Evaluation of Hydrothermal Treatment to Immobilize Hexavalent Chromium in Wastewater Using Granulated Blast Furnace Slag

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The immobilization of hexavalent chromium in wastewater using blast furnace slag as the immobilizing agent was investigated by using hydrothermal treatment. The results showed that immobilization was not attained without a hydrothermal treatment, while hexavalent chromium in solution could be immobilized through the process of hydrothermal treatment with the blast furnace slag at 250°C for 18 h. In particular, the reducing condition was attributed to the presence of sulfur in the blast furnace slag, which indicated that the sulfur could play a key role in the immobilization of hexavalent chromium in the present study. In addition, the leaching test was carried out to evaluate the level of immobilization of hexavalent chromium in the products after the hydrothermal treatment, and it was found that the degree of immobilization was very high. Based on the results obtained in the present study, the immobilization mechanism of the hydrothermal treatment of blast furnace slag in wastewater was elucidated.

KEY WORDS: hydrothermal treatment; blast furnace slag; immobilization; hexavalent chromium; wastewater; environmental control.

1. Introduction

Rapid industrialization and increase in the population are responsible for the inclusion of heavy metals in the environment. Their presence in the environment is a major concern because of their toxicity and threat to human life and environment. Therefore, the immobilization of heavy metals in the environment, for example, wastewater and waste disposal, is an important issue for safeguarding public health.

Chromium is widely used in alloying element, stainless steelmaking and electroplating. However, hexavalent chromium (Cr(VI)) is of particular concern because of its toxicity. Therefore, it has for long been an environmental concern, and the effluent standard of Cr(VI) is currently below 0.05 mg L\(^{-1}\) in Japan. Thus, the immobilization of Cr(VI) in wastewater before discharging the wastewater into the environment is necessary.

Hydrothermal treatments play an important role in the immobilization of heavy metals. They can be used not only for the synthesis and production of functional ceramics but also in the immobilization process for forming a hydrothermal phase and incorporating the heavy metals into that phase. Ida investigated the effect of hydrothermal treatment on the immobilization of heavy metals in soil. When the waste soil which contains heavy metals was hydrothermally treated, heavy metals were fixed in the tobermorite crystals. Inoue and Suito introduced hydrothermal treatment to fluorine immobilization in hot metal pretreatment slags, fluorine ions were immobilized during this treatment by the formation of hydrate phases.

A blast furnace (BF) slag is a by-product in the iron-making process, and it is estimated that 25 million tons of slag is generated annually in Japan. Although it has been widely used for cement and roadbeds, new recycling processes for producing value-added materials are demanded. Therefore, the authors have been investigating the hydrothermal treatment of BF slag, it was reported that calcium silicate hydrate (C-S-H) and tobermorite (Ca\(_5\)Si\(_6\)O\(_{16}\)(OH)\(_2\)·4H\(_2\)O) were formed as the main phases in a previous article.

In the present study, the possibility of using the BF slag to immobilize Cr(VI) in wastewater by using hydrothermal treatment as well as its immobilization mechanism has been investigated.

2. Experimental

A water quenched BF slag and synthesized slags were used in the experiments. Their composition is listed in Table 1. The synthesized slags were prepared from reagent grade chemicals such as SiO\(_2\), Al\(_2\)O\(_3\), MgO and CaO calcined from CaCO\(_3\). They were well mixed and premelted at 1,600°C in a platinum crucible in air and quenched by
being spread on an iron plate. Since BF slag generally contains approximately 1–1.5% sulfur as sulfide (S\(^2\)-), CaS was added to some synthesized slags in order to examine the effect of sulfur on the immobilization of Cr(VI). All the samples are almost glassy before the treatment.

The synthesized wastewater containing Cr(VI) was prepared by dissolving a certain amount of K\(_2\)Cr\(_2\)O\(_7\) (purity: 99.99 mass%).

The hydrothermal treatment was carried out in an autoclave as shown in Fig. 1. The details are described in the previous article.\(^9\) The powdered slag sample (1 g, \(\leq 125 \mu m\)) and the synthetic wastewater (10 mL) were placed in the autoclave (25 mL). The experimental temperature was varied from 150 to 250°C under saturated water steam pressure and the corresponding pressure range was approximately 5 to 40 atm. The experimental duration for each temperature was varied from 1 to 24 h. Experiments without hydrothermal treatment were also conducted to confirm the effect of hydrothermal treatment as follows. The sample was enclosed in polyethylene (PE) bottles in which the required amount of synthesized wastewater was present. A PE bottle containing the sample was capped and placed in a water bath (25 and 80°C), this was followed by the treatment for 1–24 h.

After the treatments, the autoclave and the bottle were cooled to room temperature, then the products were taken out from the solution and washed using distilled water and dried at 80°C before the analysis. The pH of the solution was measured by a pH-ion meter (HORIBA, F-23). After drying, the products were characterized by powder X-ray diffraction (XRD). Scanning electron microscopy with energy-dispersion analysis (SEM-EDX) was performed in order to characterize and observe the morphologies of these products. Sulfur content of sample was analyzed by LECO analyzer (CS-400). The Cr(VI) content in solutions was determined by inductively coupled plasma emission spectrometry (ICP-AES) with and the lower limit of Cr(VI) analysis of 0.002 mg L\(^{-1}\). In addition, the leaching test was carried out at room temperature with various pH ranges followed by the Japanese Environmental Quality Standards.\(^10\)

3. Results and Discussion

3.1. Immobilization of Cr(VI) by Hydrothermal Treatment

The influence of hydrothermal treatment on the immobilization of Cr(VI) was investigated using a BF slag as shown in Table 1, and the experiments were carried out with or without hydrothermal conditions. The hydrothermal treatment was carried out at 150 and 250°C and other treatments were carried out at room temperature and 80°C. The experimental temperature of hydrothermal treatment was selected so as to support the occurrence of a hydrothermal reaction since it was founded that the hydrothermal reaction involving BF slag occurred at 250°C but not at 150°C in the previous study.\(^9\) The initial Cr(VI) content was 1 000 mg L\(^{-1}\) (initial pH = 3.4), and the holding time was 24 h. As shown in Fig. 2, immobilization of Cr(VI) not observed at 25°C and 80°C without the hydrothermal conditions. However, the Cr(VI) content in wastewater for BF slag with hydrothermal treatment at 250°C decreased below the analytical detection limit of 0.002 mg L\(^{-1}\) within 24 h. This result confirmed that the hydrothermal treatment with BF slag is an effective process for immobilizing Cr(VI) in wastewater.

The effect of holding time on the immobilization of Cr(VI) in wastewater was investigated. Figure 3 shows the change in the Cr(VI) concentration of wastewater with
holding time when the BF slag is used at each temperature. The Cr(VI) content in wastewater at 150°C slightly decreased at the beginning of the treatment, which may be due to a small amount of the sulfur eluted from BF slag, reducing Cr(VI) slightly. This can be reducing from the fact that sulfur content showed a slight decline (1.50 → 1.33 mass%) during 18 h. However, the immobilization reaction was not completed, and the phase of the BF slag did not change remaining glassy at 150°C.

When the wastewater was hydrothermally treated at 250°C, immobilization was completely achieved after a holding period of 18 h. In the previous study,9) it was reported that the hydrothermal reaction of the BF slag might occur above 200°C. Accordingly, it becomes evident that the immobilization of Cr(VI) in wastewater results from the hydrothermal reaction of the BF slag.

The change of pH value in wastewater during hydrothermal treatment at 250°C is summarized in Fig. 4. The pH value was increased up to 12 with an increase in the holding time. This may be due to the reduction caused by the dissolution of sulfur from the BF slag in the wastewater as mentioned in the result at 150°C. Figure 5 shows the XRD patterns of the products obtained by the hydrothermal treatment of the BF slag in wastewater. A low intensity peak was observed near 2θ=29.9° among the halloysite in Fig. 5(b) at 250°C after 12 h of hydrothermal treatment, and this peak indicated the formation of tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O) in the glassy matrix. Further, the formation of tobermorite and uvarovite (Ca₃Cr₂(SiO₄)₃) phases was observed at 250°C after the treatment for 18 h. In addition, the slight precipitation of Chromium(III) hydroxide (Cr(OH)₃) in solution was observed.

Based on the obtained results of pH value and XRD patterns, Fig. 4 can be divided into three zones: (a) the rapid increase of pH value and progressing of reduction reaction, (b) the beginning of hydrothermal reaction, (c) the formation of hydrothermal products. The increasing of pH value at zone (a) may be by dissolution of sulfur from the BF slag. It was confirmed the content of sulfur in BF slag by LECO and sulfur content showed a dramatic decline after 6 h (initial 1.50→0.4 mass%). After zone (a), the wastewater can become the alkaline condition, its condition may be accelerated the hydrothermal reaction of BF slag.9) However, the Cr(VI) content did not decrease as a function of the holding time in the range of 6–12 h and the XRD patterns did not show significant change in Fig. 5(b). It can be expected that hydrothermal reaction was produced by the dissolution and deposition of materials through a saturated aqueous solution. In case of zone (b), reaction time was required for wastewater to be saturated, namely the incubation period in the progress of this immobilization process. Finally, at zone (c), hydrothermal reaction of BF slag was activated, and Cr ions were incorporated in the hydrothermal phase as shown in Fig. 5(c). Ida et al.12) also reported that the hydrothermal reaction immobilized the heavy metal by the formation of a hydrothermal phase. In order to clearly the effect of sulfur in this study, hydrothermal treatments by the synthesized slags with and without the sulfur were performed. Slags A and B were hydrothermally treated in the wastewater at 250°C. Figure 6 shows the change in the concentration of Cr(VI) in the wastewater versus the holding time. In the case of slag A without sul-
Fur, immobilization was not observed and the pH of the solution was found to be 4.5 after 18 h, showing a slight increase from the initial pH 3.4. Because slag A does not contain sulfur as reducing agent, the Cr(VI) in the wastewater has not been reduced to Cr(III). In addition, hydrothermal reaction involving the BF slag did not occur under acidic conditions. However, immobilization was completely achieved in the case of slag B. The pH also changed during the reaction process, as shown in Fig. 4. It was evident that sulfur in the BF slag plays a key role in the immobilization of Cr(VI) by hydrothermal treatment.

The results for SEM observation of the BF slag after hydrothermal treatment are shown in Fig. 7. Since it was difficult to observe the cross section of powdered samples, BF slag granules with a diameter of 3–5 mm were observed. The evidence of hydrothermal reaction was not identified after 12 h, but the hydrothermal reaction layer was observed after 18 h, as shown in Fig. 7(c). Figure 7(d) shows the EDX analysis results of reaction layer (I) of Fig. 7(c). Considerable Cr was detected in the hydrothermal reaction layer. Hence, Cr ions were considered to be incorporated in the hydrothermal phase when the immobilization reaction was completed, which can be confirmed by XRD analysis in Fig. 5(c).

3.2. The Mechanism of Immobilization of Cr(VI) in Wastewater with BF Slag during Hydrothermal Treatment

Based on the results obtained in this study, the mechanism of immobilization of Cr(VI) in wastewater with the BF slag during the hydrothermal treatment is discussed. Figure 8 shows the schematic diagram of the immobilization reaction in the present study.

Cr(VI) ions are known to exist as dichromates (Cr$_2$O$_7^{2-}$) in the pH range 0.8–6.4 and chromates (CrO$_4^{2-}$) is existed over the pH range 6.4.$^{[13]}$ In this study, the initial pH was 3.4 and Cr(VI) was considered to exist as dichromate ions (Cr$_2$O$_7^{2-}$).

First, it was presumed that sulfur in the slag dissolved in the wastewater as sulfide ions (S$^{2-}$), where it reacted with (Cr$_2$O$_7^{2-}$) reducing Cr(VI) to Cr(III), as shown by Eq. (1).

$$4\text{Cr}_2\text{O}_7^{2-} + 3\text{S}_2\text{O}_3^{2-} + 16\text{H}_2\text{O} \rightarrow 8\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 32\text{OH}^- \tag{1}$$

It is clear from Eq. (1), pH value of wastewater increased with the reduction of Cr(VI) to Cr(III). After the of pH value increased up to 6.4, reduction of Cr(VI) to Cr(III) was considered to be by Eq. (2).

$$8\text{Cr}_2\text{O}_7^{2-} + 3\text{S}_2\text{O}_3^{2-} + 20\text{H}_2\text{O} \rightarrow 8\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 40\text{OH}^- \tag{2}$$

When the Eqs. (1) and (2) proceed, the increase in pH value accelerate the hydrothermal reaction of BF slag as shown in Fig. 8(c). Finally, as shown in Fig. 8(d), hydrothermal reaction phase such as tobermorite and uvatovite, which incorporated Cr ions, were formed as stable phases. In addition, less-soluble Cr(III) precipitated in the solution as Cr(OH)$_3$.

3.3. Leaching Test

To evaluate stability of slag in the environment after the hydrothermal treatment, the leaching test was carried out.
Two kinds of sample were selected for tested in Fig. 4; the one is immobilization was completely finished after a holding period of 18 h and the other is was not completely finished after 12 h with hydrothermal treatment.

The total Cr content in the solution is plotted against the shaking time in Fig. 9. Figure 9(a) shows that the total Cr content in the solution rapidly increases with the shaking time at pH 6.9. This might be due to the incorporate immobilization of Cr into the hydrothermal phase. This can be explained by the fact that hydrothermal phase were not detected by XRD as described in Sec. 3.1. In contrast, when immobilization was completed by using hydrothermal treatment, the total Cr content was almost zero at various shaking times and pH ranges, as shown in Fig. 9(b). In general, the dissolution behavior of an element into an aqueous solution depends on the pH value. However, the present results in which the Cr content of the solution is constant below the analytical limit with various pH ranges suggest that Cr can be strongly stabilized in the product after the hydrothermal treatment. Accordingly, BF slag can be successfully used as an immobilizing agent for Cr(VI) ions in wastewater by performing hydrothermal treatment. In addition, since, the environmental stability of hydrothermal product with immobilized Cr(VI) is high, the BF slag can be used as a raw material for other products especially after the immobilization.

4. Conclusions

The immobilization process of hexavalent chromium in wastewater using a granulated BF slag and hydrothermal treatment was investigated. The results obtained are summarized below.

(1) The immobilization of Cr(VI) in wastewater does not occur without hydrothermal treatment, while the hydrothermal reaction involving the BF slag is an effective process for the immobilization of Cr(VI) in wastewater.

(2) The immobilization of Cr(VI) was observed only, when sulfur was contained in the slag. This is considered to be due to the reactions:

$$4Cr_2O_7^{2-} + 3S^{2-} + 16H_2O \rightarrow 8Cr^{3+} + 3SO_4^{2-} + 32OH^- \text{ (pH < 6.4)}$$

$$8Cr_2O_4^{2-} + 3S^{2-} + 20H_2O \rightarrow 8Cr^{3+} + 3SO_4^{2-} + 4OH^- \text{ (pH > 6.4)}$$

(3) Tobermorite and uvarovite were confirmed to be the major phases after the hydrothermal treatment in wastewater containing Cr(VI).

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REFERENCES