Synthesis of Hydrocalumite-like Adsorbent from Blast Furnace Slag using Alkali Fusion

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Blast furnace (BF) slag, one of the byproducts of iron- and steel-making plants, was converted into a hydrocalumite-like compound using the alkali fusion method. The slag was transformed into the precursor with reactive phases via alkali fusion, after which the precursor was added to distilled water and stirred at room temperature to synthesize the product including a hydrocalumite-like compound. The effects of the mixed ratio of NaOH to the slag (NaOH/slag ratio), fusion temperature, ratio of precursor mass to distilled water volume (W/V ratio) and crystallization reaction time on the product phase were investigated, and the removal abilities of the obtained product for certain ions from aqueous solution was examined. Optimal conditions for hydrocalumite synthesis are a NaOH/slag ratio of 1.6, fusion temperature of 600 °C, W/V ratio of 125 g/L and reaction time of more than 24 h. The product could remove more NH₄⁺, Sr²⁺, F⁻, PO₄³⁻ and AsO₄³⁻ than BF slag, while the removal of Cl⁻, SO₄²⁻ and NO₃⁻ was almost zero. These results suggest that a hydrocalumite-like adsorbent able to remove pollutant ions in aqueous solution can be synthesized from BF slag via alkali fusion.

KEY WORDS: blast furnace slag; hydrocalumite-like adsorbent; alkali fusion; cation and anion removal abilities.

1. Introduction

Blast furnace (BF) slag is the greatest byproduct of iron- and steel-making processes, and more than 25 million tons of BF slag is generated every year in Japan. Although it has been widely used for cement production, road construction, and as a concrete aggregate, the capacity for use of recycled BF slag in these fields has become saturated and the development of value-added products from such waste slag has become an important issue for sustainability. Therefore, research has recently been made in various recycling processes.

The synthesis of functional materials from BF slag has been attempted. Yamasaki et al. investigated the spherification of BF slag using a hydrothermal hot-press system, and Nakamot et al. reported that it is possible to use waste slag as a lubricant in the high straining rolling of ultrafine-grained steel by using the hydrothermal hot-pressing method. Yoshikawa et al. reported on the use of BF slag in the preparation of porous ceramics as water-retentive materials. Takazawa et al. synthesized zeolite-X from the precursor, which was obtained from BF slag via acid treatment, by an alkali reaction, and Sugano et al. synthesized zeolite-A using BF slag by alkali hydrothermal treatment using a ball mill-type reaction vessel. Nakayama et al. synthesized monolithic tobermorite from BF slag by hydrothermal synthesis, and Wajima et al. synthesized 11 Å tobermorite from BF slag using an alkali hydrothermal reaction with EDTA. Kuwahara et al. reported on the synthesis of a hydrotalcite-like compound from BF slag using co-precipitation via acid treatment. However, there are no reports for the application of alkali fusion, whereby less-active phases in raw materials are converted into highly-active phases by fusion with alkali agents, to synthesize functional materials from BF slag.

In our previous study, we converted steel-making slag into functional materials using alkali fusion, and a hydrocalumite-like compound, able to remove harmful anions, was synthesized. Hydrocalumite is an anionic clay mineral which belongs to the layered double hydroxide (LDH) family, and is expressed as 3CaO·Al₂O₃·CaX₂/m·nH₂O (X: univalent or bivalent anion, n: 20 or less). LDHs are lamellar mixed hydroxides containing positively charged main layers and they undergo anion exchange. In recent years, many studies have been devoted to investigating the ability of LDHs to remove harmful oxy-anions such as arsenate, phosphate, etc. from contaminated water. This provides a new way to convert the slag into functional materials. However, there are no reports for the synthesis of a hydrocalumite-like compound from BF slag via alkali fusion, and no information is available on the optimal synthesis conditions. Elucidation of the reaction conditions is important for designing manufacturing equipment and operating conditions.

In this study, we attempted to convert BF slag into a hydrocalumite-like compound by alkali fusion. The main purpose of this study is to determine optimal synthesis conditions and the effective utilization of a hydrocalumite-like
compound as a water purification agent. Synthesis conditions investigated include fusion temperature, mixed ratio of NaOH powder to slag (NaOH/slag), ratio of fused powder mass to solution volume (W/V ratio) and reaction time. In addition, the ability of the product to remove certain cations and anions from aqueous solution was examined for possible application in wastewater treatment.

2. Experimental

2.1. Materials

BF slag can be classified into air- and water-cooled slag according to the cooling method. These slags contain crystalline and amorphous phases, respectively. To ensure that phases in the slag were converted into functional phases by alkali fusion, BF slag used in this study (received from one of the steel-making plants in Japan) was air-cooled. The BF slag was ground by mill and sieved to under 1 mm. The chemical and mineralogical compositions of raw slag were obtained by X-ray fluorescence spectrometry (XRF) (Shimadzu, XRF-1700) and X-ray diffraction (XRD) (Rigaku, RINT-2500), respectively (Table 1, Fig. 1). Raw slag was mainly composed of CaO (41.5%), SiO$_2$ (33.9%), and Al$_2$O$_3$ (14.2%) in the form of calcite (CaCO$_3$), gehlenite (Ca$_2$Al$_2$SiO$_7$), larnite (Ca$_2$SiO$_4$). Other oxides, such as MgO, SO$_3$, Fe$_2$O$_3$, TiO$_2$, K$_2$O, and MnO occurred in lesser amounts.

2.2. Synthesis

To investigate the relationship between synthesis conditions (fusion temperature, NaOH/slag ratio, W/V ratio and reaction time) and product phases, a two-step synthesis process comprised of alkali fusion and crystallization, was carried out as shown in Fig. 2. In the alkali fusion process, 10 g of the slag was mixed with 4, 8, 12, 16, and 20 g NaOH (NaOH/slag ratio: 0.4, 0.8, 1.2, 1.6, and 2.0 g/g, respectively) and ground to obtain a homogeneous mixture. This was then heated in a nickel crucible in air at 200, 400, 600, and 800°C for 1 h. The resultant fused mixture was cooled to room temperature and ground again to obtain the fused precursor. In the crystallization process, 1.25, 2.5, or 5 g of precursor were added to 20 mL distilled water (W/V ratio: 62.5, 125 and 250 g/L, respectively) in a 50 mL polymethylene bottle and stirred with magnetic stirrer at room temperature for 3, 6, 12, 24 and 48 h. After stirring, the solid product was filtered, washed with distilled water, and dried in the drying oven at 60°C overnight.

The product phases and morphologies were analyzed by XRD and a scanning electron microscope (SEM) (Hitachi, S-4500), respectively. Concentrations of Si, Al, and Ca in the filtrate were determined by inductively-coupled plasma (ICP) (Seiko instruments SPS3000).

2.3. Ionic Removal Experiments

The ability of the BF slag and product to remove certain ions (NH$_4^+$, Sr$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, F$^-$, PO$_4^{3-}$, AsO$_2^-$ and AsO$_4^{3-}$) from aqueous solution was examined, in comparison with hydrocalumite synthesized from reagents. Hydrocalumites with chloride (HC–Cl) or nitrate (HC–

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Table 1. Chemical composition of raw slag, fused slag and product.

<table>
<thead>
<tr>
<th>Oxide (wt.%)</th>
<th>Raw slag</th>
<th>Fused slag</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>41.5</td>
<td>15.8</td>
<td>48.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>33.9</td>
<td>12.7</td>
<td>29.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.2</td>
<td>5.3</td>
<td>12.5</td>
</tr>
<tr>
<td>MgO</td>
<td>6.6</td>
<td>2.0</td>
<td>4.4</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.1</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.3</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>–</td>
<td>60.9</td>
<td>4.1</td>
</tr>
</tbody>
</table>

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Fig. 1. XRD patterns of BF slag.

Fig. 2. Flow chart of the experiment.
NO₃) in the interlayers were prepared as hydrocalumite samples. A mixture of 0.6 M CaCl₂ solution (100 mL) and 0.3 M AlCl₃ (100 mL) or that of 0.6 M Ca(NO₃)₂ and 0.3 M Al(NO₃)₃ was added drop wise under vigorous stirring conditions to 100 mL of 1 M NaCl or 1 M NaNO₃, and heated at 50°C. During the stirring, the pH was kept constant at 12 by simultaneous addition of 10% NaOH solution. After 6-h stirring, the solid product obtained by a vacuum filtration method was washed with distilled water and then dried at 80°C overnight.

Ionic removal experiment was carried out as follows. One millimolar solutions were prepared with NH₄Cl, Sr(NO₃)₂, NaCl, Na₂SO₄, NaNO₃, NaF, Na₃HPO₄·12H₂O, NaAsO₂ and Na₂HAsO₄·7H₂O. The sample (0.1 g) was added to 10 mL of 1 mM solution in a 50 mL centrifuge tube, and shaken for 12 h using a reciprocal shaker. After shaking, the solution was centrifuged at 3000 rpm for 10 min. Concentrations of NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻, F⁻, and PO₄³⁻ in the supernatant were determined using an ion chromatograph (Dionex ICS-3000), and those of Sr²⁺, AsO₂⁻ and AsO₄³⁻ in the supernatant were determined using ICP. The amount of each ion removed was calculated from the difference between the initial and final solution concentrations.

3. Results and Discussion

3.1. Alkali Fusion
We examined the effect of alkali fusion conditions (NaOH/slag ratio and fusion temperature) on the hydrocalumite synthesis. Crystallization conditions were fixed at a W/V ratio = 125 g/L and reaction time = 24 h. Figure 3 shows the XRD patterns of the product after alkali fusion with various NaOH/slag additions, (a) 0.4, (b) 0.8, (c) 1.2, (d) 1.6 and (e) 2.0, at 600°C. Hydrocalumite and calcite were present in all products. At the ratio of 0.4, high gehlenite peaks remained in the product. These peaks decreased and those for hydrocalumite increased at an increased NaOH/slag ratio of 1.2. At ratios greater than 1.2, the gehlenite concentration decreased and a mixture of hydrocalumite and calcite was obtained. The alkali fusion reaction between BF slag and NaOH powder occurs to completion at a NaOH/slag ratio of more than 1.2 and the product obtained at a NaOH/slag ratio of 1.6 showed the highest peaks for hydrocalumite.

Figure 4 shows XRD patterns of the products at various heating temperatures, (a) 200°C, (b) 400°C, (c) 600°C and (d) 800°C, and at the NaOH/slag ratio of 1.6. At 200°C, high gehlenite peaks remained in the product, but these decreased with a corresponding increase in hydrocalumite peaks at an increased temperature of 600°C. This occurs because the alkali fusion reaction between the BF slag and NaOH powder is promoted by increase in fusion temperature. At 800°C, the hydrocalumite peaks diminished and those of portlandite were confirmed. The same XRD pattern of the product was also confirmed at NaOH/slag ratio of 1.2 at 800°C, and the solution after crystallization of the precursor at 800°C contained higher amount of Si and Al than that at 200–600°C. It was reported that alkali metal (sodium) release into atmosphere occurs around 800°C. It was considered that sodium condition, such as content, chemical species, etc., in precursor at 800°C was not suitable to synthesize hydrocalumite. The product obtained from the precursor after alkali fusion at 600°C indicated the highest peaks for hydrocalumite.

Optimal fusion conditions for hydrocalumite synthesis are a NaOH/slag ratio of 1.6 and a fusion temperature of 600°C.

3.2. Crystallization
Figure 5 shows XRD patterns of the product produced at
Various W/V ratios, optimal fusion conditions as mentioned above and a crystallization time of 24 h. Hydrocalumite was synthesized under all conditions. With W/V ratio increasing from 62.5 to 125 g/L, the hydrocalumite peaks increased. These peaks decreased, together with the appearance of portlandite, at a W/V ratio of 250 g/L, because hydrocalumite crystal \([\text{Ca}_4\text{Al}_2\text{O}_6(\text{OH})_2\cdot11\text{H}_2\text{O}]\) requires more water than portlandite \([\text{Ca(OH)}_2]\). Therefore, the optimal W/V ratio for hydrocalumite synthesis was found to be 125 g/L.

Figure 6 shows XRD patterns of the precursor \((\text{NaOH}/\text{BF slag} = 1.6, \text{fusion temperature } 600^\circ\text{C})\) and products from the precursor during the crystallization process. The precursor is mainly composed of soluble sodium salts, such as sodium silicate, sodium aluminate and sodium aluminosilicate. After addition to distilled water, the sodium salt phases decreased from the immediate dissolution of soluble precursor phases, and calcite and portlandite appeared. After a 3 h reaction, hydrocalumite appeared, and with increasing reaction time, the hydrocalumite peaks increased, while those of portlandite decreased.

The reaction was monitored by analyzing the Ca, Si and Al solution contents and the intensity of the product phase, hydrocalumite, portlandite and calcite, in the solid during the reaction, as shown in Fig. 7. The change in amount of mineralogical phases in the product was represented using the intensity of the major XRD peaks in the product at given diffraction faces; hydrocalumite \((0 0 2)\), portlandite \((1 0 1)\), and calcite \((1 0 4)\). In the initial crystallization stage, Si and Al contents in the solution were 120 and 90 mmol/L, respectively. In contrast, the Ca content was zero during crystallization, due to the precipitation of crystalline phases, such as portlandite and calcite, and amorphous phases, such as amorphous calcium silicate. With increasing reaction time,
the Si and Al concentrations decreased initially, and reached a steady state after 24 h, while the Ca concentration was zero during the reaction. The hydrocalumite and calcite intensity increased in the early stage and was almost constant after 24 h of alkali reaction. Changes in Si and Al solution concentrations were correlated to the formation of amorphous calcium silicate and hydrocalumite. This means that the Si and Al in solution gradually reacted with the Ca contents, such as portlandite, to synthesize amorphous calcium silicate and hydrocalumite crystals, respectively. In addition, the Ca reacted with CO₂, which dissolves from the atmosphere into the alkali solution, to form calcite.

3.3. Synthesis at Optimal Conditions

Figure 8 shows XRD patterns of the (a) BF slag, (b) fused precursor and (c) product. The slag was composed of the crystalline phases, gehlenite, calcite and larnite (Fig. 8(a)). After alkali fusion, most of the crystalline phases were converted to soluble sodium salts, such as sodium silicate and sodium aluminate (Fig. 8(b)), and finally, the product, which included the crystalline phases, hydrocalumite and calcite, was synthesized (Fig. 8(c)).

Figure 9 shows SEM micrographs of the (a) raw slag, (b) fused precursor and (c) product. Although the slag is composed of rock-like particles (Fig. 9(a)), the fused precursor consists of particles with a melted surface resulting from the formation of sodium salts by alkali fusion (Fig. 9(b)). After synthesis, thin regular hexagonal crystals of the hydrocalumite-type compound were confirmed to be present in the product (Fig. 9(c)).

Table 1 show the chemical composition of the BF slag, fused precursor and product. The slag mainly contains CaO (41.5 wt.%), SiO₂ (33.9 wt.%) and Al₂O₃ (14.2 wt.%), and some minor elements. After alkali fusion, the obtained precursor contains higher amounts of Na₂O (57.3 wt%) and lower amounts of CaO (21.8 wt.%), SiO₂ (11.8 wt.%) and Al₂O₃ (5.1 wt.%), than the raw slag, due to the NaOH addition. After synthesis, the product has almost the same chemical composition as the raw material, which means that most elements in the slag were converted into new phases in the product. It is noted that the mixture of slag (10 g) and NaOH powder (16 g) was converted into the precursor (24 g) to synthesize the product including hydrocalumite (5.4 g).

3.4. Ability of Product to Remove Various Ions from Aqueous Solution

Figure 10 shows the removal efficiencies of (a) the slag and product, and (b) HC–Cl and HC–NO₃, for certain ions from aqueous solutions. It is noted that the all supernatant pH after the tests was approximately 12.6 regardless of the pH of the original solution. The removal efficiencies of raw slag are low, except for PO₄³⁻, owing to its Ca-containing compounds, and those of the product for all ions are higher than those of the raw slag. The product has high removal abilities for cations, NH₄⁺ (75.6%) and Sr²⁺ (100%), and anions, F⁻ (20.6%), PO₄³⁻ (99.1%), and AsO₄³⁻ (26.7%). In the case of HC–Cl and HC–NO₃, the removal abilities for cations are very low (NH₄⁺: 16–18%, Sr²⁺: 2–5%), and those for anions, SO₄²⁻, F⁻, PO₄³⁻, AsO₂⁻ and AsO₄³⁻, are high. It is considered that the product has the removal abilities for cations owing to the amorphous calcium silicate, and those for anions owing to hydrocalumite in the product. The removal efficiencies of Cl⁻, SO₄²⁻ and NO₃⁻ (representative co-existing anions in natural and wastewater) by the slag and product were small. It is unclear why the removal ability

Fig. 8. XRD patterns of (a) BF slag, (b) precursor and (c) product.

Fig. 9. SEM photographs of (a) BF slag, (b) precursor and (c) product.
of the product for $\text{SO}_4^{2-}$ was zero while HC–Cl and HC–NO$_3$ has high removal ability of $\text{SO}_4^{2-}$. The only difference from HC–Cl and HC–NO$_3$ is the presence of amorphous calcium silicate, which may influence the reaction between hydrocalumite phase and $\text{SO}_4^{2-}$. These results indicate that the removal of ions by the product from natural and waste-water would be unaffected by these co-existing anions. Therefore, the product can be used as an adsorbent for water purification.

4. Conclusion

The chemical conversion of BF slag into an adsorbent including a hydrocalumite-like compound using alkali fusion was attempted. The slag was transformed into a precursor with reactive phases through alkali fusion, and then the product was synthesized by stirring in distilled water at room temperature. Optimal hydrocalumite synthesis conditions are a NaOH/slag ratio of 1.6, fusion temperature of 600°C, W/V ratio of 125 g/L and reaction time of more than 24 h. The product has higher adsorption potential for $\text{NH}_4^+$, Sr$^{2+}$, F$^-$, $\text{PO}_4^{3-}$ and AsO$_4^{3-}$ than raw slag, and does not remove the representative anions in natural and waste water, such as Cl$^-$, $\text{SO}_4^{2-}$ and NO$_3^-$. These results suggest that the product could be applied in the environmental field, such as the removal of pollutants from wastewater.

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