Synthesis of hydrogrossular and hydroxysodalite from blast furnace slag using alkali fusion for fixation of HCl gas

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Abstract. Blast furnace (BF) slag, one of the by-products of iron- and steel-making plants, was converted into the product including hydrogrossular and hydroxysodalite using the alkali fusion method for HCl gas fixation. The slag was transformed into the alkali-fused slag with reactive phases via alkali fusion, after which the fused slag was added to distilled water with Al(OH)₃ to synthesize the product including a hydrogrossular by heating at 120 °C for 24 h. The product including hydrogrossular, hydroxysodalite and calcite can be synthesized with addition of Al(OH)₃, and could remove HCl gas at high temperature to fix Cl in the product. These results suggest that a novel product able to fix HCl gas at high temperature can be synthesized from BF slag via alkali fusion.

1. Introduction

Incineration is the most popular environmental techniques for the disposal of hazardous waste, and HCl gas is produced from the waste containing chlorine on incineration. HCl gas is one of the most problematic substances among acidic gases, and must be removed from flue gases before exhausting into the surrounding environment. HCl gas was mainly formed from the combustion of garbage and the incineration of hazardous wastes, due to the oxidative destruction of toxic halogenated organic wastes such as pesticides and various chlorinated hydrocarbons like polyvinyl chloride (PVC) or polychlorinated biphenyls (PCBs) from industrial uses on incineration [1].

Hydrogrossular is a new sorbent for HCl gas removal at high temperature. It is a hydration product in cement pastes [2-5] and can also be synthesized from by-products such as coal fly ash or molten slag under hydrothermal condition [6, 7]. The molecular formula of hydrogrossular is Ca₆Al₂(SiO₄)₃ₙₙ(OH)₆ₖₖ, where x = 0 - 3. The minerals with 0 < x < 1.5 and 1.5 < x < 3 are defined as hibschite [Ca₆Al₂(SiO₄)₃₋ₓ(OH)ₓ₋₆₋₆] and katoite [Ca₆Al₂(SiO₄)₁.₅(OH)₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆₋₆-
phases in the product with addition of Al content was investigated, and the fixation ability of each product for HCl gas at high temperature was examined.

2. Experimental

2.1. Blast furnace slag
The BF slag was water granulated slag collected from one of the steel companies in Japan. Before the experiment, the BF slag was milled under 250 μm. The chemical and mineralogical compositions of the raw slag were determined by X-ray fluorescence spectrometry (XRF) (XRF-1700, Shimadzu, Japan) and powder X-ray diffraction (XRD) (RINT-2500, Rigaku, Japan), respectively (Table 1, Figure 1). Raw slag was mainly composed of CaO (42.9%), SiO₂ (34.5%), Al₂O₃ (13.7%) and smaller contents of other oxides, such as MgO, Fe₂O₃ and SO₃, in the form of amorphous phase.

| Content (wt. %) | Raw slag | Product-1 | Product-2 | Product-3 | Product-4 | Product-5 |
|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| CaO            | 57.0     | 64.8      | 62.1      | 58.1      | 56.3      | 53.2      |
| SiO₂           | 25.8     | 19.5      | 18.7      | 18.3      | 18.2      | 18.3      |
| Al₂O₃          | 9.4      | 6.2       | 11.0      | 15.2      | 16.7      | 19.2      |
| MgO            | 2.6      | 1.0       | 1.3       | 1.2       | 1.3       | 1.2       |
| Fe₂O₃          | 0.8      | 1.6       | 1.6       | 1.5       | 1.5       | 1.3       |
| P₂O₅           | 0.5      | 0.7       | 0.6       | 0.5       | 0.5       | 0.5       |
| SO₃            | 1.6      | 0.4       | 0.5       | 1.0       | 1.0       | 1.2       |
| Cl             | 0.1      | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       |
| TiO₂           | 0.9      | 1.2       | 1.1       | 1.0       | 1.0       | 0.9       |
| MnO            | 0.7      | 1.0       | 0.9       | 0.9       | 0.8       | 0.8       |
| Na₂O           | -        | 2.5       | 1.2       | 1.4       | 1.8       | 2.6       |

Figure 1. XRD patterns of raw slag.
2.2. Synthesis
Raw slag (5 g) was mixed with NaOH powder (8 g), and milled to obtain a homogeneous mixture. This mixture was then heated in a nickel crucible at 600 °C for 6 h in an electric furnace. The resultant fused mixture was naturally cooled to room temperature and milled again to obtain the alkali-fused slag. 2.5 g of the fused slag was mixed with Al(OH)₃ powder (Wako) (0.125, 0.25, 0.375, 0.5 g), this mixture was added into distilled water (10 mL) in the pressure vessel (50 mL), and then set in an electric furnace at 120 °C for 24 h. After heating, the vessel was quenched with tap water, the solid was obtained by filtration, washed with distilled water, and dried at 60°C overnight to obtain the product. The phases of the product were analyzed using XRD.

2.3. HCl gas fixation
The HCl gas fixation experiment at high temperature using raw slag, lime (Wako, Japan) and the products was carried out using a vertical reactor, as shown in Figure 2. A silica tube (17 mm i.d., 1-m long) was used as the reactor, and its temperature was controlled by an electric furnace around the tube. The sample (0.3 g) was set in the reactor, and then N₂ gas was passed through the reactor at a rate of 1 L/min (for the volume measured at NTP) for N₂ substitution. The reactor was then heated to 800 °C (this temperature is typical for a waste incinerator) at 1 L/min of N₂ flowing through the reactor. After the temperature was reached to 800 °C, the HCl gas was fed into the reactor at 500 mL/min. An HCl concentration is 1000 ppmv in N₂ gas, which is similar to the average concentration in the exhaust gas of an incinerator in Japan. The exiting gas from the reactor was passed through distilled water (500 mL) with 0.1% NaOH solution (5 mL) by bubbling, which was sufficient for the whole HCl gas to be dissolved. The pH of the solution was measured with a pH meter (D-53, Horiba, Japan) to determine the amount of the HCl gas fixed by the sample. After pH of the solution reached to acidic (3 - 4), the HCl gas was stopped, N₂ gas was fed into the reactor, and the reactor naturally cooled to room temperature with N₂ flowing. The solid sample after HCl removal in the reactor was collected, the mineralogical phases of the product after the HCl removal were analyzed using XRD, and the Cl contents in the product before and after the HCl removal test were examined as follows. An aliquot (10 mg) of the sample was added to 0.4 M nitric acid solution (40 mL) in a centrifuge tube, and the tube was shaken with a reciprocal shaker (200 rpm) for 12 h. Then, the tube was centrifuged, and the Cl⁻ content in the supernatant was measured by ion meter (LAQUA, Horiba, Japan) in order to calculate the Cl⁻ content in the solid sample.

The Cl elution test for each solid sample after HCl removal experiments was carried out. An aliquot (10 mg) of the sample was added to distilled water (40 mL) in a tube, and the tube was shaken with a shaker for 12 h. Then, the tube was centrifuged, and the Cl⁻ content in the supernatant was measured by ion meter in order to calculate the soluble Cl⁻ content in the solid sample.

![Figure 2. Experimental apparatus for HCl gas fixation.](image-url)
3. Results and discussion

Table 1 shows the chemical compositions of the products. With increasing the addition of Al(OH)$_3$, the contents of Ca and Si in the product decrease, while those of Al and Na increase, due to the addition of Al(OH)$_3$ and NaOH. It is noted that the other contents are almost same.

Figure 3 shows the XRD patterns of the products. It is noted that the products synthesized from the fused slag with Al(OH)$_3$ at the additional ratio of Al(OH)$_3$ to the fused slag = 0, 0.05, 0.1, 0.15 and 0.2 g/g are represented as Product-1, Product-2, Product-3, Product-4 and Product-5, respectively. All products contain one of the hydrogrossular, katoite [Ca$_3$Al$_2$(SiO$_4$)$_{0.8}$(OH)$_{8.8}$], and calcite [CaCO$_3$]. Without addition of Al(OH)$_3$ to the fused slag, the mixture of katoite and calcite can be synthesized in Product-1. With addition of Al(OH)$_3$ to the fused slag, hydroxysodalite [Na$_8$Al$_6$Si$_6$O$_{24}$(OH)$_2$], one of the zeolite phases, appeared in the product, and Product-2, Product-3, Product-4 and Product-5 contained katoite, calcite and hydroxysodalite. It is noted that these three phases have the removal ability for HCl gas at high temperature.

![Figure 3: XRD patterns of the products.](image_url)

Figure 4 shows the pH of the solution with dissolving HCl gas after passing through raw slag, Ca(OH)$_2$ and the products. For blank and raw slag, the pH of the solution drastically decreased from 10 to 3-4 for 15 min, implying that the HCl gas was dissolved in the solution after passing through the reactor without removing HCl gas using raw slag. The pH remained almost constant for 40 min and then decreased when Ca(OH)$_2$ was used. By using the products, the pH of the solution withstands at least 20 min, then drastically decreased to 3-4. Therefore, the products can remove the HCl gas, but the amounts of the HCl removal are lower for the products than for Ca(OH)$_2$. It is noted that HCl removal behaviors of the product are almost same.
Figure 4. pH of the solution with dissolving HCl gas after passing through raw slag, Ca(OH)$_2$ and the product.

Figure 5. XRD patterns of the products after HCl removal test.

Figure 5 shows the XRD patterns of the products after HCl removal test. The presence of wadalite [Ca$_{12}$Al$_{10}$Si$_4$O$_{32}$Cl$_6$], sodalite [Na$_8$Al$_6$Si$_6$O$_{24}$Cl$_2$] and CaCl$_2$·2H$_2$O phase can be identified in the product after the test. CaCl$_2$·2H$_2$O was formed by absorbing moisture due to the highly hygroscopic nature of CaCl$_2$. The HCl gas is efficiently removed as wadalite, sodalite and CaCl$_2$ by katoite, hydroxysodalite and calcite at 800 °C followed by these equations:

\[
\begin{align*}
5\text{Ca}_3\text{Al}_2\text{(SiO}_4\text{)}_{0.8}\text{(OH)}_{0.8} + 12\text{HCl} & \rightarrow \text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6 + 3\text{CaCl}_2 + 28\text{H}_2\text{O} \quad (1) \\
\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{(OH}2) + 2\text{HCl} & \rightarrow \text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2 + 2\text{H}_2\text{O} \quad (2) \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad (3) \\
\text{CaO} + 2\text{HCl} & \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

Table 2 shows the Cl content in the product before and after HCl removal test. Before the HCl removal test, all products and Ca(OH)$_2$ contain little amounts of Cl (lower than 1.0 mg/g). After the removal test, the products contain 28–40 mg/g of Cl, which is 12–18 % of Cl content in Ca(OH)$_2$ after the test (219 mg/g).

| Product  | Cl content (mg/g) |
|----------|-------------------|
|          | Before test       | After test      |
| Product-1| 0.9               | 35.9            |
| Product-2| 0.8               | 39.8            |
| Product-3| 0.9               | 34.7            |
| Product-4| 0.8               | 28.1            |
| Product-5| 0.7               | 29.4            |
| Ca(OH)$_2$| 0.1             | 219.0           |

Table 3 shows the soluble Cl contents of the products and Ca(OH)$_2$. Before the HCl removal test, all products and Ca(OH)$_2$ contain little amounts of soluble Cl (lower than 1.0 mg/g). After the removal test,
the products contain 3.0 – 3.6 mg/g of soluble Cl, which is 1.3 – 1.6 % of soluble Cl content in Ca(OH)₂ after the test (219 mg/g).

Table 3. Soluble Cl content in the product before and after HCl removal test.

| Soluble Cl content (mg/g) | Product-1 | Product-2 | Product-3 | Product-4 | Product-5 | Ca(OH)₂ |
|---------------------------|-----------|-----------|-----------|-----------|-----------|---------|
| Before test               | 0.9       | 0.8       | 0.8       | 0.8       | 0.7       | 0.1     |
| After test                | 3.1       | 3.0       | 3.2       | 3.5       | 3.6       | 219.0   |

Figure 6 shows the elution percentage of Cl content from the products and Ca(OH)₂ after HCl removal test. Elution of Cl from the products indicates lower than 10 %, while that from Ca(OH)₂ is 100 %. Ca(OH)₂ shows a high HCl removal ability but Cl was included as soluble Cl after the removal, which is unfavorable for landfill disposal and cement production. The soluble Cl content in the product was very lower than that in Ca(OH)₂ after the HCl removal. These results indicate that the product including katoite and hydroxysodalite can remove HCl gas at high temperature and fix Cl in the product to use for landfill and cement production. Therefore, the product can be used as a scavenger for HCl gas treatment.

Figure 6. Elution percentage of Cl content from the products and Ca(OH)₂ after HCl removal test.

4. Conclusion
The chemical conversion of the BF slag to a scavenger including hydrogrossular and hydroxysodalite through alkali fusion was performed. The slag was converted into alkali-fused slag with reactive phases via alkali fusion, the fused slag was mixed with Al(OH)₃ powder to put into distilled water, and the product was synthesized by heating at 120 °C for 24 h. The product including katoite, hydroxysodalite and calcite was synthesized, and can remove HCl at high temperature and showed lower solubility of Cl after the HCl removal compared to lime [Ca(OH)₂]. These results suggest that the product can be applied for the HCl gas removal from a high-temperature effluent gas and be reclaimed or used for cement production after the HCl removal.

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