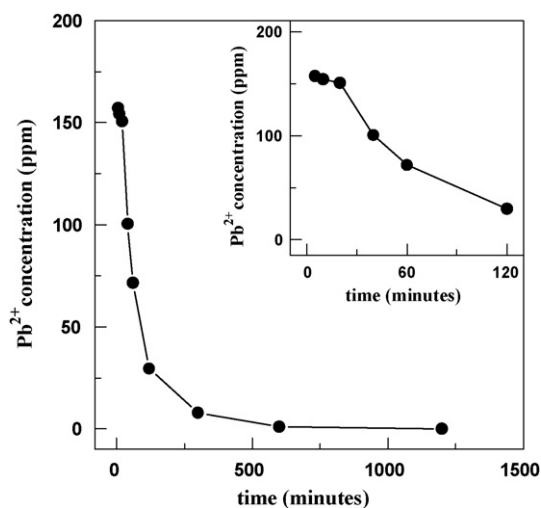


Fig. 7. Concentrations of Pb²⁺ ions left in the solution reacted with 5.2P glass for various times.

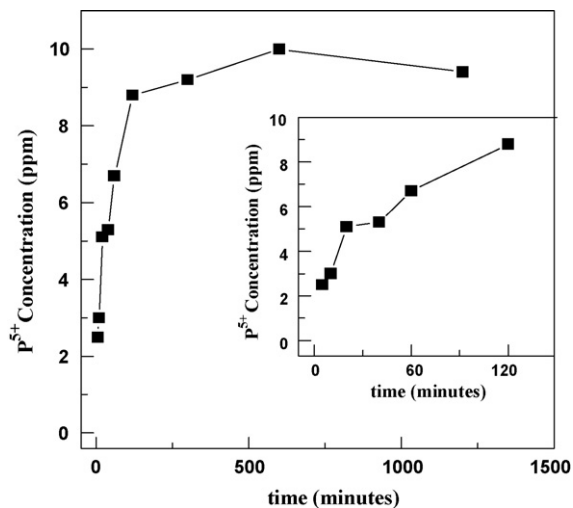


Fig. 8. Concentrations of P⁵⁺ ions left in the solution reacted with 5.2P glass for various times.

attributed to the crystals with non-stoichiometric structure that developed at this pH level through the coexistence of Ca^{2+} and Pb^{2+} ions at the Pb^{2+} site in the $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystal.

As shown in Fig. 4, Pb^{2+} ion removal capacity showed the highest at pH 2, and decreased sharply with a further increase in the pH of the reacting solution. This explains that the $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystal is only stable at the pH levels of 2 to 2.5. At the lower pH, such as pH of 1, the solubility of the crystal is too high to be stable as shown in Fig. 3.

Even if the clear XRD peaks of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals started to show after 40 min of reaction (Fig. 5), the scattered crystal precipitation of the crystals showed at the early stage of reaction, such as 10 min of reaction as shown Fig. 6. The results in Fig. 7 were compared to the previous XRD and SEM data (Figs. 5 and 6, respectively) and it can be stated that it takes some time to start precipitation of $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals on the silica-rich layer. However, once certain amounts of crystals were obtained, the crystal growth rate increased sharply and then the Pb^{2+} removal rate from the solution also increased. Because no Pb^{2+} ions were left in the solution after 10 h of reaction, the Ca^{2+} and P^{5+} ions leached from the glass surface started to form $\text{Ca}(\text{PO}_3)_2$ on the glass. In Fig. 5, $\text{Ca}(\text{PO}_3)_2$ crystal phase was found after 20 h of reaction.

Mechanism of crystal formation on glass surfaces in a solution can be stated as follows. All ions in glass generally tend to leach out of glass in an aqueous solution although their dissolution rates differ from each other. The ion-leaching rate strongly depends on the state of the ion in the glass structure and glass composition. An invert glass that has less than 50 mol% of glass formers shows strong dissolution behavior.

In the present glass composition, it is expected that the leaching rate of the Na^+ ions are much higher than any other element because the Na^+ ions are mobile network modifiers. In invert glass, quite a large amount of Ca^{2+} ions also tends to dissolve into the solution. This leads to the formation of a silica-rich layer on the glass surface. This silica-rich layer is believed to be in the form of silica gel with silanol groups because Na^+ and Ca^{2+} ions are exchanged with hydrogen ions in the solution. This silica gel layer may act as a seed to attract some ions from the solution to form crystals.

In Bioglass[®] study, hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] crystals form on the glass surface by attracting Ca^{2+} and P^{5+} ions from the solution when the Bioglass[®] is reacted in simulated body fluids with pH 7.2 [16]. In the present study, however, Pb^{2+} ions, which were already present in the solution, were more active than Ca^{2+} ions that were leached out of the glass, and therefore, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals were deposited instead of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ on the silica-rich layer. After most of the Pb^{2+} ions were removed from the solution, $\text{Ca}(\text{PO}_3)_2$ crystals formed on the glass.

5. Conclusions

When a phosphosilicate glass with an invert glass composition was reacted in the solution containing Pb^{2+} ions, the Pb^{2+} ions were eliminated by forming $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ crystals on

the glass surface. The removal capacity was the highest in the solution with pH 2 and the capacity decreased in the stronger or weaker acid solution accordingly. At a 2.0 pH, most of the 160 ppm Pb^{2+} ions were eliminated in 6 h of treatment when the ratio of the glass surface area to the volume of the solution was set at 0.1 cm^{-1} . Pb^{2+} ions in the solution can be removed more effectively when using an increased surface area of glass by pulverizing the glass into powder. This method can be a new technique to remove hazardous heavy metal ions from the industrial wastewater.

Acknowledgement

This work was supported by INHA UNIVERSITY Research Grant.

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