Precipitation of carbonate crystal on surface active glasses

CHEOL Y. KIM
Department of Ceramic Engineering, College of Engineering, Inha University,
253 Yonghyun-dong, Nam-ku, Inchon, Korea
E-mail: cheolkim@dragon.inha.ac.kr

MYEONG-SIK NAM
Department of New and Renewable Energy Research, Korea Institute of Energy Research,
71-2 Jang-dong, Yusung-ku, Taejon, Korea

Anions, such as CO_3^{2-} and SO_4^{2-} ions, in industrial wastewater can cause serious scale problem in drainage pipes and vessels, when combined with other metal ions in the water. In this study, it was attempted to remove CO_3^{2-} ions from an aqueous solution by using surface active glasses. Glasses with various compositions of SiO_2-Na_2O-B_2O_3-RO (R = Mg, Ca, Sr, Ba) system were reacted in a CO_3^{2-} ion-containing solution with various pH, then the glass surfaces were analyzed by XRD and SEM, and CO_3^{2-} ions in the reacted solution were also measured. CO_3^{2-} ions in the solution were combined with alkaline earth metal ions, which were leached out of the glass, and were precipitated on the glass surface as carbonate crystals. In this way, the carbonate ions could be removed from the solution. The removal capacity of CO_3^{2-} ions is closely related to the surface reactivity of the glass and solubility product constants of the newly formed carbonate crystals. Glass containing either SrO or BaO showed a strong uptake capacity of CO_3^{2-} ions from the solution.
© *2000 Kluwer Academic Publishers*

1. Introduction
Certain ions, such as SO_4^{2-} and CO_3^{2-} ions, found in wastewater can be deposited as sulfate or carbonate minerals in a transporting pipe. These scales produce a major obstacle to the reuse of wastewater because they have a tendency to cling to the inner surface of the pipes and vessels. Scale problems also occur in various processes and systems such as heat transfer, desalination plants, and transport of geothermal fluids [1]. Scale deposits impair productive reservoirs and foul both downhole and surface injection equipment, and shorten the operating life of an important installations [2, 3].

Many efforts in recent years have been made in an attempt to prevent these scales. Some attempts to stop the formation of deposits in pipes have been made by controlling thermodynamic factors such as temperature, pressure and solubility in a reservoir [2]. Some efforts to remove metal ions such as Pb, Ca, Sr and Ba ions, which were apt to form deposits, are made by using chemically modified materials such as ion exchange resin and biosorbent etc. [4]. Various treatment methods such as precipitation, adsorption, evaporation, electrolysis and cementation methods also have been employed to remove heavy metals from the industrial wastewater [1–3].

Our laboratory has found that some types of surface active glass has the property of attracting some ions in a solution and forming certain crystals on its surface. Hydroxyapatite crystal tends to precipitate on a bioactive glass when it is reacted in a simulated body fluid [5]. This hydroxyapatite is responsible for bonding between this implant and living tissue when the bioactive glass is implanted into a body [6]. Some surface active glasses with special compositions can attract Pb^{2+} ions from a solution and form Pb^{2+} ion containing phosphate crystal on their surfaces. The toxic Pb^{2+} ion in a solution can be removed in this way [7].

In the present study, glasses with various compositions of SiO_2-Na_2O-B_2O_3-RO (R = Mg, Ca, Sr, Ba) system were reacted in a CO_3^{2-} ion-containing solution with various pH ranging from 3 to 12.5 for various length of time. The objectives for this study are (1) to find the removal mechanism of CO_3^{2-} ions in a solution by surface active glass and (2) to find the optimum glass composition to uptake CO_3^{2-} ions from a solution.

2. Experimental methods
2.1. Sample preparation
Glasses in this experiment contained less than 50% of silica, referred to as an invert glass, to improve the chemical reactivity of the glass in a solution. Four different alkaline earth metal oxides were added to the glass batch. They were MgO, CaO, SrO and BaO. Table I shows the glass compositions for this study.

TABLE I Glass compositions for the present study

Composition name	SiO$_2$	Na$_2$O	B$_2$O$_3$	RO* (mol.%)
RO-glass	45	14	16	25

RO*; MgO, CaO, SrO, BaO.

100 g of glass batch was mixed and melted in a Pt-crucible at the temperature ranging from 1000 to 1400 °C for 2 hours depending on the glass compositions. The glass melt was poured into a graphite mold to make a bar, and the glass bar was annealed at a proper temperature before cutting and polishing. The size of the prepared glass disc was $12 \times 12 \times 27$ mm. Glass powder was also prepared by pulverizing the quenched glass and sieving it to obtain the powder with various sizes of 63, 250, 500 and 841 μm.

2.2. Reaction in a carbonate ion solution
These prepared glass specimens were reacted with a CO_3^{2-} ion-containing solution in a polyethylene bottle for various periods of time. The ratio of surface area of the sample to the volume of the reacting solution was set at 0.1 cm^{-1}, and the reacting temperature was kept at 37 °C. The solution with carbonate ions was prepared by dissolving Na$_2$CO$_3$ in distilled water. The pH range of the solution varied from 3 to 12.5 by adding appropriate amounts of 50% HCl. After the glass sample was drawn out of the reaction solution, the glass specimens were treated with acetone for a few seconds to stop the further reaction.

2.3. Analysis of the reacted surface
The reacted glass surface was analyzed with a thin-film X-ray diffractometer (Philips PW3719 operated at 40 kV, 1.5° of incident beam angle, Cu target, scan speed: 0.08/sec, 2θ: 10–70°) and scanning electron microscope (Hitachi X-4200, 20 kV). The compositional profile of the surface and fracture surface of the glass was analyzed by an X-ray energy dispersive (EDS) equipped in the SEM.

2.4. Ion concentration measurement
The CO_3^{2-} ion concentration remained in the reacted solution after the glass treatment was measured by the acid-base titration method [8]. The carbonate ion can be titrated as a base with a strong acid titrant, in which case two fair breaks (pH 8.4, pH 5.4) are obtained. A CO_3^{2-} ion-containing solution was titrated with 0.01 N HCl, and determined the volume of HCl used at pH of 8.3 (V_1) and the volume at pH of 5.4 (V_2). The amount of carbonate ions can be calculated as follows.

The amount of carbonate ions
$$= \frac{(V_1 - V_2) \times 0.01 \times \text{weight of CO}_3}{\text{Volume of Co}_3^{2-} \text{ ion containing solution}}$$

Si^{4+} ions were measured by the molybdenum blue method [9]. Si^{4+} ion in a solution turns into silico-

molybdate by adding molybdate, and the silicomolybdate produces a blue color when adding metol-sulfite and oxalic acid. The extinction at 810 nm was measured by a UV-visible spectrometer (Shimadzu, UV-2401PC), and the extinction was compared with a standard calibration curve to calculate Si^{4+} ion concentration.

3. Results and discussion
3.1. Precipitation of carbonate crystal
When various RO glass specimens (R = Mg, Ca, Sr, Ba) were reacted in a CO_3^{2-} ion-containing solution with various pH ranging from 3 to 12.5 for 1 hour, carbonate crystals were deposited on the glass surfaces. Their surfaces were analyzed by a thin-film X-ray diffractometer, and the results are presented in Fig. 1.

For MgO glass, no crystalline phase was observed throughout the entire range of pH and only an X-ray bump is shown, which indicates a typical amorphous phase. It is thought that this is due to the inertness of the glass against the reacting solution. For CaO glass, however, CaCO$_3$ crystal peak [10] was observed at pH ranging from 6 to 12.5. In both SrO and BaO glasses, well-developed crystalline phases of SrCO$_3$ and BaCO$_3$, respectively [10], were obtained within a wide range of pH. From these results, it can be stated that SrO and BaO glasses, which have better chemical reactivity than MgO and CaO glasses, effectively, removed carbonate ions from the solution. The numerical data will be shown later.

To observe microstructure and morphology of carbonate crystals formed on glass surface, the glasses were reacted in a solution with a pH of 6 for 1 hour, and examined by SEM and EDS. The results are shown in Fig. 2.

For MgO glass, an amorphous cluster, which were shown as an X-ray diffraction bump, was observed on the glass surface. Based on EDS results, the primary composition of this amorphous cluster is thought to be magnesium carbonate phase. A Cl peak was observed due to the introduction of HCl, which was added for pH control. The EDS result for CaO glass shows a strong Si peak as well as strong Ca peaks. This indicates that CaCO$_3$ crystal was formed on the silica-rich layer, but the crystal layer was thin enough for EDS to detect the silica layer beneath CaCO$_3$. For SrO and BaO glasses, however, quite thick layers of SrCO$_3$ and BaCO$_3$ crystals, respectively, covered the glass surfaces entirely. No silica peaks were observed under EDS examination. The alkaline earth metal ions easily leached out of SrO and BaO glasses due to the relatively weak binding of the divalent ions to glass network, which acts as a network modifier [11]. Therefore, these glasses have better chemical reactivity, and this promotes the formation of the silica rich layer and deposition of the carbonate crystals on it.

As a result, it can be stated that carbonate crystals precipitate more easily on the glass surfaces containing SrO and BaO than on those containing MgO and CaO.

To examine the pH dependence of carbonate crystal deposition, all glasses except MgO glass (which has lower chemical reactivity), were reacted in a CO_3^{2-}
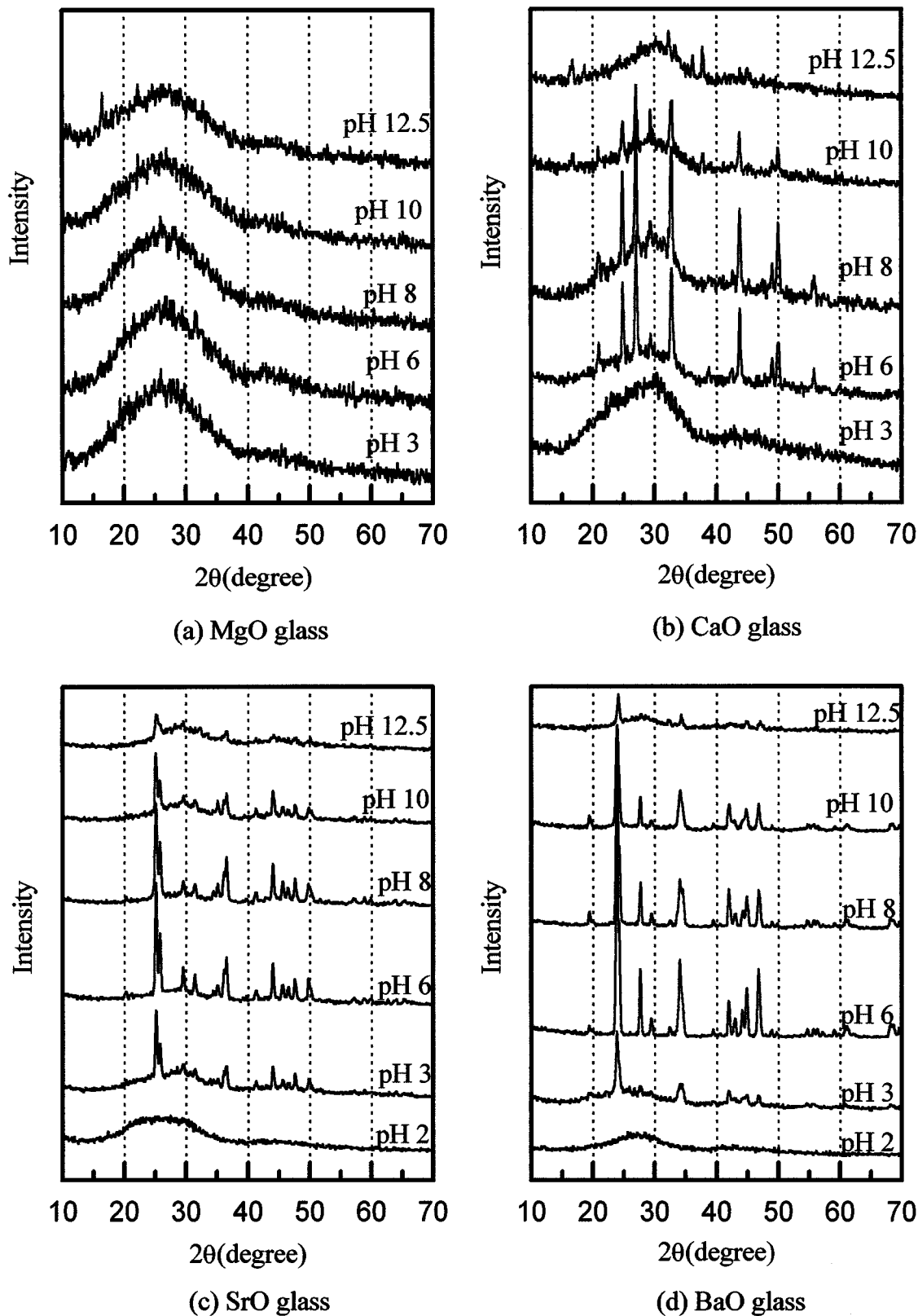
Figure 1 X-ray diffraction patterns of RO glass surface reacted in a CO_3^{2-} ion-containing solution for 1 hr.

ion-containing solution with pHs of 3, 6 and 10, respectively, for 1 hour. Their surfaces were then examined by SEM, and shown in Fig. 3. A silica gel layer is observed on the surfaces of all glasses reacted in an acidic solution of pH 3. Small X-ray diffraction peaks of carbonate crystals were observed on SrO and BaO glasses, as discussed in Fig. 1. For all glasses, reacted with the solution of a pH over 6, carbonate crystals were precipi-

tated on the glass surface as shown in Fig. 3, and the crystal formation was also confirmed earlier by XRD.

In this way, CO_3^{2-} ions can be removed from the solution by precipitating carbonate crystals on the surface active glasses in a neutral range of pH.

Fig. 4 shows the fracture surface of SrO glass, which was reacted in a CO_3^{2-} ion containing solution with a pH of 10 for 1 hour. An EDS line profile shows the
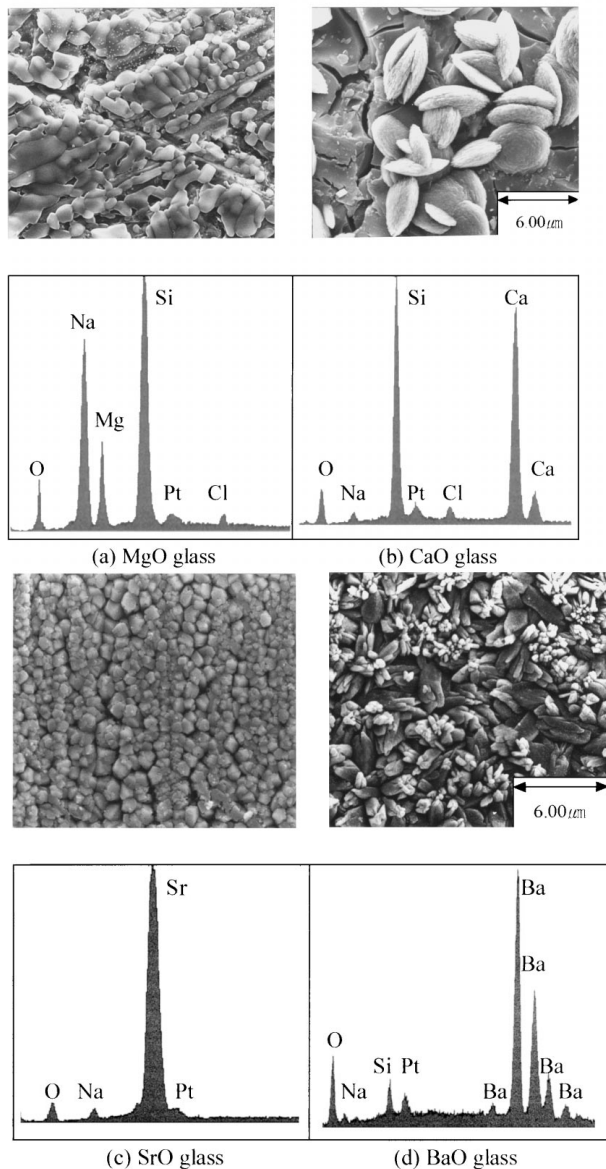
Figure 2 SEM micrographs and EDS anlaysis of RO glass surfaces reacted in a CO_3^{2-} ion containing solution with pH 6 for 1 hr.

silica rich layer beneath $SrCO_3$ crystal. This indicates that carbonate crystals were deposited on the silica gel layer not on the original glass surface. The silica rich layer was formed by ion exchange between Sr^{2+} ion in the glass and H^+ ion in the solution. Consequently, the silica rich layer is believed to be a gel layer with a silanol group. Carbonate crystal precipitated on this gel layer. No easy ion exchange was possible between Mg^{2+} in MgO glass and H^+ ions, and, therefore, no easy formation of silica gel layer was found in the MgO glass. This explains why no carbonate crystal formation was observed in the MgO glass.

3.2. Uptake of carbonate ions
After the prepared glasses were reacted in a carbonate ions-containing solution with a pH of 6 for various hours, the concentration of carbonate ions remaining in a solution was analyzed by the acid-base titration method, and the result is presented in Fig. 5.

For MgO glass which showed an excellent chemical durability due to the strong binding of Mg-O in a

TABLE II Solubility product constants of carbonate crystals

Carbonate crystal	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Solubility product constant	3.5×10^{-8}	4.5×10^{-9}	9.3×10^{-10}	5.0×10^{-9}

glass structure, only 300 ppm of carbonate ions were removed from the solution after 48 hours of reaction, which originally contained 5000 ppm of CO_3^{2-}. As mentioned earlier, only a small amount of amorphous magnesium carbonate phase was precipitated on MgO glass surface at pH 6. CaO glass was able to remove about 700 ppm of carbonate ions from the solution after 48 hours of reaction. Both SrO and BaO glasses showed a strong uptake capacity of carbonate ions. SrO and BaO glasses removed 1250 ppm and 900 ppm, respectively, of carbonate ions after 48 hours of reaction. This can be attributed to two causes. First, as discussed earlier, the silica gel layer forms easily on SrO and BaO glasses, from which Sr^{2+} and Ba^{2+} ions can be easily leached out of glasses due to the weak binding of R-O in glass structure [11]. This silica-rich layer acts as a seed for the carbonate crystal deposition. Second, the solubility product constants for $SrCO_3$ and $BaCO_3$ are lower than those for $MgCO_3$ and $CaCO_3$, as shown in Table II [12]. This low solubility also promotes the crystal precipitation.

3.3. Blockage of ions leaching
When surface active glasses are reacted in a solution, all ions in a glass can be leached out of a glass surface even if their leaching rates are different. Si^{4+} ions which are dissolved from the glasses do not participate in forming any crystal, but remain in a solution. We measured this Si^{4+} ion concentration to find out whether the newly formed crystal layer blocks the further leaching of ions from glasses. The Si^{4+} ion concentration was measured by using the molybdenum blue method with reaction time, and the result is shown in Fig. 6.

When considering their chemical durability of the prepared four different glasses from their chemical compositions, the durability for MgO and CaO glasses are far higher than those for SrO and BaO glasses, therefore, it was expected that greater amounts of Si ions would be dissolved in SrO and BaO glasses. However, the actual results as shown in Fig. 6 are quite different. The amounts of Si^{4+} ions leached out of MgO and CaO glasses are even higher than those from SrO and BaO glasses. This result suggests that the newly formed $SrCO_3$ and $BaCO_3$ crystals blocked the leaching of Si ion from the glasses. In the case of CaO glass, the thickness of $CaCO_3$ crystal was too thin to prevent from Si-ion leaching effectively, and no blocking layer was formed on the MgO glass surface.

3.4. Uptake of CO_3^{2-} ions by using glass powders
The uptake capacity of carbonate ions from the solution can be improved by increasing the surface area of glass. To do this, glass was pulverized into various size, such as 63, 250, 500 and 841 μm and then 40 grams of
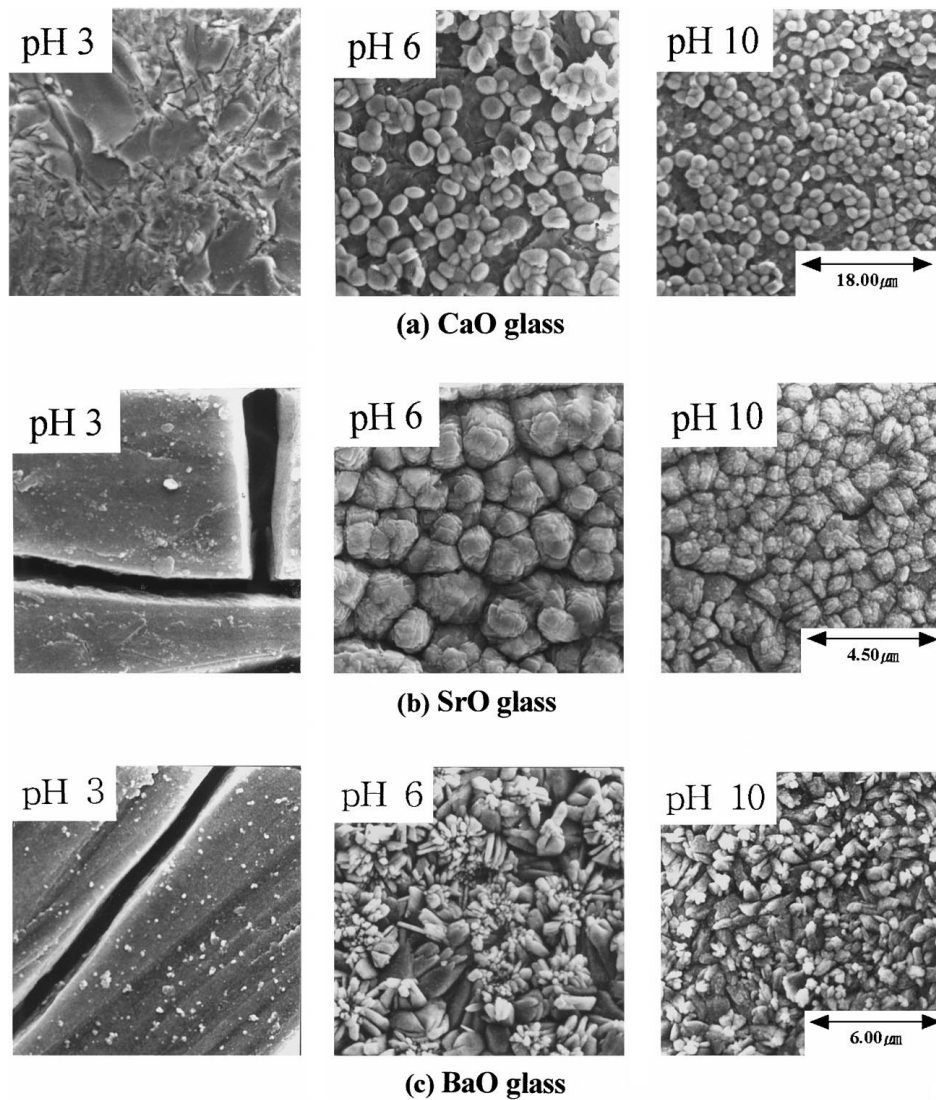
(a) CaO glass

(b) SrO glass

(c) BaO glass

Figure 3 SEM micrographs and RO glass surfaces reacted in a CO_3^{2-} ion containing solution with various pH6 for 1 hr.
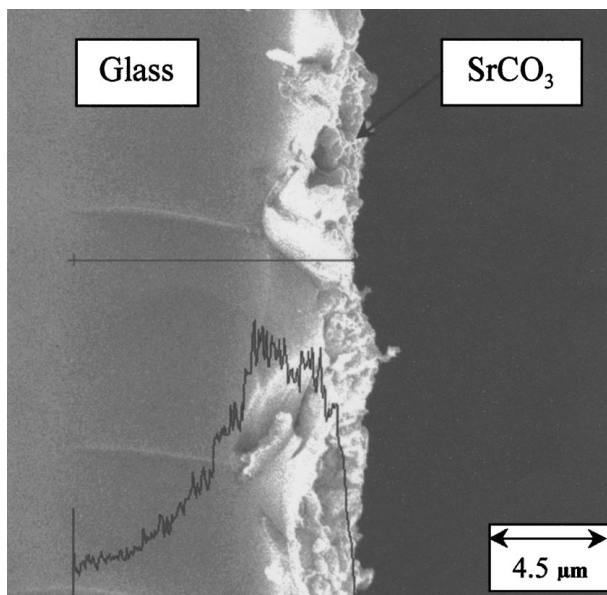

Figure 4 EDS line profile of Si and micrograph of fracture surface of SrO glass reacted in a CO_3^{2-} ion containg solution with pH 10 for 1 hr.
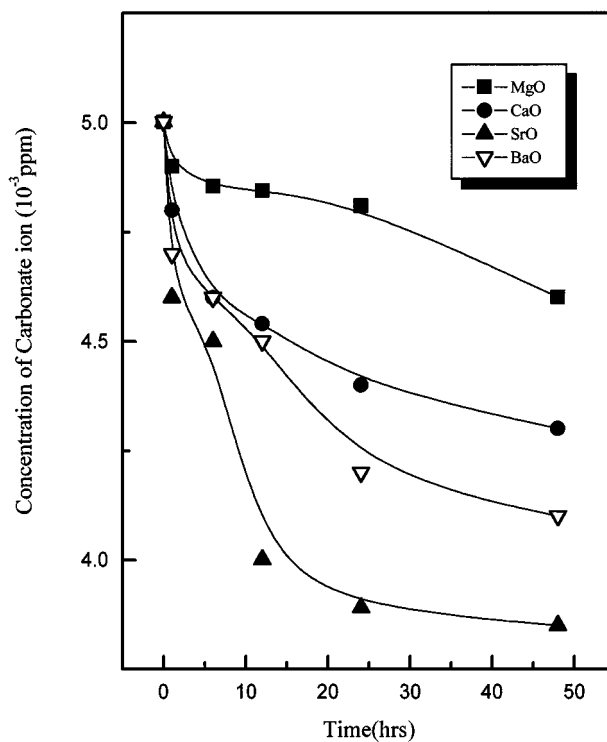

Figure 5 Concentration of carbonate ions remained in a solution after reaction with RO glasses for various periods of time.
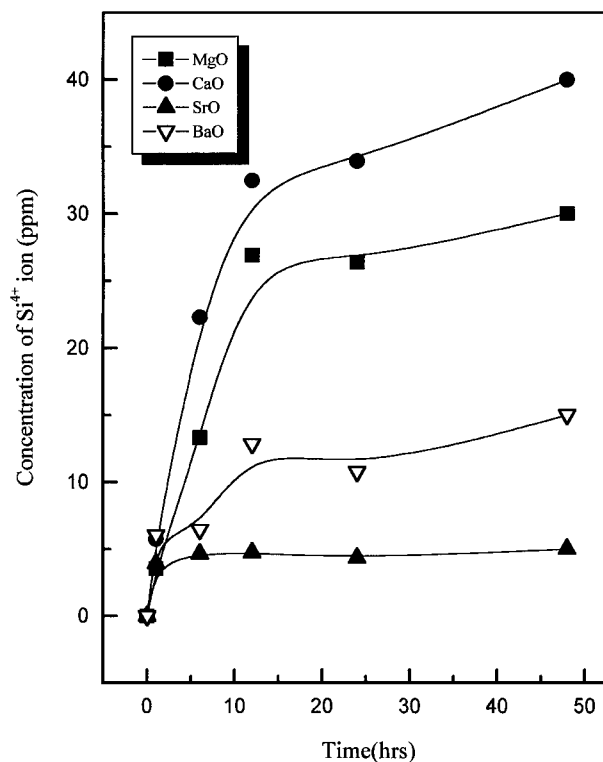
3249

Figure 6 Concentration of Si^{4+} ions leached in a CO$_3^{2-}$ ion containing solution with pH 6 for various periods of time.
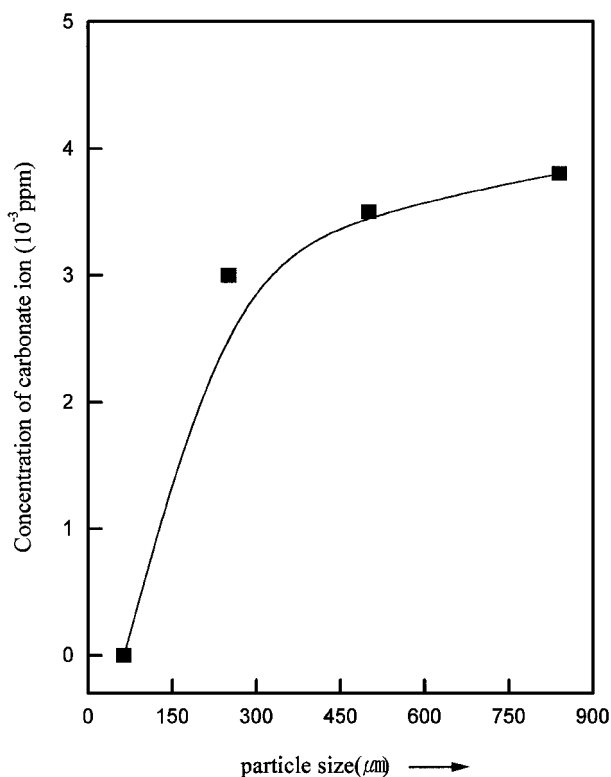

Figure 7 Concentration of CO$_3^{2-}$ ions remained in a solution after reaction with BaO Glass powders.

each size of BaO glass powder were packed into a glass tube with filter paper at the bottom. 100 ml of carbonate ion-containing solution was flown into the glass tube at a flow rate of 25 ml/min. Carbonate ions in a collected solution after this filtration by BaO glass powder were measured by the method mentioned earlier. The experiment was performed for all different sizes of glass

powders. The carbonate ion concentration against glass powder size was plotted in Fig. 7.

By using glass powder with less than 63 μm, the entire 5000 ppm of carbonate ion which was originally present in the solution were removed completely under these experimental conditions.

By controlling the flow rate of solution and, the size and quantity of glass powder, we are able to remove all carbonate ions in wastewater by just flowing the solution over glass powder. In this way, surface active glass powder may be used as a carbonate ion removal filter.

4. Conclusions

When various alkaline earth metal ion-containing glasses are reacted with a solution of carbonate ions, and the following conclusions can be drawn.

1. Carbonate crystal precipitates by combining alkaline earth metal ions, which are leached out of the glasses, with CO$_3^{2-}$ ion present in a solution on a silica gel layer formed on the surface active glass.

2. All glasses except MgO glass have a strong uptake capacity for carbonate ions from solutions in the pH ranging from 6 to 10.

3. Carbonate crystals formed on both SrO and BaO glasses showed a blocking effect against further leaching of Si ion from the glass surface.

4. The carbonate ion removal rate increases sharply with surface area, and 5000 ppm of carbonate ions in the solution were completely eliminated by the BaO glass in a particle size of 63 μm.

References
1. N. ANDRITSOS, A. J. KARABELAS and P. G. KOUTSOUKOS, *Langmuir* **13** (1997) 2873.
2. LEE N. MORGENTHALER and ZARA I. KHATIB, *Environment Treatment & Control* (1991) 37.
3. I. GAVRIELI, A. STARINSKY, B. SPIRO, Z. AIZENSHTAT and H. NIELSEN, *Geochimca et Cosmochimica Acta* **17** (1995) 3525.
4. JACK Z. XIE, HSUAO-LUNG CHANG and JOHN J. KILBANE, *Bioresource Technology* **57** (1996) 127.
5. C. Y. KIM, A. E. CLARK and L. L. HENCH, *J. Non-Cryst. Solids* **113** (1989) 195.
6. L. L. HENCH, *J. Am. Ceram. Soc.* **7** (1991) 1487.
7. HYUN-JUN KIM, Master's Thesis, Inha Univ. (1996).
8. R. A. DAY, JR. and A. L. UNDERWOOD, "Quantitative Analysis" (Prentice-Hall, Inc., 1974) p. 123.
9. T. R. PARSONS, Y. MAITA and C. M. LALLI, "A Manual of Chemical and Biological Methods for Seawater Analysis" (Pergamon Press, 1984) p. 22.
10. Joint Committee on Powder Diffraction Standards; Card No. 24-30, Copyright JCPDS-ICDD (1990).
11. MILO. B. VOLF, "Chemical Approach to Glass" (Elsevier Science Publishing Compony, New York, 1984) p. 118.
12. D. A. SKOOG, D. M. WEST and F. J. HOLLER, "Analytical Chemistry (6ed.)" (Saunders College Publishing, 1994) A1-A3.