

## Use of Magnesium-Aluminium and Zinc-Aluminium Hydroxycompounds as Adsorbents of Uranium Ions in Aqueous Solutions

Toshio MAKI\*

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It was found that precipitates formed by adding NaOH solution to the mixed solutions of  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Mg/Al molar ratios of 2 to 4 and to the mixed solution of  $\text{ZnSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Zn/Al molar ratio of 2, respectively, can be used as efficient adsorbents of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions in aqueous alkaline carbonate solutions. The ideal structural formulas of the precipitates formed from the mixed Mg-Al solution with Mg/Al ratio of 2.0 and the mixed Zn-Al solution with Zn/Al ratio of 2.0 were estimated to be  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]^{2+}[\text{SO}_4 \cdot 3\text{H}_2\text{O}]^{2-}$  and  $[\text{Zn}_4\text{Al}_2(\text{OH})_{12}]^{2+}[\text{SO}_4 \cdot 3\text{H}_2\text{O}]^{2-}$ , respectively.

It has been shown that 0.1 g of the Mg-Al and Zn-Al double hydroxysulphate powders (particle size 70–170  $\mu$ ) uptake >97% of the U(VI) ions from 50 ml of an aqueous alkaline carbonate solution containing 100 ppm of U(VI) within 2 h at room temperature. The rates of adsorption of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions for the Mg-Al and Zn-Al double hydroxysulphate powders were both about 2 times that for the hydrous Ti(IV) oxide powders. Five weight percent sodium bicarbonate solution was found to be effective for the desorption of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions from the double hydroxysulphate powders. Adsorption capacity of the double hydroxysulphates was discussed in relation to their structure.

**KEY WORDS:** Adsorption/ Desorption/  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ion/ Double hydroxysulphate/ Brucite-like layer/

### I. INTRODUCTION

The hexavalent uranium ions are present in the form of  $\text{UO}_2^{2+}$  in aqueous acidic media and of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  in aqueous alkaline carbonate media, respectively.<sup>1,2)</sup> Although anion exchange resins or hydrous Ti(IV) oxides are generally used for uptake of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions from aqueous alkaline carbonate solutions such as sea water, they are still considerably costly.

The present author has found that the magnesium-aluminium hydroxysulphate and zinc-aluminium hydroxysulphate can be used as efficient adsorbents of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions in aqueous alkaline carbonate solutions.

Methods of preparation of magnesium-aluminium double hydroxides from mixed solutions of magnesium and aluminium chlorides, as well as the microstructures of the resultant hydroxycarbonates have been investigated extensively by Feitknecht<sup>3)</sup> and Gastuche *et al.*<sup>4,5)</sup> Gastuche *et al.* concluded that, in addition to aluminium and magnesium hydroxides, two hydroxycarbonates having Mg/Al ratios of about 5 and 2 are formed, essentially pure, from solutions with Mg/Al molar ratios of about

\* 牧 俊夫: Laboratory of Ceramic Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611.

5 and 2 (Mg/Mg+Al molar ratios of 0.83 and 0.67), respectively.<sup>4)</sup> The structure of the hydroxycarbonates proposed consists of positively charged brucite-like layer as a basic unit, and the positive charge is balanced by an interlayer sheet containing carbonate groups and water molecules.<sup>5)</sup> There are some minerals having such a structure,<sup>6)</sup> and the hydrotalcite ( $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$ ) is an example. Brindley and Kikkawa prepared the mixtures of Mg-Al hydroxyperchlorates and Mg-Al hydroxycarbonates by precipitation with a small excess of caustic soda from mixed solutions of Mg and Al perchlorates.<sup>7)</sup>

In the present study two series of magnesium-aluminium and zinc-aluminium hydroxycompounds were prepared by precipitation with a caustic soda solution at various pH from mixed solutions of magnesium and aluminium sulphates, and of zinc and aluminium sulphates, respectively, and capacities of their precipitates to adsorb  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions from aqueous solutions were investigated in relation to their microstructure.

## II. EXPERIMENTAL

### 1. Sample Preparation

Mg-Al and Zn-Al mixed solutions, 0.1 M in total cation content and with (Mg or Zn)/Al molar ratios of 1.0, 2.0, 3.0 and 4.0, were prepared from solutions of  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ , respectively. Caustic soda solution (4N) was added to each of these mixed solutions and changes of their pH values were measured successively. The precipitates formed by adding 4N NaOH solution up to pH 9.0 or 10.5 for Mg-Al series and up to pH 7.5 for Zn-Al series were boiled for 10 min together with liquid media, and, after cooled to room temperature, they were separated from liquids by suction-filtration. In all the experiments described above, distilled water was reboiled to expel  $\text{CO}_2$  just before its use.

The precipitates separated as pasty cakes were oven dried at 105°C for more than 48 h and pulverized to the grain size of 80–200 mesh. For comparison, powders of magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , hydrous basic zinc sulphate,  $\text{ZnSO}_4\cdot 4\text{Zn}(\text{OH})_2$ ,<sup>8)</sup> and aluminium trihydroxide,  $\text{Al}(\text{OH})_3$ ,<sup>9)</sup> were prepared by adding 4N NaOH solution to the 0.1N solutions of  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$ , up to pH 10.5, 7.5 and 8.0, respectively. Also for comparison, powders of hydrous Ti(IV) oxides were prepared by adding about 4N  $\text{NH}_4\text{OH}$  solution to 0.04N  $\text{Ti}(\text{SO}_4)_2$  solution.<sup>10)</sup> All the powdered samples were oven dried at 105°C over 48 h, and then subjected to analyses for their characterization.

### 2. Adsorption and Desorption of U(VI) Ions

The pH of solution of  $\text{UO}_2\text{Cl}_2\cdot \text{H}_2\text{O}$  was first raised up to 10.5 by addition of 0.01N  $\text{Na}_2\text{CO}_3$  solution and then lowered to 8.0 by addition of 0.01N HCl solution. The alkaline solution thus prepared, which contained 100 ppm of U(VI) in the form of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ,<sup>11)</sup> was used as the adsorptive solution. The adsorbent (0.100 g) composed of the powders of 80–200 mesh in grain size was shaken back and forth, with

100 strokes per minute, with 50 ml of the adsorptive solution in a flask of 100 ml in capacity at 25°C for 2 h. After separation of solid from liquid, the uranium remaining in the solution was extracted with a mixed solution of TBP and isoctane (25: 75 in vol. ratio), and its uranium content was determined spectrophotometrically by comparing the absorbance of its liquid with those of the standard samples.<sup>11)</sup> The amounts of U(VI) adsorbed by the powders were calculated by subtracting the amounts of U(VI) in the organic extract from the amounts of U(VI) initially present in the adsorptive solution. The adsorption capacities of the powdered samples measured under the condition described above were represented by wt. percentages of U(VI) ions adsorbed by the powders to those initially present in the adsorptive solution. The desorption of U(VI) from the powders was performed by shaking *ca.* 0.1 g of U(VI)-adsorbed powders with 50 ml of a 5 wt.% NaHCO<sub>3</sub> solution at 60°C for 1 h.

### 3. Sample Characterization

X-ray diffraction, chemical analysis, thermal analyses(DTA and TGA), infrared absorption spectra and X-ray fluorescence spectral analysis were used to characterize the powdered samples before and after adsorption of U(VI). The samples were pelleted in KBr for infrared absorption spectroscopy. The (Mg or Zn)/Al ratios of the samples were determined mainly by X-ray fluorescence spectral analyses and by chemical analyses as an adjunct. The samples to be subjected to X-ray fluorescence spectral analyses were prepared by melting their mixtures with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. The chemical analyses of the samples were performed first by dissolving 0.100 g of the samples into a conc. HCl(35wt.%) solution, and then neutralizing the solution with a NH<sub>4</sub>OH solution to precipitate hydrous aluminium gels. The amounts of magnesium retained in the solution after separation of aluminium were determined by the chelate titration method.

## III. RESULTS

### 1. Formation of Mg-Al and Zn-Al Hydroxysulphates

Changes of the pH of the Mg-Al and Zn-Al mixed solutions having the (Mg or Zn)/Al ratio of 2.0 with amount(ml) of 4*N* NaOH added are shown by the solid lines (C) and (C') in Fig. 1 (A) and (B), respectively. The results for the solutions containing each of the magnesium, zinc and aluminium sulphate alone were also shown by the dotted lines (a), (a') and (b or b'), respectively, in these figures. Both the solid lines (c) and (c') consist of two steps, the first steps suggesting the formation of aluminium hydrogels and the second the formation of some double hydroxycompounds. The results for the pH changes of the solutions having (Mg or Zn)/Al ratios of 1.0, 3.0 and 4.0 were not shown in the figure, but they were almost the same in shape as those shown by the curves(c) or (c'), except that the widths of the first and second steps decreased with increasing the (Mg or Zn)/Al ratios of the solutions. The (Mg or Zn)/Al ratios of the precipitates formed from the Mg-Al or Zn-Al mixed solutions,

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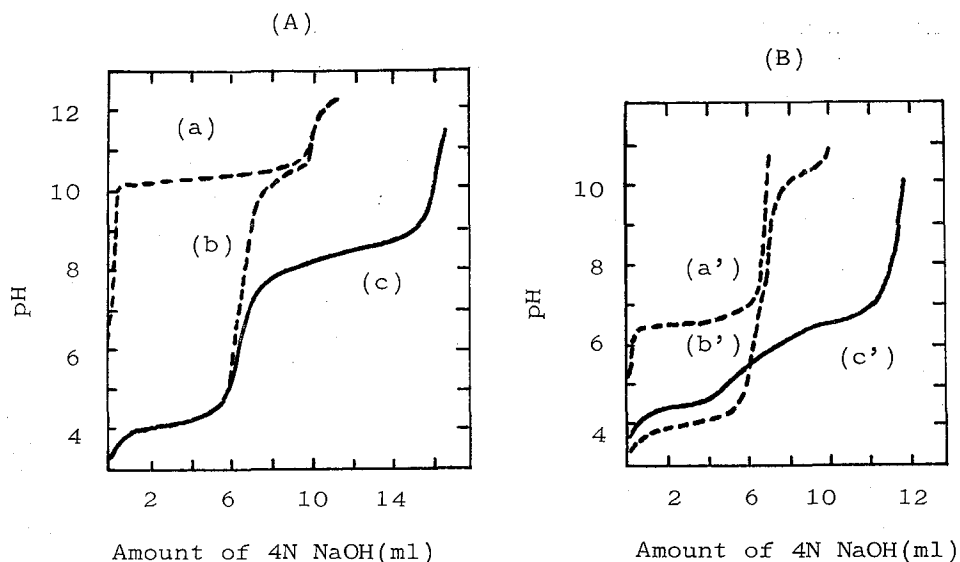


Fig. 1. Changes of pH of Mg-Al and Zn-Al solutions with amount of NaOH solution added.  
 (A): (a) 4N NaOH solution was added to a MgSO<sub>4</sub> solution, 0.1N in Mg content.  
 (b) 4N NaOH solution was added to a Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, 0.1N in Al content.  
 (c) 4N NaOH solution was added to a solution, 0.1 M in total cation content, prepared by mixing MgSO<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in Mg/Al molar ratio of 2.0.  
 (B): (a') 4N NaOH solution was added to a ZnSO<sub>4</sub> solution, 0.1N in Zn content.  
 (b') 4N NaOH solution was added to a Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, 0.1N in Al content.  
 (c') 4N NaOH solution was added to a solution, 0.1 M in total cation content, prepared by mixing ZnSO<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in Zn/Al molar ratio of 2.0.

Table I. (Mg or Zn)/Al molar ratios in initial solutions and those in precipitates

(a) Mg/Al molar ratios					
Mg/Al in solution		1.0	2.0	3.0	4.0
Mg/Al ratios in precipitates	*pH 9.0	0.9	1.9	2.5	2.5
	*pH 10.5	1.0	2.0	2.9	3.9
(b) Zn/Al molar ratios					
Zn/Al in solution		1.0	2.0	3.0	4.0
Zn/Al ratios in precipitates	*pH 7.5	1.0	2.0	2.9	4.0

\* pH of solutions after completion of precipitation.

which were determined by X-ray fluorescence or chemical analyses, are given in Table I. The table shows that the Mg/Al ratios of the precipitates, 2.5 and 2.5, formed by adding 4N NaOH solution up to pH 9.0 are less than those of their mother solutions, 3.0 and 4.0, respectively. This fact indicates that some of the Mg<sup>2+</sup> ions were retained

in their solutions at pH 9.0. The Mg/Al ratios of the other precipitates are all the same as those of their mother solutions. In order to investigate the effect of aging period of the precipitates on their Mg/Al ratios, the precipitates together with their mother solutions, without being subjected to the boiling procedure, were placed in the air-tight polyethylene jars, held for 7 days at 60°C, and the Mg/Al ratios of the precipitates separated from their solutions were determined. The results obtained were the same as those shown in Table I.

Figures 2 and 3 show DTA curves for some of the samples described in Section II-1. Figures 4 and 5 show their TGA curves. Figures 6 [(b)-(e)] and 7[(b)-(e)] show their X-ray diffraction patterns. Figures 8[(b)-(e)] and 9[(b)-(e)] show their infrared absorption spectra.

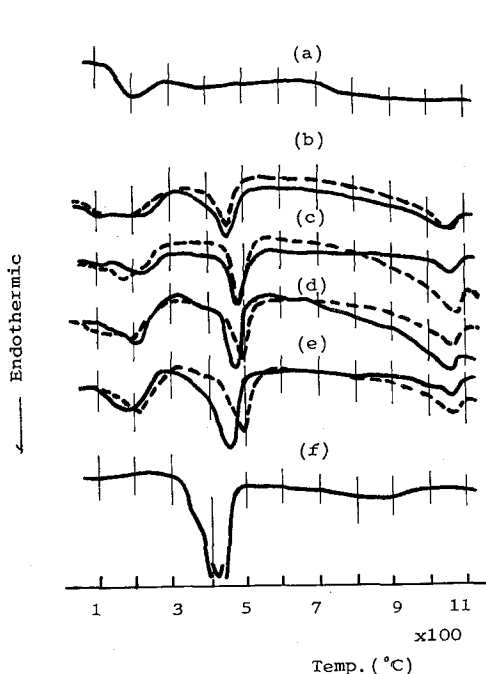


Fig. 2. DTA curves for powdered samples of Mg-Al series,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .

- (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{Mg}(\text{OH})_2$  (f) prepared by adding NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$  solutions up to pH 8.0 and 10.5, respectively.
- (b)-(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Mg/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e) up to pH 10.5 (solid line) and 9.0 (dotted line), respectively.

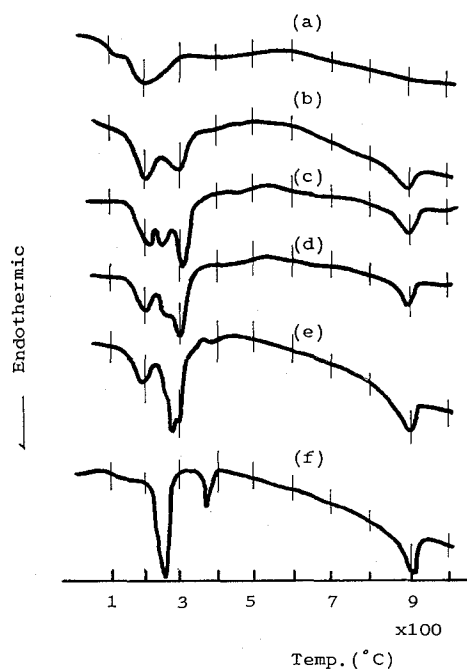


Fig. 3. DTA curves for powdered samples of Zn-Al series,  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .

- (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  (f) prepared by adding NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{ZnSO}_4$  solutions up to pH 8.0 and 7.5, respectively.
- (b)-(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{ZnSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Zn/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e) up to pH 7.5, respectively.

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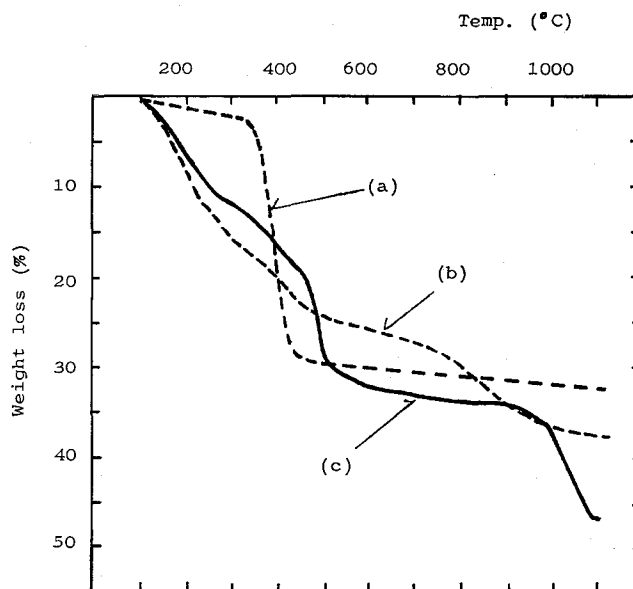


Fig. 4. TGA curves for powdered samples of Mg-Al series,  $Mg(OH)_2$  and  $Al(OH)_3$ .  
 (a) and (b):  $Mg(OH)_2$  (a) and  $Al(OH)_3$  (b) prepared by adding NaOH solution to  $MgSO_4$  and  $Al_2(SO_4)_3$  solutions up to pH 10.5 and 8.0, respectively.  
 (c): Precipitates prepared by adding NaOH solution to mixed solution of  $MgSO_4$  and  $Al_2(SO_4)_3$  with Mg/Al molar ratio of 2.0 up to pH 10.5.

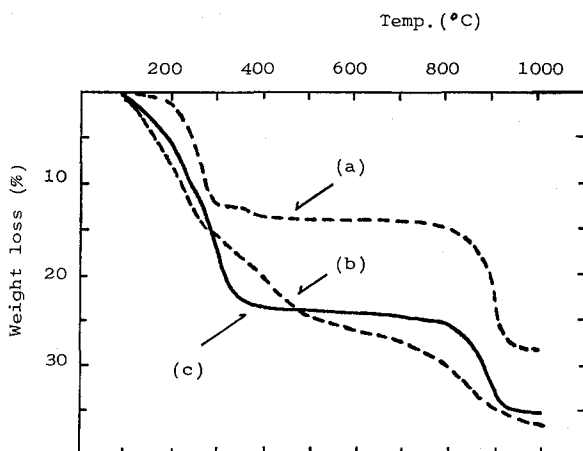


Fig. 5. TGA curves for powdered samples of Zn-Al series,  $ZnSO_4 \cdot 4Zn(OH)_2$  and  $Al(OH)_3$ .  
 (a) and (b):  $ZnSO_4 \cdot 4Zn(OH)_2$  (a) and  $Al(OH)_3$  (b) prepared by adding NaOH solution to  $ZnSO_4$  and  $Al_2(SO_4)_3$  solutions up to pH 7.5 and 8.0, respectively.  
 (c): Precipitates prepared by adding NaOH solution to mixed solution of  $ZnSO_4$  and  $Al_2(SO_4)_3$  with Zn/Al molar ratio of 2.0 up to pH 7.5.

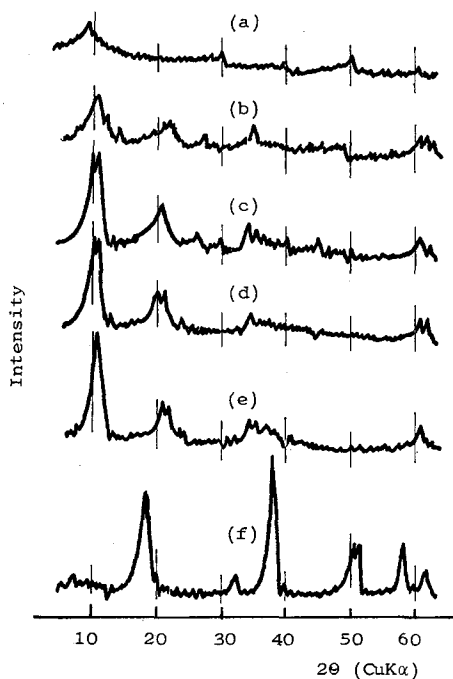


Fig. 6. X-ray diffraction patterns of powdered samples of Mg-Al series,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .

- (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{Mg}(\text{OH})_2$  (f) prepared by adding NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$  solutions up to pH 8.0 and 10.5, respectively.
- (b)–(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Mg/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e) up to pH 10.5, respectively.

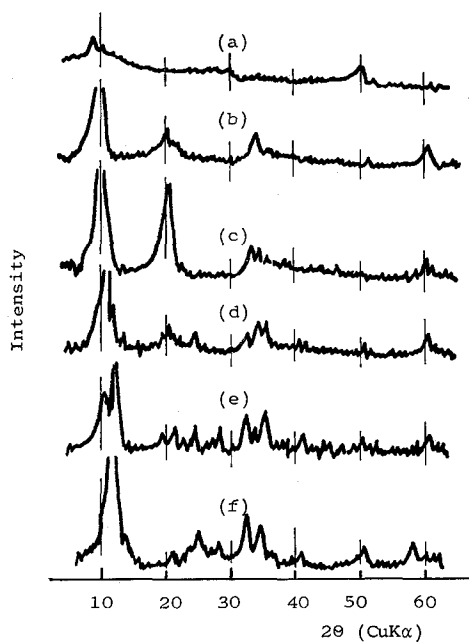


Fig. 7. X-ray diffraction patterns of powdered samples of Zn-Al series,  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .

- (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  (f) prepared by adding NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{ZnSO}_4$  solutions up to pH 8.0 and 7.5, respectively.
- (b)–(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{ZnSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Zn/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e) up to pH 10.5, respectively.

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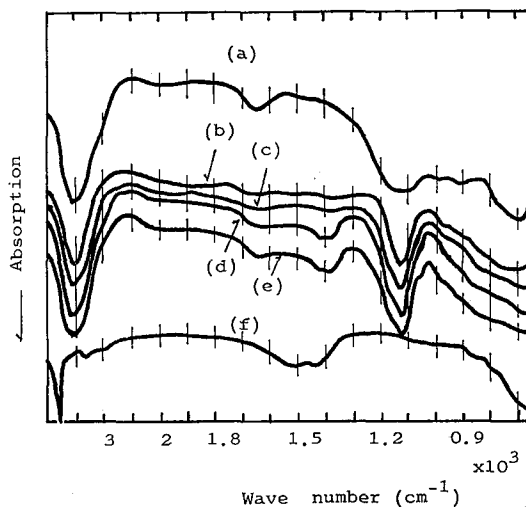


Fig. 8. IR spectra for powdered samples of Mg-Al series,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .  
 (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{Mg}(\text{OH})_2$  (f) prepared by adding NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{MgSO}_4$  solutions up to pH 8.0 and 10.5, respectively.  
 (b)-(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{MgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Mg/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e) up to pH 10.5, respectively.

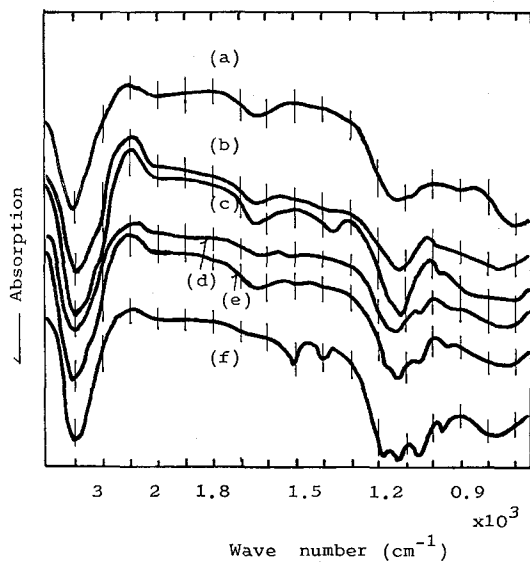


Fig. 9. IR spectra for powdered samples of Zn-Al series,  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .  
 (a) and (f):  $\text{Al}(\text{OH})_3$  (a) and  $\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2$  (f) prepared by addition NaOH solution to  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{ZnSO}_4$  solutions up to pH 8.0 and 7.5, respectively.  
 (b)-(e): Precipitates prepared by adding NaOH solution to mixed solutions of  $\text{ZnSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  with Zn/Al molar ratios of 1.0 (b), 2.0 (c), 3.0 (d) and 4.0 (e), respectively.



## 2. Adsorption and Desorption Capacities

Under the experimental conditions described in Section II-2, the capacities to adsorb U(VI) ions were  $100 \pm 3\%$  for all the powdered precipitates formed by adding NaOH solution to the Mg-Al mixed solutions with Mg/Al ratios of 2.0, 3.0 and 4.0, respectively, all up to pH 10.5. The capacity to adsorb U(VI) ions for the powdered sample formed by adding NaOH solution to the Zn-Al mixed solution with Zn/Al ratio of 2.0 up to pH 7.5 was also  $100 \pm 3\%$ . The capacities of the samples of the Zn-Al series, however, decreased as their Zn/Al ratios increased; the capacity of the sample with Zn/Al ratio of 4.0 was *ca.* 50% and that of the sample including no aluminium [ $\text{Zn}_5(\text{OH})_8\text{SO}_4$ ] was effectively nil. It was found by chemical analyses that, for the samples of the Mg-Al series, the  $\text{SO}_4^{2-}$  ions initially present in the samples were liberated by *ca.* 60 wt.% to the solutions in exchange for the  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions adsorbed.

Among the solutions tested, *i.e.*, 5 wt.% solutions of  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , and  $\text{Na}_2\text{SO}_4$ , the  $\text{NaHCO}_3$  solution gave the best result in desorbing the  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  ions from the samples, *e.g.*, the desorption ratios in wt.%, *i.e.*, the ratios of the amounts of U(VI) ions desorbed from the samples to those once adsorbed by the samples, were *ca.* 80 wt% for all the powdered Mg-Al and Zn-Al samples with large adsorption capacity.

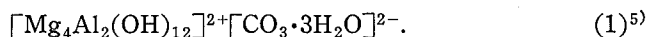
Compared to the results described above, the adsorption capacity of the powdered hydrous Ti(IV) oxide prepared in the present experiment was lower, *i.e.* *ca.* 50%, under the same condition as that applied to the other samples. The adsorption capacity of the hydrous Ti(IV) oxide, however, increased with increasing immersion time, reaching to *ca.* 100% after immersed for 24 h. This means that the adsorption rate is much lower for the hydrous Ti(IV) powders than for the Mg-Al and Zn-Al powders.

## IV. DISCUSSION

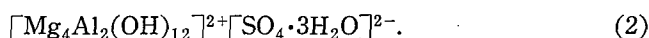
### 1. Manesium-Aluminium Hydroxysulphate

Gastuche *et al.* investigated extensively the materials formed by dialysis of the precipitates formed by the reaction of NaOH solution with mixed Mg-Al solutions.<sup>4)</sup> They found that from solutions with Mg/Al ratios ranging from about 2 to 5 hydroxycarbonates having the same ratios of Mg/Al as those of the mother solutions were precipitated, essentially pure, and from solutions with Mg/Al ratios less than 2 and larger than 5 the mixtures of hydroxycarbonate and  $\text{Al}(\text{OH})_3$ , as well as those of hydroxycarbonate and  $\text{Mg}(\text{OH})_2$ , were precipitated, respectively.

Based on chemical and X-ray powder data, they proposed that the structures of the hydroxycarbonates consist of positively charged brucite-like layers in which aluminium replaces magnesium up to a maximum of about one in three sites, and the positive charge is balanced by an interlayer sheet containing carbonate groups and water molecules.<sup>5)</sup> An ideal structural formula proposed by them for the Mg-Al hydroxycarbonate with maximum Al for Mg substitution was



Since the Mg/Al ratios of our initial solutions were in the range between 2.0 and 4.0 except for the solution having Mg/Al ratio of 1.0 (Table I), the precipitates formed by adding NaOH solution up to pH 10.5 are considered to be the compounds with the same Mg/Al ratios as those of their mother solutions, and an ideal structural formula for the Al-rich material would be almost the same as that of formula (1). The only difference would be that  $\text{CO}_3$  in the formula is replaced by  $\text{SO}_4$ . Therefore, an ideal structural formula for the precipitate formed from our solution with Mg/Al ratio of 2.0 could be written as



Carbonate ion ( $\text{CO}_3$ ) in the formula (1) is considered to have been taken from water containing  $\text{CO}_2$ , because water having been in contact with air was probably used for dialysis of the precipitates in the experiments by Gastuche *et al.* In the present experiment, the initial solutions were prepared from magnesium- and aluminium sulphate, and the precipitates formed were not dialyzed. Therefore, it seems reasonable to speculate that the precipitates obtained from the solution with Mg/Al ratio of 2.0 be the hydroxysulphate with the formula (2).

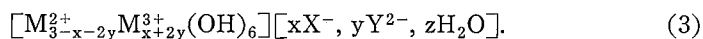
The experimental results described in Section III-2 are all in consistent with the author's speculations described above: The endothermic peaks observed at 1050°C in DTA curves [Fig. 2 (b), (c), (d) and (e)], and the weight loss observed at 1000–1100°C in TGA curves [Fig. 4 (c)] indicate that the compounds formed from the mixed sulphate solutions with Mg/Al ratios of 2.0, 3.0 and 4.0 contain  $\text{SO}_4$ , which is liberated as  $\text{SO}_3$  at about 1050°C. The presence of  $\text{SO}_4$  in the compounds is also indicated by the single sharp absorption peak at 1100  $\text{cm}^{-1}$  and the weak absorption peak at 970  $\text{cm}^{-1}$  in the infrared spectra<sup>12)</sup> [Fig. 8 (b), (c), (d) and (e)]. Generally, the free sulphate ion, which is symmetrical, being not coordinated to a metal, gives only a sharp single absorption peak at 1110  $\text{cm}^{-1}$ . If the sulphate ion coordinates to the specified ion, the peak at 1110  $\text{cm}^{-1}$  will split into 2 to 3 bands to lower the symmetry.<sup>12)</sup> The weak absorption peak at 970  $\text{cm}^{-1}$  is reported to be due to a perturbation of  $\text{SO}_4^{2-}$  caused by a crystal field formed, for example, by  $[\text{Co}(\text{NH}_3)_6]^{2+}$  ion in the structure,  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ .<sup>13)</sup> Therefore, the absorption peak observed at 970  $\text{cm}^{-1}$  in the present experiment would be due to the perturbation of the free  $\text{SO}_4^{2-}$  ions caused by a crystal field formed by  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]^{2+}$  ion in formula (2). The fact that the weight loss of the compounds occurred first in two steps, *i.e.* at about 200 and 500°C, would indicate that the former was due to liberation of water molecules and the latter of hydroxyls both from the hydroxysulphates having the formula like that of (2). The structural formula of the compound with Mg/Al ratio of 2.0 derived from the TGA curve (c) shown in Fig. 4 and the analytical data given in Table I was in fair agreement with the formula (2). X-ray diffraction patterns and infrared spectra of the samples (hydroxysulphate) prepared from the mixed Mg–Al solutions with Mg/Al ratios of 2.0, 3.0 and 4.0 were all the same [Fig. 6 (c), (d) and (e); Fig. 8 (b), (c), (d) and (e)], but entirely different from those of  $\text{MgSO}_4$  [Fig. 6 (f)], respectively, indicating that the

precipitates formed from the mixed Mg–Al solutions with Mg/Al ratios of 2.0–4.0 are the pure hydroxysulphates having fundamentally the same structure as that of  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]^{2+}[\text{SO}_4 \cdot 3\text{H}_2\text{O}]^{2-}$ .

## 2. Zinc-Aluminium Hydroxysulphate

Structure of the precipitates formed by the reaction of NaOH solution with mixed Zn–Al solutions has not yet been investigated in detail. From the extensive work on the synthetic hydroxycarbonate and the consideration of structurally related compounds, Brown and Gastuche<sup>5)</sup> proposed an ideal general structural formula for compounds in which both divalent (Mg, Ni<sup>2+</sup>, Ca, Co<sup>2+</sup>, Zn, Mn<sup>2+</sup>, Cd, Fe<sup>2+</sup>) and trivalent (Al, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>3+</sup>, Ni<sup>3+</sup>) metal cations are in the brucite-like layers, developing on them a positive charge that is balanced by interleaved anion-water sheets.

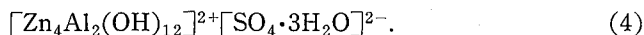
The formula proposed is:



Charge	+(x + 2y)	-(x + 2y)
	Brucite-like layer	Interlayer sheet

where M<sup>2+</sup> are divalent cations,  
 M<sup>3+</sup> are trivalent cations,  
 X<sup>-</sup> are monovalent anions,  
 Y<sup>2-</sup> are divalent anions,  
 X + 2y ≤ 1,

and the number of large atoms in interlayer sites is three ideally.<sup>5)</sup> The formula (2) is an example of this formula (3), an ideal structural formula for a compound prepared from the mixed Zn–Al solution with Zn/Al ratio of 2.0 can be written as



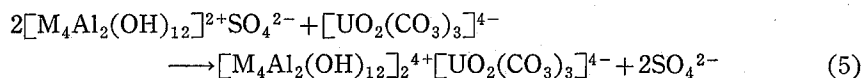
The structural formula of the sample prepared by adding NaOH solution up to pH 7.5 to the mixed Zn–Al solution having Zn/Al ratio of 2.0 was estimated from the TGA curve(c) shown in Fig. 5 and the analytical data given in Table I. The formula estimated was in fair agreement with the formula (4). The sample with Zn/Al ratio of 2.0 mentioned above showed the X-ray diffraction pattern and the infrared spectrum both similar to those of the samples prepared from the mixed Mg/Al solutions with Mg/Al ratios of 2.0, 3.0, and 4.0, indicating that the sample with Zn/Al ratio of 2.0 has the structure fundamentally similar to that of the magnesium-aluminium hydroxysulphate mentioned above. The X-ray diffraction patterns and the infrared spectra of the samples prepared from the solutions with Zn/Al ratios of 3.0 and 4.0, however, were combinations of the two compounds, *i.e.*, those of the zinc-aluminium hydroxysulphate and the hydrous basic zinc sulphate,  $\text{Zn}_5(\text{OH})_8\text{SO}_4$ <sup>8)</sup>, respectively. This fact indicates that the samples prepared from the solutions with Zn/Al ratios over 3.0 are the mixtures of these two compounds. The reason why the formation region of the hydroxysulphate is narrower for the Zn–Al series than for the Mg/Al series is attributed to the special character of Zn ions to prefer tetrahedral coordination in

hydroxycompounds in contrast to that of Mg ions which take only octahedral coordination.<sup>14)</sup> Of course, the more detailed investigation is needed for its clarification.

The sulphate ions in Zn-Al hydroxysulphate are presumed to be symmetrical, being similar to those in Mg-Al hydroxysulphate, but unsymmetrical in hydrous basic zinc sulphate, being coordinated tightly to Zn<sup>2+</sup> ions present at the surface of the positively charged layer [(Zn<sub>5</sub>(OH)<sub>8</sub>]<sup>2+</sup>. These speculations are evidenced by a single sharp band observed at 1110 cm<sup>-1</sup> in infrared spectrum of Zn-Al hydroxysulphate with Zn/Al ratio of 2.0 [Fig. 9 (c)] and splitted absorption bands observed near 1110 cm<sup>-1</sup> in infrared spectrum of hydrous basic zinc sulphate [Fig. 9 (f)].

### 3. Mechanisms of Adsorption and Desorption of U(VI) ions by Mg-Al and Zn-Al hydroxysulphates

Figure 11 shows an idealized structure of the Mg-Al or Zn-Al hydroxysulphate, [M<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>]<sup>2+</sup>[SO<sub>4</sub>·3H<sub>2</sub>O]<sup>2-</sup>, where M is Mg or Zn. As discussed in Section IV-2, the interlayer SO<sub>4</sub><sup>2-</sup> ions are not closely coordinated to specified M<sup>2+</sup> or Al<sup>3+</sup> ions present in the brucite-like layer, but located a little apart on the surface of the brucite-like layer, being nearly free and symmetrical and thus neutralizing the positive charges of the brucite-like layer as a whole. In such a structure, the bond between SO<sub>4</sub><sup>2-</sup> ions and brucite-like layer would not be strong, and the SO<sub>4</sub><sup>2-</sup> ions would easily be replaced by some other anions. Furthermore, the SO<sub>4</sub><sup>2-</sup> ion<sup>15)</sup> is large in size compared with other anions such as Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, and accordingly the replacement of the SO<sub>4</sub><sup>2-</sup> ions by large anions such as [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup><sup>16)</sup> would be easy. The high power of the Mg-Al and Zn-Al hydroxysulphates to adsorb [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> ions, which has been confirmed by the present experiment, can thus be explained by the easy replacement of SO<sub>4</sub><sup>2-</sup> ions in the hydroxysulphates by [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> ions. The mechanism can be represented by the formula (5),



where M is Mg or Zn. As described previously (Section III-2), adsorption of [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> ions from their solutions by the Mg-Al and Zn-Al hydroxysulphates as well as liberation of SO<sub>4</sub><sup>2-</sup> in exchange have been confirmed by the chemical analyses. Changes in infrared spectra of the Zn-Al hydroxysulphate powders caused by their immersion in the U(VI)-containing solution offer further evidence for this mechanism [see Fig. 10, (a) to (c)]: The sharp absorption at 1110 cm<sup>-1</sup> assigned to ν<sub>3</sub> stretching vibration of SO<sub>4</sub><sup>2-</sup> decreased and the absorption at 1370 and 1500 cm<sup>-1</sup> assigned probably to two C-O stretchings of CO<sub>3</sub> in [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup><sup>12,13)</sup> increased when the powders were immersed in the U(VI)-containing solution.

Hydrous basic zinc sulphate prepared by adding 4N NaOH solution to 0.1N ZnSO<sub>4</sub> solution was estimated from weight losses shown in Fig. 5, curve(c), to have the formula, Zn<sub>5</sub>(OH)<sub>8</sub>·0.5H<sub>2</sub>O. It has a similar structure to that of Zn-Al hydroxysulphate, consisting of positively charged base unit layers, *i.e.* [Zn<sub>5</sub>(OH)<sub>8</sub>]<sup>2+</sup><sup>14)</sup>, and negatively charged interlayers. Its capacity to adsorb [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> ions, however, was little. This could be explained by the strong bond between the SO<sub>4</sub><sup>2-</sup> ions and

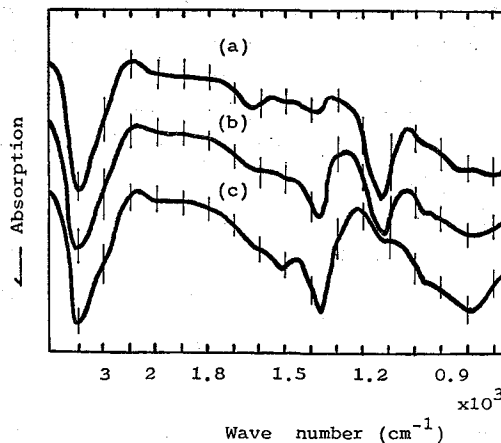


Fig. 10. IR spectra of double hydroxysulphate with Zn/Al molar ratio of 2.0 before and after immersion in U(VI)-containing solution.

- (a): Before immersion.
- (b): After immersion in U(VI)-free solution prepared by adding dil.HCl solution to 0.01N Na<sub>2</sub>CO<sub>3</sub> solution up to pH 8.0.
- (c): After immersion in solution of pH 8.0 containing 100 ppm of U(VI) in the form of [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> ions.

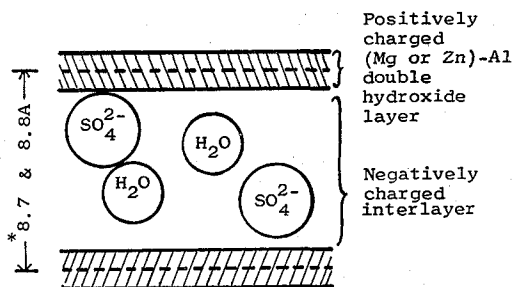
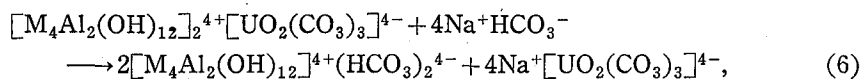


Fig. 11. Idealized structure of Mg-Al and Zn-Al hydroxysulphate, [M<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>]<sub>2</sub><sup>4+</sup>·SO<sub>4</sub><sup>2-</sup>·3H<sub>2</sub>O (M: Mg, Zn).

\* Thicknesses of Mg-Al and Zn-Al hydroxide layers calculated from 2θ of their X-ray basal reflections, respectively.

the Zn<sup>2+</sup> ions present at the surface of the positively charged base unit layers in hydrous basic zinc sulphate.

The desorption of [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> from the double hydroxysulphate caused by immersion in a NaHCO<sub>3</sub> solution can be represented by the formula (6),



where M is Mg or Zn.

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