Recovery of Calcium from BF Slag and Synthesis of Zeolite A Using Its Residue

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The elution and recovery of Ca from blast furnace slag and the alkali hydrothermal synthesis of zeolite A using the residue from the elution treatment were investigated using a ball-milling-type reaction vessel. The superior elution was obtained by using citric and formic acid solutions from which Ca could be selectively eluted from the slag. Whereas hydrochloric acid solution and ion-exchanged water were ineffective for Ca elution. Ca ions eluted in the solution were recovered as calcium formate by evaporation of water.

From the formic acid eluted slag residue after three elution treatment cycles of the slag for 7.2 ks, zeolite A was synthesized in 1 mol/L NaOH solution with a reaction time of 86.3 ks at 343 K, without the addition of any other materials.

KEY WORDS: slag; zeolite A; elution treatment; hydrothermal synthesis; heat-storage materials.

1. Introduction

In 2008, 78.5 million tons of pig iron were produced in Japan, resulting in 27.3 million tons of blast furnace slag (BF slag) as a by-product, of which 82% was water-quenched slag and 18% was slow-cooled slag. Nearly 100% of the slag is re-used as raw materials for cement, roadbed, and concrete aggregate. However, the amount of BF slag produced in Japanese steel industry tends to become much higher than the total amount of slag consumption in these fields and therefore, exploring new applications of BF slag has become increasingly important.

Heat storage systems have a high potential to effectively utilize the energy sources because of the need for the reduction of the difference between the amounts of electric power consumption in the daytime and nighttime. Zeolites, one of the candidate materials used for heat storage, are composed of aluminosilicate containing molecular-sized pores in their crystal structure, and their general chemical formula is indicated by $\text{M}_m[\text{Al}_n\text{Si}_{m-n}\text{O}_{2m+n}]\cdot x\text{H}_2\text{O}$. Zeolite A, in particular, with a composition of $\{\text{Na}_{12}[\text{Al}_4\text{Si}_2\text{O}_{10}]\cdot 27\text{H}_2\text{O}\}_8$, has a Si/Al molar ratio of 1 and contains the largest amount of Al among the various zeolites. It has been reported that the amount of water vapor absorbed by the zeolite is approximately 30% of its total mass. Zeolites are hydrothermally synthesized by heating the raw materials at a high temperature for a certain period of time under high pressure, and the raw materials used generally consist of compounds such as the oxides of Si and Al (hereafter referred to as Si source and Al source, respectively), an alkali source, and water. However, it seems that the relatively high production cost of zeolite prevents its practical use as a heat storage material.

The major components of BF slag are SiO$_2$, Al$_2$O$_3$, CaO, and MgO. Because Ca and Mg can be substituted for Na in the synthesis of zeolite A, BF slag is a readily available raw material for the synthesis of zeolite A. The use of BF slag as a raw material for the synthesis of zeolite A would also result in a significant reduction in the manufacturing cost of the zeolite. Another potential advantage of the use of BF slag in zeolite production is the environmental contribution to resource management by the effective recycling of industrial waste. Other utilizations of zeolites include the purification of industrial liquid waste and soil, the humidity control materials for buildings, deodorants, and so on. Consequently, the development of a low-cost manufacturing process for zeolites is of paramount importance.

We have previously reported the successful synthesis of zeolite A using water-quenched BF slag in combination of the optimization in the composition so as to CaO+MgO being less than 15 mass% (CaO+MgO). Slag compositions may be possibly optimized by the addition of Si and Al sources or the removal of Ca from the slag. In the previous study, the former method was investigated, and the Si and Al sources employed were amorphous SiO$_2$ and NaAl$_2$O$_4$, respectively. However, the large amount of addition of these reagents results in the increase of manufacturing cost. On the other hand, if Ca can be selectively eluted from BF slag, zeolite A may be synthesized using only BF slag.

There are many reports on the elution behavior of metallic ions from slag and other oxides. Futatsuka et al. investigated the elution behavior of Si, P, and Fe ions from steel making slag using simulated seawater. Zhang et al. dis-
cussed the elution of Si, Al, Fe, and Mg from ores using organic acids such as oxalic, citric, and tannic acids. However, there is no report on the direct elution and recovery of Ca from BF slag. In this study, therefore, the elution behavior of Ca in BF slag was investigated using various acids at room temperature. The optimized conditions of the type of acid, the acid concentration (pH), and the elution time period were evaluated, and the synthesis of zeolite A using the slag subjected to elution treatment was carried out.

2. Experimental

The raw material used in this study was water-quenched BF slag that was supplied from one of the steel mill works in Japan. The chemical composition of the BF slag is listed in Table 1. It is known that S content in BF slag is usually approximately 1%. Therefore, it seems that S content in the slag was similar to that of the conventional slag, though it was not analyzed. The slag was ground into a powder with a size less than 30 μm by an agate mortar. The elution treatment was carried out using hydrochloric, formic, acetic, lactic, citric, and tartaric acids. Citric acid was prepared using the monohydrate. For comparison, the treatment in use of ion-exchanged water was also carried out. The experimental apparatus for alkali hydrothermal synthesis used in this study, which was previously explained in detail, is shown in Fig. 1. The slag powder with a weight of 1.0 g, thirty numbers of SiC balls with a diameter of 10 mm, and 30 mL of acid solution were put into the vessel. The elution treatment was carried out for various time periods at room temperature. The rotation velocity of the vessel was 75 rpm. After the elution treatment was terminated, all the content was removed from the vessel. Then, filtration was conducted, and the residue obtained was washed by distilled water. The elution treatment using the residue was repeated under the same conditions. For comparison, the elution treatment without rotation of the vessel was carried out, in which the slag powder was statically hold in an acid solution for a given time period. To understand the elution behavior of the metallic ions, the ion concentrations of Al, Ca, Mg, and Si in the filtrate were measured after several time periods in elution treatment using ICP-AES (SHIMADZU, ICPS-8100). The filtrate was heated at 343 K to recover the eluted Ca by evaporating the water. The residue was analyzed for phase identification of compounds by X-ray diffraction.

Zeolite A was synthesized in aqueous NaOH solution using the residue after elution treatment of the slag. Two hundred and forty numbers of SiC balls with a diameter of 5 mm, and 15 mL of NaOH aqueous solution in 1 mol/L were put into the vessel together with the residue obtained by elution treatment at 343 K for 86.4 ks. The rotation velocity of the vessel was 75 rpm. After the synthesis reaction was terminated, the synthesized products were removed from the vessel. Following filtration and washing of these products using distilled water, they were dried at the synthesis temperature. The products were then analyzed for phase identification of compounds by X-ray diffraction. The ratio of identified phases in the product was determined by the calibration curve method using MgO as the standard reagent. The calibration curve was created using commercial zeolite A and MgAl2O4 powders. The outer appearance of the products was observed using a scanning electron microprobe (SEM, XL30FEG, Philips). The heat of water adsorption was measured using a Tian-Calvét type twin calorimeter; details of this apparatus have been previously reported.

3. Results and Discussion

3.1. Elution Treatment of Ca from BF Slag

Figure 2 shows the concentration of Ca ion eluted from the slag into various acid solutions after holding for 7.2 ks at room temperature. The pH values of acetic, tartaric, lactic, formic, citric, and hydrochloric acid solutions were controlled so as to be 2. With the exception of the result

| Table 1. Chemical composition of water-quenched blast furnace slag (mass%). |
|-----------------|---|---|---|---|---|---|
| SiO₂ | Al₂O₃ | CaO | MgO | Total-Fe | FeO | Si/Al (molar ratio) |
| 33.8 | 14.7 | 42.5 | 6.65 | 0.25 | 0.05 | 1.95 |

Fig. 1. Schematic diagram of ball-mill type reaction vessel for elution treatment and alkali hydrothermal treatment.

Fig. 2. Concentration of Ca ion eluted into various acid solutions at room temperature for 7.2 ks.
obtained using tartaric acid, the concentration of Ca ion eluted into the acids by ball milling treatment is higher than that by static treatment. The use of inorganic acids such as HCl resulted in very little elution of Ca ion into the acid solution. The use of organic acids resulted in a much higher concentration of eluted Ca compared with the use of the inorganic acids. In the case of formic and lactic acids, in particular, the concentration of Ca ion reached approximately 1100 mg/L. Namely, the residues obtained by treatment using formic and lactic acids, and hydrochloric acid have the highest and the lowest elution ability of Ca, respectively. The chemical compositions of both of these residues were analyzed. Figure 3 shows the chemical composition of these residues and BF slag on the pseudo-binary phase diagram of the SiO2–Al2O3–(CaO+MgO) system. The hatched area indicates the chemical composition range where zeolite A can be synthesized, as reported in a previous study.3) The chemical composition of the residue remains virtually unchanged from that of BF slag upon treatment with hydrochloric acid. The ball milling treatment using citric and formic acids changes the chemical compositions of CaO+MgO from 50.3 mass% to 41.7 and 46.7 mass%, respectively. In addition, the ball milling treatment using formic acid does not change the Si/Al ratio, which is desirable for the synthesis of zeolite A. Therefore, formic acid was selected as an acid solution used for the elution treatment, and is discussed hereafter.

The change in concentration of Al, Ca, and Si ions eluted from BF slag by ball milling treatment in formic acid with various initial acid concentrations is shown in Fig. 4. The data show that the initial acid concentration has a strong effect on the concentrations of eluted Ca and Si ions. At an initial pH value of 2, the concentrations of Ca and Si are such high values as 1150 and 80 mg/L, respectively. The dependence of Ca and Si concentrations on initial pH may be explained as follows. When the initial pH values were controlled as 2, 3, and 5, pH values obtained after elution treatment changed to 6, 10, and 11, respectively. The elution of Ca ion was prevented in the case of acid solution with a higher initial pH value because the solution became alkaline more readily when the initial concentration of the acid was low. Therefore, it can be concluded that the initial pH value of 2 is needed for the synthesis of zeolite A.

The CaO+MgO composition of the residue obtained by the ball milling treatment for a time period of 7.2 ks, however, was outer in a concentration range on the pseudo-binary phase diagram (Fig. 3) within which zeolite A can be synthesized. Little change in CaO+MgO composition was obtained by employing an extended treatment time longer than 7.2 ks. The concentration of Ca and Mg ions were saturated in the solution, and therefore, a second elution treatment was carried out in a new acid solution using the residue obtained by the first treatment, employing cycle times of 1.8 and 7.2 ks. Figure 5 shows the relation between the composition ratio of the residue to BF slag and the number of elution cycles. No difference in the CaO composition of the residue was observed between the cyclic periods of 1.8 and 7.2 ks. The compositions of SiO2 and Al2O3 in the residue obtained by treatment for 7.2 ks are higher than that for 1.8 ks. In treatment with an elution time period of 1.8 ks, the longer filtration time was required because the membrane filter became clogged during filtering.

Tashiro et al. reported the elution behavior of cation in the slag of the CaO–SiO2–CaF2 system in water at 317 K. The peak concentrations of Ca and Si were obtained in the elution time range from 36 to 54 ks. As the elution time was increased, CaO–SiO2–H2O gel was formed on the slag surface, and then precipitated.7) It seems that a similar behavior takes place in this study considering that the slag composition is similar to the slag composition used in their study, although formic acid solution was used in the present study. The elution time for which the Ca concentration had the peak value...
in this study was 1.8–7.2 ks. This time was shorter than that reported by Tashiro et al., possibly because the ball milling process accelerated the elution process. For these reasons, the elution treatment for 7.2 ks is better than that for 1.8 ks.

In case of 7.2 ks elution time, the composition ratio of Ca and Mg in the residue decreases rapidly after three cycles, and then it tends to be a constant value with the further increase of cycle numbers. The composition ratio of Si shows a similar behavior to that of Ca until three cycles, but it tends to decrease slightly with an extended cycle numbers. There is very little elution of Al in the slag after two cycles; however, after three cycles, Al elution evidently appears. Si and Al are the constituent elements of zeolite A. From the view point of the synthesis of zeolite A, the loss of these elements is required to be minimized, attaining to the lowest possible level. Figure 6 shows the chemical composition of the residue after the elution treatment on the phase diagram of the SiO$_2$–Al$_2$O$_3$–(CaO+MgO) system together with that of BF slag. The chemical composition of the residue after three cycles reaches an area on the phase diagram in which zeolite A can be synthesized. The further increase of treatment cycle number shifts the chemical composition of the residue to the outside of this area. Consequently, the optimum cycle number in elution treatment is three cycles with each treatment time period of 7.2 ks.

A white powder was obtained from the filtrate after one cycle treatment followed by evaporation of water in air at 343 K for 172.8 ks. This powder with a weight of 0.38 g was recovered from BF slag with a weight of 1.0 g. The XRD pattern of this powder is shown in Fig. 7. The powder was identified as calcium formate, (HCOO)$_2$Ca which is the same one utilized as a flower picking and concrete admixture, and so, this process may have a potential to supply calcium formate at low cost.

### 3.2. Synthesis of Zeolite A from Residue

The direct synthesis of zeolite A was carried out using the residue obtained after three cycle treatments. Table 2 shows the chemical composition of the residue used. The alkali hydrothermal treatment was carried out at 343 K for 86.4 ks in 1 mol/L NaOH solution. The synthesized products obtained by conventional process using BF slag, amorphous SiO$_2$, and NaAlO$_2$ which was studied in the past by the authors was compared with products obtained by the present process. Figure 8 shows the XRD patterns of the products obtained by the direct synthesis of zeolite A together with the XRD of the synthesized product obtained by conventional process. From comparison of both XRD patterns, the larger amount of zeolite A can be synthesized by the present process. Na–P1 (Na$_6$Al$_x$Si$_{12–x}$O$_{40}$·12H$_2$O) with a 5/3 Si/Al ratio was formed by this process, whereas tobermorite and hydrogarnet (3CaO·Al$_2$O$_3$·(3–x)SiO$_2$·2xH$_2$O (x = 0–3)) were formed by use of BF slag, amorphous SiO$_2$, and NaAlO$_2$ (conventional raw materials). Na–P1 may be formed due to the suppression of the formations of tobermorite and hydrogarnet with the higher content of CaO, because the composition of CaO+MgO in the residue is lower than 10 mass% and the Si/Al ratio is higher than that of the previous raw materials. Zeolite A content in the products synthesized by the conventional and the present processes were 45% and 51%, respectively.

Figure 9 shows the scanning electron micrographs of BF slag powder, the residue obtained after elution treatment, and the product obtained by hydrothermal treatment using the residue. BF slag before the elution treatment has a smooth surface, whereas, the residue obtained after the elution treatment by formic acid has a rough surface, the particle size being much reduced. The product synthesized has

#### Table 2. Calculated chemical composition of BF slag after three formic acid cycle treatments (mass%).

|          | SiO$_2$ | Al$_2$O$_3$ | CaO | MgO | Si/Al (molar ratio) |
|----------|---------|-------------|-----|-----|---------------------|
|          | 59.5    | 29.7        | 10.0| 0.8 | 1.70                |

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a similar shape to that including zeolite A⁶; however, its average size is smaller.

There are some patents regarding on the pretreatment of BF slag for the synthesis of zeolite A. One method is as follows: after dissolution of BF slag by hydrochloric or nitric acid, silica gel is formed from the solution. Al source is added to the solution, and then the hydrothermal synthesis is carried out.⁸ Another method is as follows: BF slag with the addition of Na₂CO₃ powder is heated at 1023–1173 K. The obtained material is treated in an acid solution with pH value of lower than 4, followed by washing with water. The hydrothermal synthesis is then carried out.⁹ Both of these methods require additional material. Heating is necessary for the latter method. The present method is more advantageous over these previous methods reported in patents, because the elution treatment is carried out at room temperature and zeolite A can be synthesized using simply the residue without any use of other materials.

3.3. Heat of Water Absorption of Product

The amounts of the heat of water absorption of the products obtained in this study and commercial zeolite A was measured using a Tian-Calvét type twin calorimeter. Figure 10 shows the relation between the heat of water adsorption and zeolite A content in the product. This relation is not proportional. The heat of water adsorption of all product obtained in this study is higher than that predicted by the proportional relation based on commercial zeolite A. This is because commercial zeolite A has a high Si content and Si shows hydrophobicity,⁹ whereas the Si content in the product obtained by the present method is higher than that in case of the Si/Al ratio of 1. Despite this, the heat in zeolite A produced in this study was higher than that predicted from the proportional relation between zeolite A content and the heat of water absorption. The reason is that Na–P₁ is also formed in the product and is also a hydrophilic zeolite with Si/Al = 5/3. The pore size of Na–P₁ is 0.31 nm and 0.44 nm in short and long diameters, respectively. This pore size is similar to zeolite A. Na–P₁ also has good water absorption properties because it is capable of absorbing twelve H₂O molecules, whereas zeolite A can absorb twenty seven water molecules. The formation of Na–P₁ together with zeolite A thus accounts for the higher heat of water adsorption than that of commercial zeolite A.

4. Conclusions

The optimum conditions for the elution treatment of Ca in BF slag using various acids were examined as well as the synthesis of zeolite A. Zeolite A was synthesized using the slag treated in acid solutions, and the following results were obtained.

Citric and formic acid solutions were more favorable to the elution of Ca in BF slag, whereas water and hydrochloric acid solution have no effect. The use of a ball-milling-type reaction vessel increased the elution rate of Ca from the slag. Calcium formate was obtained from the filtrate after the elution treatment and evaporation of water. The optimum elution conditions for the synthesis of zeolite A were found to be the use of formic acid solution with pH 2 at room temperature for 7.2 ks, repeating three times of this elution treatment. The composition of the residue obtained by this process was 29.7 mass%Al₂O₃ - 59.5 mass%SiO₂ - 10.0 mass%CaO - 0.8 mass%MgO. Zeolite A could be synthesized from this residue by the alkali hydrothermal treatment at 343 K for 86.4 ks in 1 mol/L NaOH solution in the ball-milling-type reaction vessel. The product obtained in these conditions shows higher water absorption ability than commercial zeolite A, although the zeolite A content in the product was 51%. The improved water absorption ability appeared to be due to the formation of Na–P₁ together with zeolite A, which was one of zeolite compounds with high water absorption ability.

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