Introduction

Steel converter slag is produced in large quantities worldwide as a by-product in primary steel-making process; for example, approximately 90 kg of slag is produced per ton of steel\(^1\). In the EU alone, with a primary steel production of approximately 110 million tons, 10 million tons of slag is produced annually\(^2\). In Japan, approximately 98 million tons of crude steel is produced annually, thus generating approximately 13 million tons of steel converter slag as a by-product\(^3\). Steel slag is utilized in construction industry to replace cement; however, cement can be replaced only by 10–20% with steel slag because of the latter’s low hydration reactivity\(^4\). Converter slag is also used as an aggregate; however, volume stability problems owing to the presence of free lime are common\(^5\). Thus, the use of steel slag in these applications is limited, and a major portion of converter slag is disposed as a backfill material or in landfills. Therefore, exploring new uses of the slag has become increasingly important.

Hydrogarnet is known to be a major hydration product in solidified cement pastes\(^6-9\), and can also be synthesized by hydrothermal treatment of by-products, such as coal ash or molten slag\(^10,11\). Garnet minerals have a cubic structure with the general formula \(X_3Y_2(SiO_4)_3\). The \(X\) site is usually occupied by divalent cations \((Ca^{2+}, Mg^{2+}, and Fe^{2+})\) and the \(Y\) site is occupied by trivalent cations \((Al^{3+}, Fe^{3+}, and Cr^{3+})\) in an octahedral/tetrahedral framework, with \([SiO_4]^{4-}\) occupying the tetrahedral positions. The anhydrous end members of the \(Ca_3(Al, Fe)_2(SiO_4)_3\) series are grossular \((Ca_3Al_2(SiO_4)_3)\) and andradite \((Ca_3Fe_2(SiO_4)_3)\). Hydrogarnet \((Ca_3(Al, Fe)_2(SiO_4)_3(OH)_{4(3-y)}; 0 < y < 3)\) includes a group of minerals in which the \([SiO_4]^{4-}\) tetrahedral is partially or completely replaced by \(OH^-\). The Al-containing hydrogarnet includes hydrogrossular \((Ca_3Al_2(SiO_4)_3(OH)_{4(3-y)}; 0 < y < 3)\) with katoite \((Ca_3Al_2(OH)_{12})\) as the end member. The Fe-containing hydrogarnet is designated as hydroandradite \((Ca_3Fe_2(SiO_4)_3(OH)_{4(3-y)}; 0 < y < 3)\) and Fe-katoite \((Ca_3Fe_2(OH)_{12})\). The nomenclature of minerals in the hydrogarnet group is \(Ca_3(Al, Fe_{1-x})_2(SiO_4)_3(OH)_{4(3-y)}; 0 < x < 1; 0 < y < 3\).

Hydrogarnet is considered to be very useful in the fixation of hydrogen chloride (HCl) gas, which is generated from municipal solid waste.
combustors and industrial waste incinerators\textsuperscript{12}, at high temperatures. In recent years, significant attention has been paid to reducing the level of atmospheric pollution caused by HCl gas. Current techniques for removing HCl use calcium hydroxide (Ca(OH)\textsubscript{2}) and calcium carbonate (CaCO\textsubscript{3}) at low temperatures (below 300°C) because they are relatively simple, easy to operate, and have low capital costs\textsuperscript{13–15}. However, these techniques may evolve polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by “de novo” synthesis in municipal waste incineration process\textsuperscript{16}, and cause hot corrosion of the incinerator body. It was found that hydrogarnet could capture HCl gas above 400°C in a fixed bed reactor, and HCl removal at high temperatures leads us to expect the suppression of the downstream formation of hazardous by-products, such as PCDDs and PCDFs\textsuperscript{17}. Therefore, hydrogarnet may be considered a promising sorbent material of HCl, and applied in incinerators or combustors with minor modifications.

In our previous studies, blast furnace slag was converted into an Al-containing hydrogarnet using alkali fusion, and it was confirmed that this material could fix HCl gas at 800°C\textsuperscript{18}. Blast furnace slag is mainly composed of Ca, Si, and Al, while steel converter slag primarily contains Ca, Fe, and Si. It is possible to convert steel converter slag into a Fe-containing hydrogarnet, using alkali fusion, which can then be used to fix HCl gas at high temperatures. However, little information is available on the chemical conversion of steel converter slag via alkali fusion and the removal ability of Fe-containing hydrogarnet for HCl gas at high temperatures.

In this study, a hydrogarnet containing iron was synthesized from steel converter slag using alkali fusion, and the ability of this product to remove HCl gas at a high temperature (800°C) was examined for its potential applications in effluent gas treatment.

2. Experimental

2.1 Steel converter slag

The steel converter slag used in this study was received from a steel-making plant in Japan. The converter slag was ground in a mill and sieved to a particle size of less than 1 mm. The chemical and mineralogical compositions of the raw slag were determined by X-ray fluorescence spectrometry (XRF; XRF-1700, Shimadzu, Japan) and X-ray diffraction (XRD; RINT-2500, Rigaku, Japan), respectively (Table 1 and Fig. 1). The raw slag was mainly composed of CaO (49.3%), Fe\textsubscript{2}O\textsubscript{3} (20.6%), and SiO\textsubscript{2} (12.8%), found as calcite (CaCO\textsubscript{3}), magnetite (Fe\textsubscript{3}O\textsubscript{4}), and quartz (SiO\textsubscript{2}), respectively. Other oxides such as Al\textsubscript{2}O\textsubscript{3}, MgO, MnO, P\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}, SrO, Cr\textsubscript{2}O\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, and Na\textsubscript{2}O were also present in smaller amounts.

\begin{table}
\centering
\caption{Chemical compositions of raw slag, precursor, and the product}
\begin{tabular}{|c|c|c|}
\hline
 & Raw slag & Precursor & Product \\
\hline
CaO & 49.3 & 47.0 & 48.1 \\
Fe\textsubscript{2}O\textsubscript{3} & 20.6 & 21.4 & 20.0 \\
SiO\textsubscript{2} & 12.8 & 13.1 & 13.1 \\
Al\textsubscript{2}O\textsubscript{3} & 2.4 & 2.5 & 2.6 \\
MgO & 8.8 & 8.7 & 8.8 \\
MnO & 2.6 & 3.0 & 3.0 \\
P\textsubscript{2}O\textsubscript{5} & 1.7 & 1.4 & 1.7 \\
TiO\textsubscript{2} & 0.5 & 0.5 & 0.6 \\
SrO & 0.1 & 0.1 & 0.1 \\
Cr\textsubscript{2}O\textsubscript{3} & 0.1 & 0.1 & 0.1 \\
V\textsubscript{2}O\textsubscript{5} & 0.1 & 0.1 & 0.1 \\
Na\textsubscript{2}O & 0.6 & 2.0 & 1.9 \\
\hline
\end{tabular}
\end{table}

Figure 1. XRD patterns of (a) raw slag, (b) fused slag, (c) precursor, and (d) the product.
was cooled to room temperature and ground again to obtain an alkali-fused slag. In the agitation step, this fused slag was added to 200 mL of distilled water in a 500 mL polymethylpentene bottle and stirred with a magnetic stirrer at ambient temperature for 24 h to prepare a precursor. During the crystallization step, the stirred solution was heated in a water bath at 80°C, while it was being stirred. During the stirring, a part of the slurry (2 mL) was collected, the solid product was filtered, washed with distilled water, and dried in an oven at 60°C overnight to obtain the hydrogarnet product, and the filtrate solution at regular intervals.

The product phases and morphologies were analyzed by XRD and scanning electron microscopy (SEM) (Hitachi, S-4500), respectively. The concentrations of Si, Fe, and Ca in the filtrate were determined using inductively-coupled plasma (ICP) (Seiko instruments SPS3000). The change in the amounts of mineralogical phases in the product during the crystallization process was represented using the intensity of the major XRD peaks in the product at specific diffraction faces, namely hydrogarnet (4 0 0), hydrocalumite (0 0 3), and portlandite (0 0 1).

### 2.3 HCl removal

The experiments, in which HCl gas was fixed using the product obtained at 800°C (temperature typical for waste incinerators) were performed in a vertical reactor, as shown schematically in Fig. 2. The reactor was a fused silica tube (17-mm inner diameter and 1-m long). The reactor was surrounded by an electric furnace to control its temperature. A sample of the product (0.1 g) was placed in the reactor, and N₂ was passed through the reactor at a rate of 1 L/min (the volume being measured at NTP) to replace the atmosphere in the reactor. The reactor was then heated to 800°C with N₂ flow continuing through the reactor at 1 L/min. Once the required temperature was reached, the reaction gas (1000-ppmv HCl in N₂) was fed at 500 mL/min into the fixed-bed reactor. This concentration of 1000 ppmv is representative of the average HCl concentration in incinerator exhaust gas in Japan. The gas exiting the reactor was detected by Fourier transform infrared (FT-IR) spectroscopy to monitor its HCl concentration, after which, it was passed through distilled water in scrubbing bottles. The difference in the HCl concentration passing through the reactor with and without the sample was determined.

The HCl feed gas was stopped at the end of the experiment, N₂ was fed into the reactor until the reactor cooled to room temperature, and then the solid sample in the reactor was collected. The Cl elution test for all the product samples that were used in the HCl removal experiments was carried out. An aliquot (0.02 g) of each of the samples was added to distilled water (10 mL) in a 50-mL centrifuge tube and the tube was shaken using a reciprocal shaker for 30 min. The tube was then centrifuged for 10 min, and the Cl concentration in the supernatant was determined (LAQUA, Horiba, Japan) to calculate the soluble Cl⁻ content of the solid sample. The Cl content in the samples were also measured by the same elution test procedure using a 1 M HNO₃ solution.

### 3. Results and Discussion

#### 3.1 Synthesis

Figure 1 shows the XRD patterns of the raw slag, fused slag, precursor, and the Fe-hydrogarnet product. It is to be noted that the product was synthesized for 6 h crystallization time. The slag was composed of calcite, quartz, and magnetite crystalline phases (Fig. 1(a)). After the alkali fusion, most of the crystalline phases were converted to lime and soluble sodium salts (Fig. 1(b)), and the precursors, including portlandite and hydrocalumite, were formed after the aging process (Fig. 1(c)). Finally, by heating at 80°C the crystallized hydrogarnet was formed; thus, the product that included the hydrogarnet and portlandite crystalline phases was synthesized (Fig. 1(d)).

Figure 3 shows the SEM micrographs of the raw slag, fused slag, precursor, and the product. Although the slag was composed of rock-like agglomerate particles (Fig. 3(a)), the fused slag consisted of particles with a melted surface, resulting from the formation of sodium salts by alkali fusion (Fig. 3(b)). After the aging process, aggregates of thin regular hexagonal crystals, such as a hydrocalumite-type compound, were confirmed to be present in the precursor (Fig. 3(c)). Finally, octahedral crystals of hydrogarnet were observed.
Conversion of Steel Converter Slag into HCl Gas Scavenger Using Alkali Fusion

Table 1 summarizes the chemical compositions of the raw slag, fused slag, precursor, and the hydrogarnet product. The slag mainly contained CaO (49.3%), Fe₂O₃ (20.6%), SiO₂ (12.8%), and some other minor elements. The precursor and the product had chemical compositions that are almost identical to that of the raw material, implying that most elements in the slag were converted to new phases in the product. A mixture of slag (20 g) and NaOH powder (32 g) was converted to fused slag (50 g) to form the precursor (23.5 g), and to synthesize the product containing hydrogarnet (22.4 g).

Figure 4 shows the XRD patterns of the product during the crystallization step. After the stirring prior to the heating for crystallization (0 h), hydrocalumite and portlandite appeared in the product. After crystallization heating for 0.5 h, hydrogarnet appeared; with continued crystallization heating, the intensities of the hydrogarnet peaks increased, while those of the hydrocalumite peaks decreased.

The reaction was monitored by analyzing the Ca, Si, and Fe contents in the solution, and the change in the intensities of the hydrogarnet, hydrocalumite, and portlandite phases in the solid during the crystallization step, as shown in Fig. 5. In the initial crystallization stage, the Si, Fe, and Ca contents in the solution were 1380, 10, and 32 mg/L, respectively. The contents of Ca and Fe were lower than 100 mg/L during the crystallization because of the precipitation of the crystalline phases, such as hydrocalumite and portlandite as well as amorphous phases formed by the reaction among Ca, Si, Fe, and other elements (Mg, Al, Fe, Na, etc.). With increasing crystallization time, the Si concentration decreased within 30 min, then increased, and finally, reached a steady state after 1 h; on the other hand, the Ca concentrations of Ca and Fe were almost constant during the crystallization. The hydrogarnet peak intensity increased in the early stage and remained almost constant after 1 h of crystallization reaction, while the intensities of the hydrocalumite peaks decreased within 1 h. The intensity of portlandite was almost constant during the crystallization reaction. Changes in the Si, Fe, and Ca concentrations in the solution were correlated with the formation of the hydrogarnet crystals from hydrocalumite. This means that hydrocalumite reacted with Si in the solution to be converted into hydrogarnet crystals within 1 h, after which the excess Si in the solid was released into the solution.
Thus, Fe-hydrogarnet could be synthesized from steel converter slag at 80°C in 1 h via alkali fusion at 600°C. After the synthesis, the waste solution contained Fe, Si, and Ca (10, 1500, and 40 mg/L, respectively), with a high alkalinity. It may be used as a flocculant or coagulation aid for acid turbid water treatment.

### 3.2 HCl removal

Figure 6 shows the results for the removal of HCl gas using the raw slag, lime (Ca(OH)₂), and the product. With the raw slag, the HCl gas concentration after passing through the reactor drastically increased within 5 min and was almost constant with no HCl removal taking place. With slag and lime, the behavior of the HCl gas concentration was very similar. It rapidly increased within 30 min, and then gradually increased to 1000 ppmv for 120 min. Furthermore, the HCl gas concentration after passing through lime was always lower than that through slag because of the calcite content in the slag. Lastly, when the hydrogarnet product was used, the behavior of the HCl gas concentration was different from that observed with lime and slag. The HCl concentration gradually increased for 120 min because of HCl removal by hydrogarnet and portlandite. The HCl removal amounts of slag, lime, and the product were 443, 675, and 393 mg/g, respectively.

Table 2 shows the soluble Cl contents of the raw slag, product, and lime. Lime and slag showed high HCl removal ability; however, Cl was included as soluble Cl after the removal, which is unfavorable for landfill disposal and cement production. The soluble Cl content in the hydrogarnet product was lower than that in slag and lime by 50% after the HCl removal. The soluble Cl content in the product might depend on the portlandite phase. Therefore, the Cl fixation percentages of slag, lime, and the product were 52.2%, 65.6%, and 72.0%, respectively.

These results indicate that the product, containing hydrogarnet and portlandite, can remove HCl gas at high temperatures and fix Cl, and hence, can be used as a scavenger in HCl gas treatment.
4. Conclusions

A product, containing hydrogarnet with HCl removal ability, was synthesized from steel converter slag using alkali fusion. The slag could be converted into a precursor with reactive phases through alkali fusion and stirring in distilled water; subsequently, a product, containing hydrogarnet and portlandite, was synthesized by heating the precursor at 80°C for more than 1 h. The obtained product had HCl removal ability at high temperatures; furthermore, the fixation of Cl by the product was higher than that with raw slag and lime. These results suggest that the product can be applied for HCl gas removal in high-temperature effluent gas treatment.

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