

**Original Paper**

## Synthesis of Hydrotalcite-Like Materials from Various Wastes in Aluminum Regeneration Process

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**Abstract**

Syntheses of hydrotalcite-like materials (HT), functional inorganic materials having layered structure of complex hydroxide, were carried out using aluminum dross, white dust and waste solution containing Mg in an aluminum regeneration process as a raw material. The removal of toxic anions such as As(III) and As(V) were investigated with the various HTs calcined at 673K.

The CO<sub>3</sub><sup>2-</sup> type HT can be synthesized from the aluminum dross, white dust and MgCl<sub>2</sub> solution by a co-precipitation method. The characteristics of HT obtained from the wastes are almost the same as that synthesized from reagents. It is possible to remove As(III) and As(V) in aqueous solution with various HT calcination products. Three stages of batch adsorption operation is suitable to remove As(III) and As(V) with the HT calcination product. The HT derived from the above wastes can be used as an excellent material for the removal of various toxic heavy metal ions.

**Key words:** Hydrotalcite-like material, Anion exchanger, Toxic oxoacid anion

**Introduction**

The amount of aluminum consumed in Japan occupies about 15% in the world. A large amount of electrical energy is needed to produce aluminum by the molten salt electrolysis, but the energy for aluminum recycling is about 3% compared with that for molten salt electrolysis. The aluminum recycling is important from the viewpoint of resources and energy conservations. However, the various wastes such as aluminum dross, white dust, MgCl<sub>2</sub> waste solution and so on are exhausted in the recycling process of aluminum products<sup>1-3</sup>. The main component of aluminum dross, which floats on the surface of molten aluminum in the furnace, comprises metal aluminum, aluminum oxides and nitrides. The waste of fine powder recovered in the bag filter after an Al scrap melting process is called as white dust. The MgCl<sub>2</sub> waste solution is discharged in a magnesium removal process from Mg/Al alloys using Cl<sub>2</sub> gas. Especially, the aluminum dross is appointed as the managed wastes because of the possibility of ammonia generation and spontaneous ignition by the

reaction with moisture in air. Only a small part of the aluminum dross is used as a deoxidizer for steel making and a cement mixture. It is important to develop the new technology to use aluminum dross effectively<sup>4-9</sup>.

In this study, the synthesis of hydrotalcite-like materials (HT), which have a structure of layered double hydroxides and are one of the inorganic anion exchangers<sup>10-15</sup>, was carried out using reagents and the wastes discharged in an aluminum recycling process as a raw material. The removal of toxic metal ions such as As(III) and As(V) was investigated using the HT and the HT calcination product.

**Experimental**

Five gram of aluminum dross or white dust and 200 cm<sup>3</sup> of 1.0 mol/dm<sup>3</sup> HCl or aqua regia were put into a beaker, and leaching of the aluminum component was conducted for 3 h. After the leaching, the filtrate was recovered by a solid-liquid separation with a vacuum filtration equipment. Then, MgCl<sub>2</sub> waste solution was added to the filtrate containing Mg and Al. The Mg/Al molar ratio in the solution was set to 2.5. The Mg/Al mixed solu-

tion was quantitatively added to  $\text{Na}_2\text{CO}_3$  solution at pH 10.5 under stirring. In order to maintain the reaction pH at about 10.5, 30w/v% NaOH was dropped in the Mg/Al mixed solution. After these operations, an agitation was continued for 2 days. The solid product obtained by a vacuum filtration method was washed with distilled water and then dried at 343K. In the case of synthesis from reagents, the Mg/Al mixed solution was prepared using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and the above operation was carried out according to the same way. Identification of crystal structure and analysis of the chemical composition of the reaction products were carried out with an X-ray diffraction equipment (Nihon Denshi Co. Ltd., JDX-3530) and an energy-distributed fluorescence X-ray analysis equipment (Nihon Denshi Co. Ltd., JED-2110), respectively.

In order to investigate As(III) and As(V) removal with the reaction products, 0.3 g of various HTs and HT calcination products at 673K were put into  $30\text{ cm}^3$  of various As(III) and As(V) solutions. After the contact operation for 1 h at room temperature, the amounts of As(III) and As(V) remained in the mother liquor were measured. Concentration of metal ions in aqueous solution was measured with an inductively-coupled plasma spectrometer (Shimadzu Co. Ltd., ICPS-1000III).

## Results and discussion

The chemical composition of aluminum dross, white dust and Mg-containing waste solution is shown in Table 1. The weight percent for each metal component was calculated by defining the total metal content in leachants as 100%. The contents of Al and Mg in the aluminum dross, which are also the main metal composition of HT, are 85.3% and 5.6%, respectively, in case of leaching with aqua regia. On the other hand, 83.8% of Al and 4.7% of Mg are contained in  $1.0\text{ mol/dm}^3$  HCl used as a leachant. Impurity components such as Fe, Si, Ca, K, Na and so on exist in the aluminum dross, and these are originally contained in Al scrap. The contents of Al and Mg in the white dust

are 81.9% and 13.2%, respectively. The amounts of Si, Fe, Ca in the white dust are smaller than those in the aluminum dross. Though it is not shown in the table, about 13% of Cl component is contained in the white dust from the results determined by an EDX analysis method. The  $\text{MgCl}_2$  waste solution contains 98.2% of Mg. The ratio of Cl/Mg and  $\text{Mg}^{2+}$  concentration of the waste solution are 2.2 and  $3.2\text{ mol/dm}^3$ , respectively. The mixed solution of the leachant (b) and the  $\text{MgCl}_2$  waste solution (d), that of the leachant (c) and the  $\text{MgCl}_2$  waste solution (d) are used as a raw material of HT synthesis.

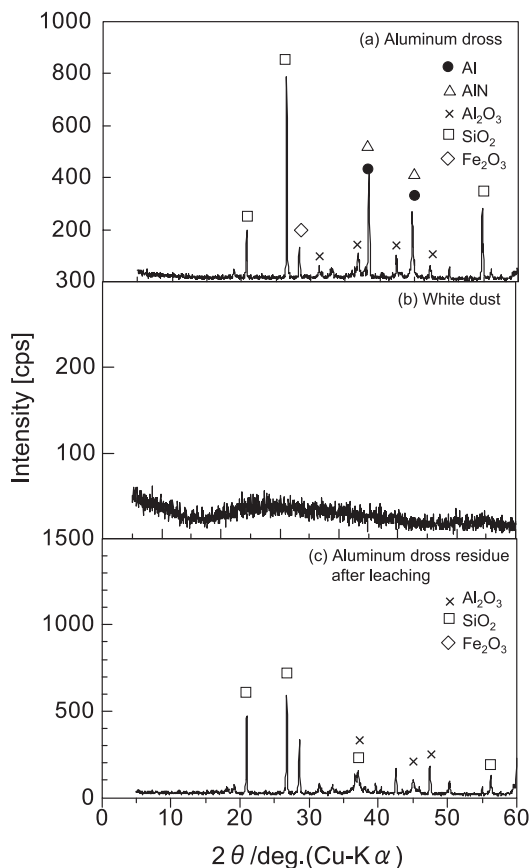
The XRD pattern of aluminum dross, white dust and aluminum dross after leaching with  $1\text{ mol/dm}^3$  HCl is shown in Fig. 1. The aluminum dross contains Al, AlN,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  as a crystalline material. No peak derived from crystalline materials is found in the XRD pattern of the white dust, which means a typical amorphous material. After the leaching of aluminum dross with  $1.0\text{ mol/dm}^3$  HCl to dissolve Al and Mg components, almost half of the aluminum dross is dissolved, and the rest remains as solid residue (Fig. 1(c)). The XRD pattern of this solid residue has the peaks of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , and the peaks of Al and AlN disappear after the leaching operation. The Al and AlN in the aluminum dross are one of the harmful components because they cause the spontaneous combustion and the generation of  $\text{H}_2$  and  $\text{NH}_4$  gases<sup>8)</sup>. Therefore, the leaching of Al compound in the aluminum dross is caused by the oxidation reaction of Al and AlN by HCl solution, and as a result, the aluminum dross residue can be made harmless by the acid leaching operation.

The SEM photograph of aluminum dross and white dust is shown in Fig. 2. The fine aluminum dross particles are coagulated, and large particles with over 20 micrometer are confirmed in Fig. 2(a). The aluminum dross particle size has also wide distribution. The particle shape and size distribution of the white dust particle is almost similar to those of the aluminum dross.

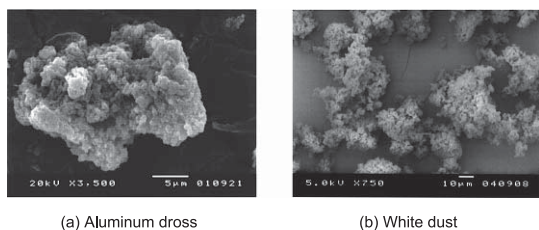
The XRD pattern of HT synthesized from reagent, aluminum dross and white dust is shown in

**Table 1** Chemical composition of aluminum dross, white dust and Mg-containing waste solution.

Material	Leachant	Metal composition [wt%]							
		Al	Mg	Si	Ca	Fe	Na	K	Pb
(a) aluminum dross	aqua regia	85.3	5.6	1.8	1.9	4.4	0.5	0.4	0.1
(b) aluminum dross	$1.0\text{ mol/dm}^3$ HCl	83.8	4.7	2.6	1.5	5.3	1.2	0.8	0.1
(c) white dust	aqua regia	81.9	13.2	0.4	0.3	0.8	—	—	—
(d) $\text{MgCl}_2$ waste solution		—	98.2	—	1.5	—	0.2	0.1	—

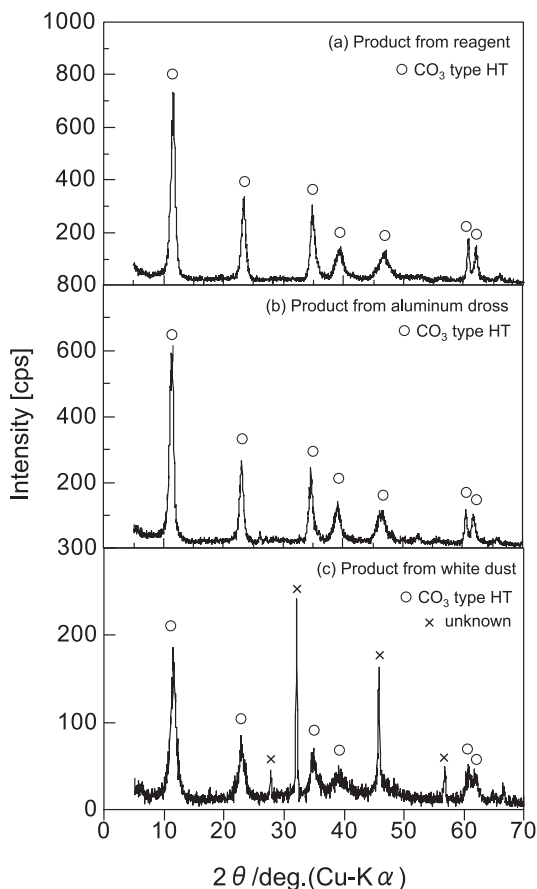


**Fig. 1** XRD pattern of aluminum dross, white dust and aluminum dross after leaching with 1 mol/dm<sup>3</sup> HCl.



**Fig. 2** SEM photograph of aluminum dross and white dust.

Fig. 3. The peak pattern of hydrotalcite-like materials  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+} [(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]^{x-}$ ,  $x = 0.2 - 0.33$ <sup>8)</sup> is identified for both products obtained from aluminum dross (Fig. 3(b)) and white dust (Fig. 3(c)). In case of white dust, some unknown peak appears in the XRD pattern due to the formation of by-product. These reaction products are identified as CO<sub>3</sub><sup>2-</sup> type HT having CO<sub>3</sub><sup>2-</sup> anions as an exchangeable ion, and these are almost the same of HT reagent (Fig. 3(a)). The results indi-



**Fig. 3** XRD pattern of HT synthesized from reagent, aluminum dross and white dust.

cate that it is possible to synthesize HT with almost same ability of HT reagent by using the aluminum dross, white dust and MgCl<sub>2</sub> waste solution.

The distribution diagram of As(III) and As(V), which is one of typical toxic oxoacid anions in aqueous solution, is shown in Fig. 4 as a function of pH. As(III) in aqueous solution exists as a form of anionic species such as AsO<sub>2</sub><sup>-</sup> over pH 10. On the other hand, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup> are formed in aqueous solution in the case of As(V). Figure 4 reveals that the anionic species of As(III) and As(V) are predominant in the alkali condition. Hydrotalcite is also well-known that it can be used as a pH buffer reagent to adjust pH, and the pH in aqueous solution can be controlled so as to be alkali condition with the HT. It is thought that the As(III) and As(V) anions can be removed with hydrotalcite according to an anion exchange reaction.

Generally, CO<sub>3</sub><sup>2-</sup> is very stable in the HT

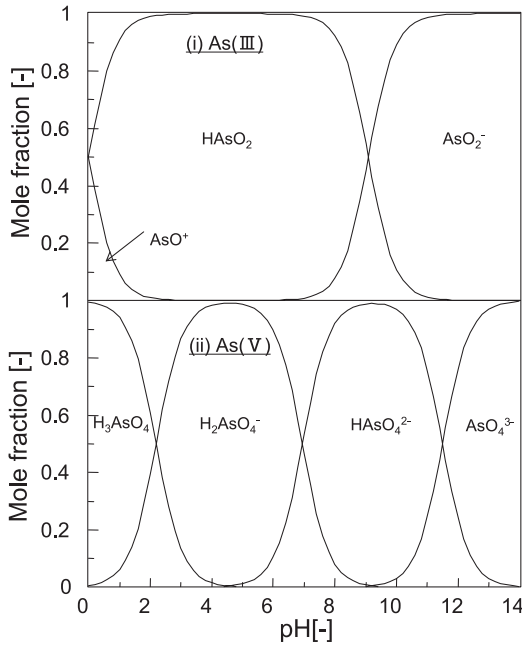


Fig. 4 Distribution diagram of As(III) and As(V) in aqueous solution.

structure<sup>8</sup>), and the anion exchange amounts between  $\text{CO}_3^{2-}$  in the HT and various oxoacid anions are not so large. From the other report<sup>14,15</sup>) or our previous studies<sup>7-9</sup>), the removal amounts of various anions with the HT calcination product (Mg/Al complex oxide) are larger than those with the  $\text{CO}_3^{2-}$  type HT. There are two processes for anion uptake, that is, the direct uptake reaction with rehydration and the anion exchange reaction, in using the HT calcination product for the removal of various anions. These anions are mainly taken by the HT calcination product with a rehydration reaction to neutralize the positive charges in HT. In this study, the removal of As(III) and As(V) was carried out using the HT calcinations product.

As already mentioned, the pH condition is important to form anion species of As(III) and As(V) in aqueous solution. At first, the pH buffer effect of HT calcination product was investigated in removing As(III). The relationship between As(III) removal and equilibrium pH is shown in Fig. 5. The black circle (●) and white circle (○) mean the removal percent of As(III) and the equilibrium pH after As(III) removal, respectively. Even if the initial pH changes from 4 to 11, the equilibrium pH is kept to be about pH11 by the buffer action of HT calcination product. The broken line shows the equilibrium pH of HT before calcination in the absence of As(III). The equilibrium pHs of HT prod-

ucts before and after calcination are different, and the pH is kept at about 8.5 in case of HT before calcination. The removal percent of As(III) shows about 90% in the initial pH range from 4 to 11. According to Fig. 4,  $\text{AsO}_2^-$  species is predominant in this equilibrium pH. That is the reason why the high removal percent of As(III) can be obtained with the HT calcination product in the wide initial pH range.

The adsorption isotherm of As(III) with the HT calcined at 673K is shown in Fig. 6. The adsorption amount of As(III) is increasing with an increase in equilibrium concentration of As(III). In  $100 \text{ g/m}^3$  of equilibrium As(III) concentration, about  $60 \text{ mg/g}$  of As(III) can be adsorbed with the HT calcination product. In order to estimate the minimum required amount of HT calcination product to get the outlet solution containing  $0.1 \text{ g/m}^3$  of As(III) by multi-stage batch operations, McCabe-Thiele analysis is applied to this adsorption isotherm. That is, the objective of this analysis is to determine the optimized additional amounts of adsorbent for every stage so as to minimize the sum of additional amount in each stage. When the concentration of As(III) in the inlet solution ( $C_0$ ) and that in the outlet solution ( $C_3$ ), the number of stage and treatment volume are respectively as-

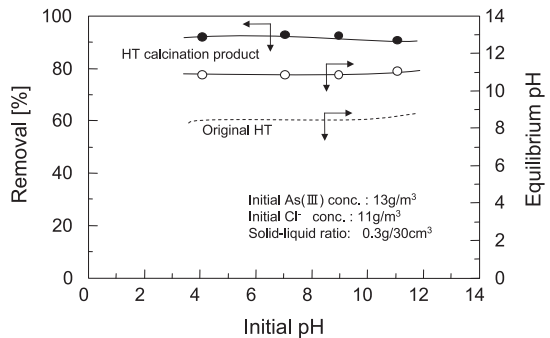


Fig. 5 Relationship between As(III) removal and equilibrium pH.

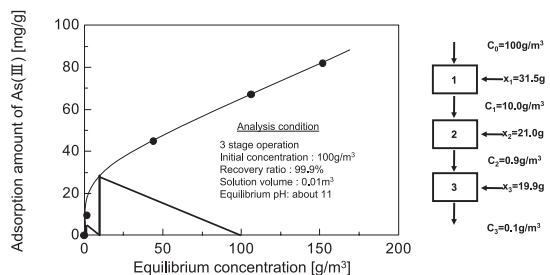


Fig. 6 Adsorption isotherm of As(III) with HT calcined at 673K.

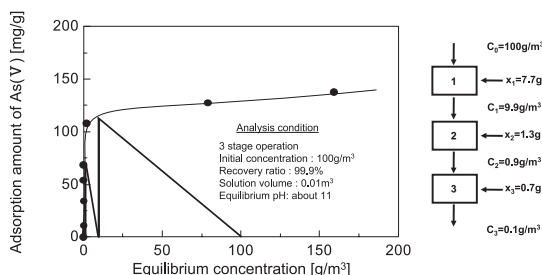


Fig. 7 Adsorption isotherm of As(V) with HT calcined at 673K.

sumed to be 100 g/m<sup>3</sup>, 0.1 g/m<sup>3</sup>, 3 stages and 0.01 m<sup>3</sup>, the required amount of HT calcination product in each stage ( $x_1, x_2, x_3$ ), the As(III) concentrations of outlet solution in the 1<sup>st</sup> and 2<sup>nd</sup> stages ( $C_1, C_2$ ) are theoretically determined to be as follows;  $x_1 = 31.5$  g,  $x_2 = 21.0$  g,  $x_3 = 19.9$  g,  $C_1 = 10.0$  g/m<sup>3</sup> and  $C_2 = 0.9$  g/m<sup>3</sup>. From this result, the theoretical minimum value of additional amount is estimated to be 72.4 g ( $x_1 + x_2 + x_3$ ).

The adsorption isotherm of As(V) with the HT calcined at 673K is shown in Fig. 7. In the low concentration region below 10 g/m<sup>3</sup>, the removal amount of As(V) sharply increases until about 100 mg/g of adsorption amount. The adsorption amount becomes almost constant in the high concentration region over 50 g/m<sup>3</sup> of equilibrium concentration. The reason why the adsorption isotherm between As(III) and As(V) is different is not clarified yet, but the effect of the differences of ion size and valency is considered as one of factors. McCabe-Thiele analysis is carried out for the adsorption isotherm of As(V) as the same way in Fig. 6. The concentration of As(V) in the inlet solution ( $C_0$ ) and that in the outlet solution ( $C_3$ ), the number of stage and treatment volume being respectively assumed to be 100 g/m<sup>3</sup>, 0.1 g/m<sup>3</sup>, 3 stages and 0.01 m<sup>3</sup>, the required amount of HT calcination product in each stage ( $x_1, x_2, x_3$ ), the As(V) concentrations of outlet solution in the 1<sup>st</sup> and 2<sup>nd</sup> stages ( $C_1, C_2$ ) are theoretically determined to be the following values;  $x_1 = 7.7$  g,  $x_2 = 1.3$  g,  $x_3 = 0.7$  g,  $C_1 = 9.9$  g/m<sup>3</sup> and  $C_2 = 0.9$  g/m<sup>3</sup>. It is found from this result that 9.7 g ( $x_1 + x_2 + x_3$ ) of additional

amount is required as the theoretical minimum value.

The results of McCabe-Thiele analysis for As(III) and As(V) removal are shown in Table 2. The operation condition of McCabe-Thiele analysis is the same as Fig. 6 except for the stage number. Stage number of batch adsorption operation changes from 1 to 50. Actually, the batch adsorption operation of 50 stages may be similar to the situation in a column adsorption operation. For As(III) and As(V) removals with the HT calcination product, the total required amounts of that remarkably decrease with a decrease in the stage number of batch operation. A large difference of the required amount is found between 1 stage and 2 stages for both cases. However, especially in case of the As(V) removal, the difference of the required amount is not so large between 3 stages and 50 stages. Because the solid-liquid separation of HT or HT calcination product is somewhat difficult, the increase in stage number should be avoided from the engineering viewpoint. From these results, it is thought that about 3 stages operation is suitable to remove As(III) and As(V) with HT or HT calcination product.

## Conclusion

As one of an effective usages of the wastes generated in an Al regeneration process, the syntheses of HT were conducted using aluminum dross, white dust and MgCl<sub>2</sub> waste solution as a raw material. The removal of As(III) and As(V) were investigated with the HT calcination product.

The CO<sub>3</sub><sup>2-</sup> type HT can be synthesized from the above wastes by the combination of acid leaching and co-precipitation. The XRD pattern of HT obtained from the wastes are almost similar to that from reagents. Toxic oxoacid anions such as As(III) and As(V) in aqueous solution can be adsorbed by using the HT or HT calcination product. In case of multi-stage batch adsorption operation, the theoretical required amounts of HT calcination product decreases with a decrease in the stage number. Three stage operations is desirable for the removal of As(III) and As(V) from the McCabe-

Table 2 Results of McCabe-Thiele analysis for As(III) and As(V) removal with HT calcination product.

Toxic material	Recovery [%]	Total amount of HT calcination product [g]			
		1 stage $x_1$	2 stages $x_1 + x_2$	3 stages $x_1 + x_2 + x_3$	50 stages $x_1 \dots + x_{50}$
As(III)	99.9	2210	148	72.4	29.3
As(V)	99.9	77.7	12.1	9.7	8.3

Inlet concentration: 100 g/m<sup>3</sup>, Outlet concentration 0.1 g/m<sup>3</sup>, Recovery: 99.9%, Solution volume: 0.01 m<sup>3</sup>.

Thile analysis. The hydrotalcite derived from the above wastes can be used as an excellent material for the removal of various toxic heavy metal ions.

### Acknowledgement

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