Removal of Toxic Anions in Aqueous Solution by Anion Exchanger Synthesized from Steelmaking Slag

Norihiro MURAYAMA¹*, Tomoaki TAKAGI¹, Takashi TSUDA¹, Kai MORIYAMA¹, Junji SHIBATA¹ and Etsuro UDAGAWA²

¹Department of Chemical, Energy and Environmental Engineering, Kansai University, Japan
²Research Laboratories, JFE Mineral Co. Ltd., Japan

Abstract
Layered double hydroxides (LDHs) were synthesized by a co-precipitation method using steelmaking slag as a raw material. The adsorption of toxic anions including As(III), B, Cr(VI) and Se(IV) in aqueous solution was investigated in order to clarify the removal property of anionic species by the obtained products.

The order of removal for four anionic species with the steelmaking slag-derived LDHs (slag-LDHs) is as follows; Se(IV) > Cr(VI) > As(III) > B in the low equilibrium concentration below 10 mg/dm³. The order implies that the valency of anionic species is mainly related to the anion adsorption order in the low concentration, that is, an anion with larger valency is easily captured in the LDHs structure. On the other hand, the saturated adsorption amount is considered to be the following order; As(III) > Se(IV) > Cr(VI) > B as a standard of mass. No remarkable difference in the crystalline materials is found before and after the As(III) adsorption operation. It is found that the steelmaking slag-derived LDHs are applicable as an anion removal agent for the dilute aqueous solution containing anionic species.

Key words: Steelmaking slag, Layered double hydroxide, Anion exchanger, Dilute solution

1. Introduction
Significant amounts of mineral wastes such as ash, slag, dross, dust and tailing are generated all over the world. Steelmaking slag and blast furnace slag are major byproducts originating from iron manufacturing and processing¹. It has been reported that the global production of slag was estimated to be in the range of 240–290 million tons per year. In Japan, about 38 million tons of steelmaking slag are also generated annually from a steel-manufacturing process²–⁴.

More recently, there is a strong interest in synthesizing various ion exchangers or adsorbents to recover valuable materials or to remove harmful materials. Layered double hydroxides (abbreviated as LDHs hereafter) are known as an antacid and an anion exchanger⁵,⁶. For example, they can be applied to the removal agent for toxic anionic species such as As, B, Cr and Se in aqueous solution⁷,⁸. The LDHs are classified as a metal complex hydroxide composed of divalent and trivalent metal ions, exchangeable anions and water, respectively. For the purpose of cheaper LDHs production and more effective recycling of steelmaking slag, the LDHs synthesis using steelmaking slag as a raw material has been investigated⁵,⁷–⁹.

The authors⁷,⁹ reported the possibility of steelmaking slag-derived LDHs (abbreviated as slag-LDHs) including the effective LDHs preparation method from steelmaking slag and the fundamental removal ability of As, B, Cr and Se at 20 mg/dm³ of aqueous solution. However, the quantitative evaluation for the anion removal ability of slag-LDHs and its removal mechanism have not been investigated adequately. Therefore, detailed experimental data and consideration for the slag-LDHs are desired, from the viewpoint of practical use in the field of environmental purification like
a waste water treatment for toxic anionic species. In this study, two kinds of slag-LDHs were synthesized by a co-precipitation method using steelmaking slag. The removal tests of As(III), B, Cr(VI) and Se(IV) in aqueous solution using the slag-LDHs were carried out under various experimental conditions. The adsorption isotherms of toxic anions were investigated, to clarify the removal property of slag-LDHs and to find the possibility of application of slag-LDHs to the toxic anion removal in dilute solution.

2. Experimental

The slag-LDHs (anion removal agent) used in this study were similar to the samples reported in our previous papers7,9. The details of original steelmaking slag and the synthesis method of slag-LDHs shown in the above papers are summarized below.

Two kinds of slag-LDHs were used in the anion removal tests mentioned later. These are also two kinds of physically-treated steelmaking slag (“~2 mm slag” and “~0.15 mm slag”) as a raw material before LDHs synthesis. The original steelmaking slag before getting the ~2 mm slag and ~0.15 mm slag are entirely the same, but the difference between them is only physical treatment method to the original slag. The ~2 mm slag indicates the powder sample grounded to be less than 2 mm. Therefore, the chemical composition of ~2 mm slag is essentially identical to the original slag. On the other hand, the ~0.15 mm slag is the fine parts classified with a sieve of ~0.15 mm screen mesh from the original slag. As a result, the chemical composition of ~0.15 mm slag is found to be different from the original slag7,9.

The slag-LDHs syntheses were conducted by a co-precipitation method7,9 shown below. The ~2 mm slag or ~0.15 mm slag of 12.5 g was added to 500 cm³ of 1.0 mol/dm³ HCl, and then the slag was leached for 24 h using a magnetic stirrer. The leachate was filtrated to remove the leaching residue. The resulting slag leachate of 400 cm³ was dropped at the flow rate of 7 cm³/min to 200 cm³ by a co-precipitation method7,9 shown below. The resulting precipitate was washed with water, and then it was dried for 24 h at 343 K.

Crystalline substances in the reaction products were identified by an x-ray diffraction analysis (XRD, RINT-TTR III, Rigaku Co., Ltd Japan). Surface morphology of the reaction products was observed by using a field emission type scanning electron microscope (FE-SEM, S-4800, HITACHI Co., Ltd Japan).

The slag-LDHs were used as a starting material of anion removal tests. The removal tests were carried out by contacting the slag-LDHs with the single component solution containing As(III), B, Cr(VI) and Se(IV) at various initial concentrations and solid-liquid ratios. These solutions were prepared by diluting the standard solution of As, B, Cr and Se (Wako Pure Chemical Industries Co., Ltd Japan), respectively. Initial pH before the removal operation was set to be 10. The solution was agitated continuously with a vertical shaker (TAITEC Co., Ltd., SR-2DW). After 2 h of shaking operation the solution was filtered, and the concentration of the remaining As(III), B, Cr(VI) and Se(IV) was analyzed using an inductively coupled plasma atomic emission spectrometer (ICPS-7000 Ver.2, Shimadzu Co. Ltd., Japan).

3. Results and Discussion

3.1 Property of slag-LDHs

Table 1 shows the chemical composition of slag-LDHs. The percentages of each metal are calculated according to the metal concentrations in the leachate obtained by dissolving the slag-LDHs with 2.0 mol/dm³ HNO₃. The main metal component is found to be Mg, Al and Si in both slag-LDHs. The Fe in the ~2 mm slag-LDHs shows high content (17.5%), and the existence of Fe can contribute to the removal ability of slag-LDHs remarkably7,9. On the other hand, the Ca content is about 4% in both slag-LDHs. The detected other metals are mainly caused by a trace amount of Ti and Mn. It is also clarified that the chemical compositions of both slag-LDHs are almost the same to the previous sample synthesized under the similar condition7,9 and that they show well reproducibility, though a slight difference in chemical composition is observed due to the sampling error of slag.

| Sample           | Content [mass%] |
|------------------|-----------------|
|                  | Mg  | Ca  | Al  | Si  | Fe  | Others |
| ~0.15 mm slag-LDHs | 38.7 | 3.5 | 33.9 | 21.5 | 1.1 | 1.3    |
| ~2 mm slag-LDHs   | 36.1 | 4.3 | 24.5 | 15.0 | 17.5| 2.6    |
Figures 1 and 2 show the XRD patterns and the SEM photographs of slag-LDHs. The peak pattern of Mg-Al LDH (Magnesium Aluminum Hydroxide Hydrate, Mg₆Al₂(OH)₁₈·4.₅H₂O) is observed in both reaction products synthesized from steel-making slag. A little higher background in the XRD pattern of –2 mm slag-LDHs than that of –0.15 mm slag-LDHs is recognized, suggesting that the crystallinity of slag-LDHs synthesized from –2 mm slag is a little lower or that amorphous metal hydroxide and amorphous silica are formed simultaneously. Therefore, it is considered that the reaction products are mainly composed of the mixture of Mg-Al LDH, metal hydroxide and amorphous silica. As shown in Figure 2(a) and (b), about 20 μm of particles are confirmed in the SEM photographs, implying that fine LDH crystals are coagulated.

3.2 Adsorption isotherm of toxic anionic species with slag-LDHs

The removal tests of As(III), B, Cr(VI) and Se(IV) in aqueous solution were carried out using two kinds of slag-LDHs. Figure 3 shows the adsorption isotherm of various toxic anions with –0.15 mm slag-LDHs. Though it is not shown in the figure, the equilibrium pHs after adsorption are in the range of 8 to 10, suggesting that the dominant anionic species of As(III), B, Cr(VI) and Se(IV) in this pH range are considered to be AsO₄²⁻, HSeO₃⁻, B(OH)₄⁻, CrO₄²⁻ and SeO₃²⁻ by the simple calculation using pKa values. In case of lower equilibrium concentration below 10 mg/dm³ (Figure 3(a)), the order of removal amount is as follows; Se(IV) > Cr(VI) > As(III) > B. Rapid increase in the removal amounts of Se(IV) and Cr(VI) occurs at almost 0 mg/dm³ concentration followed by a slight increase to 10 mg/dm³. The removal amount of B is also found to be essentially low. It is considered that the order is determined by the difference in the valency of anionic species, that is, the anionic species...
species with larger valency are more easily removed. On the other hand, the saturated adsorption amount (Figure 3(b)) is the following order; As(III) > Se(IV) > Cr(VI) > B as a standard of mass. This implies that somewhat peculiar As(III) adsorption may take place in the higher concentration region, though the affinity of slag-LDHs to As(III) is not so high. The shapes of all adsorption isotherms indicate almost Langmuir type. In the range of higher equilibrium concentration over 600 mg/dm³, the removal amounts of all anionic species seem to show each constant value, respectively. The saturated adsorption amounts of As(III), B, Cr(VI) and Se(IV) are approximately estimated to be about 32 mg/g, 21 mg/g, 19 mg/g and 5 mg/g, respectively.

Figure 4 shows the adsorption isotherm of various toxic anions with –2 mm slag-LDHs. Compared with the removal amounts with the –0.15 mm slag-LDH, those with the –2 mm slag-LDHs are found to be larger for all anionic species, suggesting that the –2 mm slag-LDHs have better removal ability for anionic species. The order of removal amount is very similar between both slag-LDHs, but there are some exceptions. For example, the obvious difference between Figure 3(b) and Figure 4(b) appears on the adsorption behavior in the high concentration region, that is to say, the adsorptions of all anionic species with –2 mm slag-LDHs (Figure 4(b)) do not seem to be saturated despite high As(III) concentration, especially in case of As(III). The reason for the difference is not clarified yet. It is considered, however, that this may be caused by the effect of Fe content in the slag-LDHs as one of important factors, because Fe has strong affinity to As.

In order to investigate the peculiar adsorption behavior, the slurries were filtered by vacuum, and the obtained filtrates were analyzed by ICP-OES. The results are shown in Figure 5. As(III) and Se(IV) in the filtrates were not detected, while B and Cr(VI) were detected in the filtrates. This implies that slag-LDHs have better adsorption ability for As(III) and Se(IV) than for B and Cr(VI).

Figure 6 shows the XRD patterns of slag-LDHs. The peaks of Mg(OH)₂, Fe₂O₃, and SiO₂ are observed, suggesting that slag-LDHs are composed of these materials.

Table 1 shows the chemical composition of slag-LDHs. Fe, Al, and Si are the main components, and the ratio of Fe to Al is about 1:1. The ratio of Fe to Al is important for the removal of As(III) and Se(IV), because Fe has strong affinity to As and Al has strong affinity to Se.

In conclusion, slag-LDHs synthesized from steelmaking slag have excellent adsorption ability for As(III) and Se(IV), and the removal amount is very similar between –0.15 mm and –2 mm slag-LDHs. The adsorption behavior is affected by the content of Fe in slag-LDHs.
behavior to As(III) mentioned above, the change in the surface property of slag-LDHs was studied before and after an As(III) removal operation. Figure 5 indicates the XRD patterns of –2 mm slag-LDH before and after the As(III) removal operation with 1,000 mg/dm³ of initial As(III) concentration. No remarkable difference in the crystalline materials is found before and after the As(III) adsorption. After the As(III) adsorption, the background of XRD (Figure 5(b)) also becomes slightly high, compared with that of the original slag-LDHs shown in Figure 5(a). Any peak patterns based on the As compounds like ferric arsenite or ferric arsenate are not identified after the As(III) adsorption. On the other hand, the same tendency can be confirmed on the SEM observation (Figure 2(c)), because no difference in the surface morphology is found before and after the As(III) adsorption. Though it is not shown as the figure, almost no difference in the XRD and SEM photograph is also not confirmed, even if 5 times repeated adsorption operations are applied with the 1,000 mg/dm³ of initial As(III) concentration. It appears that the main mechanism of As(III) removal may be an anion exchange reaction, according to the results of XRD and SEM observation.

3.3 Removal of toxic anionic species from dilute aqueous solution

In order to investigate the removal ability of toxic anionic species in dilute aqueous solution, the removal tests using 50 mg/dm³ of dilute solution were performed under various solid-liquid ratios. Figure 6 indicates the removal percentage of toxic anionic species. The As(III) removals in Figure 6(a) are increasing with an increase in the additional amount of slag-LDHs. In case of the solid-liquid ratio at 0.1 g/20 cm³, 0.2 g/20 cm³, 0.5 g/20 cm³ and 1.0 g/20 cm³, the As(III) removal percentages by the –0.15 mm slag-LDHs are about 62%, 82%, 91% and 95%, respectively. The As(III) removals by the –2 mm slag-LDHs are also about 87%, 93%, 98% and 99%, respectively. These results show that the slag-LDHs have high potential as an excellent anion removal agent. It is considered that the gap of As(III) removal is mainly caused by the difference in the Fe content in the slag-LDHs, because of the strong affinity to As.

On the other hand, Figure 6(b) shows the removal amount of toxic anionic species. The removal amount is calculated by an unit conversion...
of the results in Figure 6(a). The removal amount of As(III) is decreasing with an increase in the additional amount of slag-LDHs. This means that the usage percentage to adsorption site in the slag-LDHs declines oppositely, with increasing the additional amount. For example, if the saturated adsorption amounts of As(III) by the –0.15 mm slag-LDHs are supposed to be 32 mg/g (Figure 3(b)), the usage percentage decreases approximately from about 19% (case (i)) to 3% (case (iv)). Therefore, the balance between As(III) removal (%) and As(III) removal amount (mg/g) should be considered simultaneously in designing a practical removal process.

It is found from a series of experimental results that the slag-LDHs are performed as an anion removal agent for toxic anionic species in dilute aqueous solution.

4. Conclusion

By using the –0.15 mm slag-LDHs and –2 mm slag-LDHs, the removals of toxic anions including As(III), B, Cr(VI) and Se(IV) in aqueous solution were conducted under various experimental conditions. From the results, the potential of slag-LDHs was investigated as an excellent anion removal agent.

The order of removal for four anionic species with the slag-LDHs is as follows; Se(IV) > Cr(VI) > As(III) > B in the low equilibrium concentration region. The order implies that the valency of anionic species is mainly related to the anion adsorption order, that is, an anion with larger valency is more easily captured in the slag-LDHs. On the other hand, the saturated adsorption amount is considered to be the following order; As(III) > Se(IV) > Cr(VI) > B as a standard of mass. No remarkable difference in the crystal-line materials is not found before and after the As(III) adsorption operation. It is found that the slag-derived LDHs are applicable as an anion removal agent for dilute anionic species in aqueous solution.

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