

Thermal analysis of hydrotalcite synthesised from aluminate solutions

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Abstract The aluminate hydrotalcites are proposed to have either of the following formulas: $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3^{2-}) \cdot x\text{H}_2\text{O}$ or $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3^{2-}, \text{SO}_4^{2-}) \cdot x\text{H}_2\text{O}$. A pure hydrotalcite phase forms when magnesium chloride and aluminate solutions are mixed at a 1:1 volumetric ratio at pH 14. The synthesis of the aluminate hydrotalcites using seawater results in the formation of an impurity phase bayerite. Two decomposition steps have been identified for the aluminate hydrotalcites: (1) removal of interlayer water (230 °C) and (2) simultaneous dehydroxylation and decarbonation (330 °C). The dehydration of bayerite was observed at 250 °C. X-ray diffraction techniques determined that the synthesis of aluminate hydrotalcite with seawater and a volumetric ratio of 4.5 results in very disordered structures. This was shown by a reduction in the mass loss associated with the removal of interlayer water due to the reduction of interlayer sites caused by the misalignment of the metal-hydroxyl layers.

Keywords Hydrotalcite · Aluminate · Bayer liquor · Spectroscopy

Introduction

Hydrotalcites consist of stacked layers of metal cations (M^{2+} and M^{3+}) similar to brucite-like structures. Substitution of divalent cations for trivalent ones, of similar radii, gives rise to positively charged layers [1, 2]. The general formula for these structures is: $[\text{M}_{1-x}^{2+} \text{M}_x^{3+}(\text{OH})_2]^{x+}$

$\text{A}_{x/m}^{m-} \cdot n\text{H}_2\text{O}$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation, and A an interlamellar anion with charge $m-$. Hydrotalcite phases exist for $0.2 \leq x \leq 0.33$ [3]. The resultant positive charge, caused by the substitution of aluminium, is neutralised through the intercalation and adsorption of anions. Carbonate and sulfate have a high affinity for the hydrotalcite interlayer, which limits the removal of other anions from solution if present in high concentrations.

The purification of Bayer refinery process streams through the addition of magnesium compounds can produce a variety of layered double hydroxides, one of which is hydrotalcite [4]. There are numerous papers on the thermal analysis of hydrotalcite [5–9], however to the best of the authors knowledge, the thermal analysis of hydrotalcite formed from seawater and aluminate solutions has yet to be reported. For the full understanding of the formation of hydrotalcite produced from the seawater neutralisation of Bayer refinery liquors, hydrotalcites were synthesised in the laboratory using aluminate and magnesium solutions. One of the aims of this investigation is to establish conditions where only a hydrotalcite phase forms by the addition of different magnesium sources to an aluminate solution.

Experimental

Anhydrous sodium aluminate (NaAlO_2) was used to prepare a 0.2 M solution of sodium aluminate ($\text{Na}[\text{Al}(\text{OH})_4]$). The pH of solution was decreased to pH 12 using 0.1 M hydrochloric acid (HCl). The pH of Bayer liquor is generally greater than 12, therefore aluminate solutions were prepared in a similar pH range. The aluminate hydrotalcites were prepared by a similar method as the co-precipitation method.

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Table 1 Masses and chemicals used to prepare synthetic seawater

Salt	g/L of salt
NaCl	23.926
MgCl ₂ ·6H ₂ O	10.83
Na ₂ SO ₄	4.008
CaCl ₂ ·2H ₂ O	1.519
KCl	0.667
NaHCO ₃	0.196
KBr	0.098
H ₃ BO ₃ (boric acid)	0.026
SrCl ₂ ·6H ₂ O	0.024
NaF	0.003

Three magnesium solutions were prepared using AR grade chemicals: (1) 0.05 M magnesium chloride hexahydrate (MgCl₂·6H₂O), (2) synthetic seawater (Table 1 has the masses and chemicals used), and (3) seawater collected from Inskip Point, QLD, Australia in 2008. The concentration of magnesium in synthetic seawater and seawater is approximately 0.05 M. The formation of the aluminate hydrotalcites involved the addition of one of the three magnesium solutions to the 0.2 M aluminate solution at a rate of 0.5 mL/s. A white precipitate forms instantly and is stirred at 400 rpm for 2 h. The precipitate was vacuum filtered and washed thoroughly with de-ionised water before being placed in an oven (85 °C) overnight to dry. A summary of the aluminate hydrotalcites synthesised are given in Table 2.

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu K α radiation (1.54052 Å). Thermal decomposition of the hydrotalcite was carried out in a TA[®] Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm³/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.5 °C/min up to 1000 °C at high resolution. With the quasi-isothermal, quasi-isobaric heating program of the instrument the

furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and carbon dioxide were analysed.

Results and discussion

X-ray diffraction

X-ray diffraction shows that poorly crystalline hydrotalcite structures formed, Fig. 1. Bayerite (Al(OH)₃) is a major impurity product that forms. The change in synthesis conditions resulted in different impurity phases forming for the nine aluminate hydrotalcites. The purest aluminate hydrotalcite is Alum 1, which was synthesised using MgCl₂·6H₂O at pH 14. Alum 8 and 9 are the most disordered hydrotalcites that formed. Alum 7 was made using the same experimental conditions but with MgCl₂·6H₂O instead of seawater, and the XRD pattern appears to be much more crystalline than Alum 8 and 9. Similar trends are observed for the other aluminate hydrotalcites that are synthesised with either synthetic seawater or seawater (Inskip Point). It is suggested that a species in seawater causes a disordering effect on the hydrotalcite structure. The formation of small quantities of hydrocalumite (Ca₂Al(OH)₆Cl·2H₂O) may cause a distorting effect of the d(003) signal, due to overlapping, for aluminate hydrotalcites formed from seawater.

Thermal analysis

Alum 1–3 (pH 14 with equivalent volumes of Mg and Al solutions)

The three aluminate hydrotalcites (Alum HTs) show a number of common broad bands stretching from 30 to

Table 2 Experimental conditions used to prepare the nine aluminate hydrotalcites

Sample name	Experimental conditions
Alum 1	100 mL of 0.2 M NaAlO ₂ (pH 14) + 100 mL of 0.05 M MgCl ₂ ·6H ₂ O
Alum 2	100 mL of 0.2 M NaAlO ₂ (pH 14) + 100 mL of synthetic seawater
Alum 3	100 mL of 0.2 M NaAlO ₂ (pH 14) + 100 mL of Inskip seawater
Alum 4	100 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 100 mL of 0.05 M MgCl ₂ ·6H ₂ O
Alum 5	100 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 100 mL synthetic seawater
Alum 6	100 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 100 mL of Inskip seawater
Alum 7	60 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 270 mL of 0.05 M MgCl ₂ ·6H ₂ O
Alum 8	60 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 270 mL of synthetic seawater
Alum 9	60 mL of 0.2 M NaAlO ₂ (pH 12—lowered by HCl addition) + 270 mL of Inskip seawater

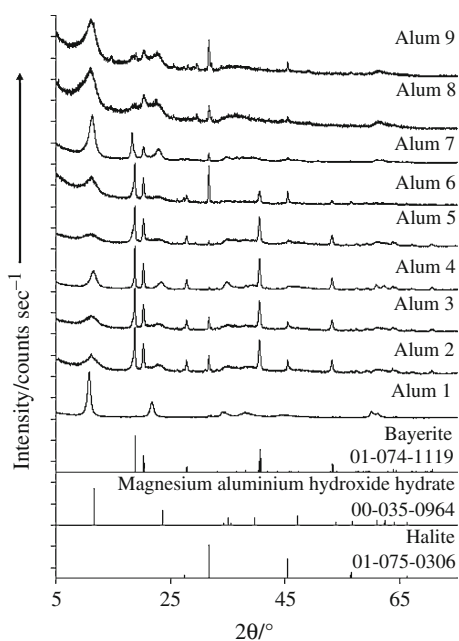


Fig. 1 XRD patterns of aluminate hydrotalcites synthesised using different synthesis conditions

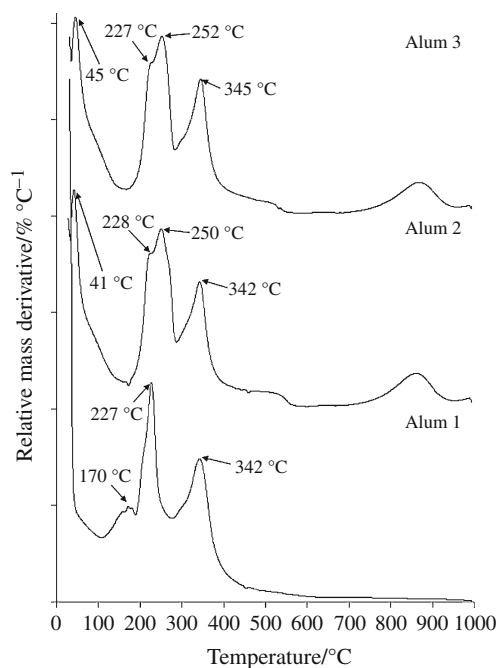
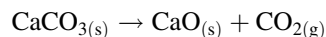


Fig. 2 DTG curves of aluminate hydrotalcites prepared at pH 14 using a 1:1 volumetric ratio (Mg:Al)

450 °C, shown in Fig. 2. Significant differences occur at higher temperatures for aluminate hydrotalcites synthesised with seawater with two mass losses being observed at around 530 and 870 °C. These mass losses are due to the formation of other species other than hydrotalcite due to the presence of ions other than magnesium in seawater. The complimentary mass spectrum (figure not shown)

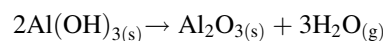
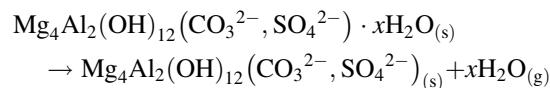
shows that carbon dioxide (CO_2) is released at 520 °C, indicating that this mass loss is associated with the decarbonation of aragonite (identified by XRD). The following decomposition of aragonite is proposed:



The mass loss at around 870 °C is due to the melting of residual salt, which is present in large volumes in seawater. The results show that a considerable amount of residual salt is present in seawater samples, with mass percentages of around 5% being obtained. The slight dehydration of bayerite may also contribute to this mass loss (Table 3).

At lower temperatures, the DTG curves are more complex due to the decomposition of the aluminate hydrotalcite structure. An initial mass loss at temperatures below 110 °C is due to the removal of adsorbed water to the external surface of the hydrotalcite structure. It is observed that a greater amount of adsorbed water is removed for Alum 2 and 3 (seawater Alum HTs) and is proposed to be due to wet residual salt.

The next mass loss observed for the three Alum HTs occurs at temperatures below 300 °C. Alum 1 showed a mass loss of 6.86% at 171 °C and another larger mass loss of 11.70% at 227 °C, to give a total mass loss of 18.56%. Alum 2 observed a combined mass loss of 13.40%, while Alum 3 observed a total mass loss of 12.64%. The decrease in combined mass loss is believed to be due to less inter-layer water in the structure caused by the misalignment of the hydroxyl layers of seawater Alum HTs. Both Alum 2 and 3 appeared to be comprised of two decomposition steps at around 225 and 250 °C. The mass spectra of these Alum HTs detected the evolution of water and OH units between 200 and 260 °C. The mass loss at 225 °C is due to the removal of interlayer water, while the second mass loss is assigned to the dehydration of bayerite. X-ray diffraction results clearly show the presence of bayerite in the seawater Alum HTs and therefore the dehydration of this precipitate is only observed for Alum 2 and 3. The dehydration of synthetic bayerite has been previously reported by Du et al. [5]. The Alum HTs were synthesised at pH 14, which means a 2:1 hydrotalcite structure would form: $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3^{2-}, \text{SO}_4^{2-}) \cdot x\text{H}_2\text{O}_{(s)}$. The dehydration of the Alum HT structure and bayerite are shown below:

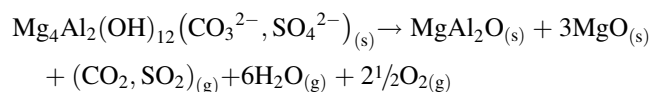


The final decomposition step observed for the three Alum HTs is at around 345 °C. The presence of this peak in all three samples indicates that this mass loss is associated with the hydrotalcite structure, as Alum 1 contains no

Table 3 Percentage mass loss values and decomposition temperatures observed for the nine aluminate hydrotalcites

Peak assignments	Alum 1			Alum 2			Alum 3		
	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%
Adsorbed water	0–108	–	9.13	0–172	41	12.67	0–167	45	12.37
Interlayer water/bayerite dehydration	108–189	171	6.86	172–287	228, 250	13.40	167–283	227, 252	12.64
	189–275	210, 227	11.70						
Dehydroxylation and decarbonation	275–600	342	16.27	287–432	342	9.64	283–482	345	11.54
Decarbonation (CaCO ₃)	–	–	–	432–599	530	2.26	482–582	522	0.91
Bayerite dehydration/melting NaCl	–	–	–	599–950	860	5.43	582–950	871	5.37
	Alum 4			Alum 5			Alum 6		
	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%
Adsorbed water	0–113	–	8.99	0–172	37	11.86	0–167	44	11.72
Interlayer water/bayerite dehydration	113–261	184, 219	17.71	172–306	257, 281	16.04	167–287	221, 253	14.09
Dehydroxylation and decarbonation	261–682	329	15.05	306–472	365	9.25	287–430	339	8.81
Decarbonation (CaCO ₃)	–	–	–	472–610	535	1.90	430–606	523	2.08
Bayerite dehydration/melting NaCl	682–950	832	1.92	–	–	–	606–950	877	8.18
	Alum 7			Alum 8			Alum 9		
	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%	Temp. region/°C	Peak maxima/°C	Mass loss/%
Adsorbed water	0–151	45	12.70	0–166	44	14.56	0–160	–	14.59
Interlayer water/bayerite dehydration	151–264	230, 241	10.91	166–291	237	8.58	160–301	228	9.89
Dehydroxylation and decarbonation	264–950	311, 362	12.82	291–514	327	11.08	301–535	334	9.74
Decarbonation (CaCO ₃)	–	–	–	–	–	–	535–665	630	1.85
Bayerite dehydration/melting NaCl	–	–	–	514–950	895	8.20	665–950	872	6.74

impurity products. This mass loss is assigned to the simultaneous dehydroxylation and decarbonation of the hydrotalcite structure, as shown below:



No significant changes in thermal stability are observed, all decomposition steps associated with the hydrotalcite structure occur within a couple of degrees of each other.

Alum 4–6 (pH 12 with equivalent volumes of Mg and Al solutions)

Unlike the Alum HTs prepared at pH 14, there are significant differences between the Alum HTs synthesised at pH 12, Fig. 3. There are significant changes in the shape of the DTG curves and decomposition temperatures of the three hydrotalcites. Alum 4 is considerably similar to Alum 1,

showing three decomposition steps at 184, 219 and 329 °C. The thermal stability of Alum 4 is lower than Alum 1. Smaller mass losses associated with interlayer water and the dehydroxylation of the hydrotalcite lattice is observed for Alum 4 compared to Alum 1. Therefore, it is proposed that at lower synthesis pH, smaller concentrations of OH ions are incorporated into the hydrotalcite structure. The incorporation of a greater amount of OH units in the hydrotalcite structure increases thermal stability due to an increase in hydrogen bonding, which requires additional energy to break the bonds. The X-ray diffraction pattern also shows that Alum 4 has bayerite in the sample. The dehydration of bayerite is not observed at 252 °C, however a small mass loss of 1.92% at 832 °C may be due to the dehydration of bayerite (no residual salt in sample).

The DTG curves of Alum 5 and 6 differ considerably to Alum 4. The presence of bayerite and halite in the sample introduced additional peaks in the DTG curves. Alum 5 observed three decomposition steps between 200 and

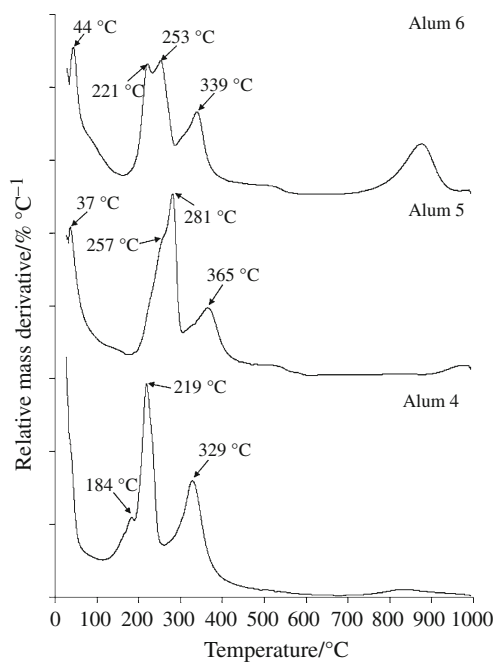


Fig. 3 DTG curves of aluminate hydrotalcites prepared at pH 12 using a 1:1 volumetric ratio (Mg:Al)

400 °C at 257, 281 and 365 °C. The dehydration of bayerite occurred at relatively the same decomposition temperature (257 °C) as Alum 2 and 3. Compared to Alum 4 the thermal stability of the hydrotalcite structure increased significantly. The intercalation of a larger quantity of sulfate anions into this particular hydrotalcite is thought to have caused the increased thermal stability. Intercalation of sulfate anions causes a complex network of hydrogen bonding to occur between the sulfate anions, water, carbonate and the hydroxyl surface of the hydrotalcite layers, which requires a larger amount of energy to break the bonds and therefore causes a delay in decomposition temperature. The intercalation of sulfate anions for Alum 2 and 3 is limited by the concentration of carbonate in seawater. At high pH the dissolution of carbon dioxide is increased, therefore saturated carbonate solutions are expected. At lower pH, the concentration of carbonate would be reduced which would allow for a greater amount of sulfate anions to be intercalated.

Alum 7–9 (pH 12 and the volume of Mg solution is 4.5 times that of the Al solution)

Increasing the volume of magnesium caused a broadening effect on the DTG curves of the aluminate hydrotalcites synthesised with seawater, while Alum 7 (synthesised using magnesium chloride) showed additional peaks, Fig. 4. Unlike the other Alum HTs synthesised with magnesium chloride, Alum 7 observed additional peaks at 45, 241 and

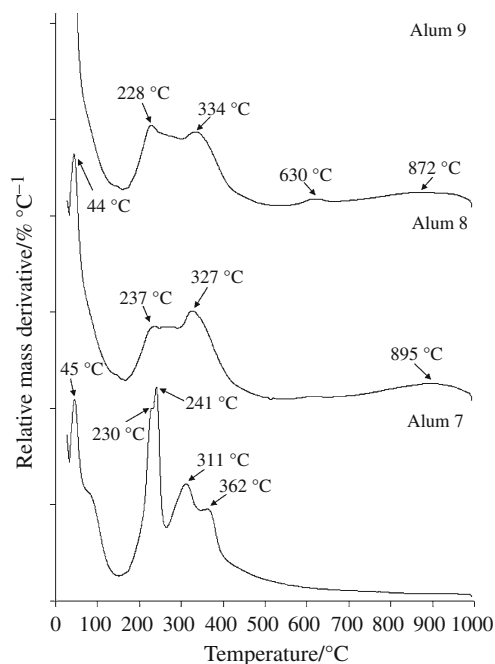


Fig. 4 DTG curves of aluminate hydrotalcites prepared at pH 12 using a 4.5:1 volumetric ratio (Mg:Al)

311 °C. XRD determined that bayerite formed under these synthesis conditions, which is also observed for Alum 4. It is thought that at high pH the hydrotalcite structure forms preferentially over the formation of bayerite for magnesium chloride solutions. The complexity of the seawater system is proposed to remove hydroxide ions from solution for Alum 2 and 3, via the formation of Ca hydroxide species, therefore the pH is reduced and thus the formation of bayerite occurs. A greater concentration of bayerite appears to form for Alum 7 compared to Alum 4, indicated by a mass loss at 241 °C observed in the DTG curve of Alum 7. There is additional adsorbed water associated with Alum 7, indicated by a mass loss increase of almost 4% compared to Alum 1 and 4. The thermal stability of interlayer water remains relatively similar to Alum 1. The dehydroxylation and decarbonation of the aluminate hydrotalcite has begun to split into two peaks: (1) 311 °C and (2) 362 °C. The mass spectrum shows the evolution of water vapour and OH units at 310 °C signifying the dehydroxylation of the hydrotalcite, while the release of predominately CO₂ 355 °C indicates that the decarbonation of the structure occurs at 362 °C. Therefore, different interlayer bonding of the carbonate, hydroxide and water molecules exists in Alum 7. It is proposed that a smaller amount of complex bonding between carbonate and water exists in this hydrotalcite.

The DTG curves of the seawater Alum HTs 8 and 9 are extremely broad, ranging from 200 to 350 °C. Two peaks can be separated at around 230 and 330 °C assigned to the removal of interlayer water and the decomposition of the

hydroxyl layers, respectively. It is believed a third peak at around 250 °C due to the dehydration of bayerite causes the broadening of the peak. XRD has shown that Alum 8 and 9 are very disordered, while Alum 1, 4 and 7 are significantly more ordered. Alum 1 is the most ordered hydrotalcite structure investigated and as such has the largest number of intercalation sites within the interlayer region of the structure. It, therefore, has the greatest mass loss of interlayer water. For disordered structures, a reduction in the number of interlayer sites is caused by the misalignment of the metal-hydroxyl layers. This is reflected in a decrease in mass loss percentages for Alum 8 and 9.

Conclusions

This investigation successfully synthesised hydrotalcite structures using aluminate solutions and a magnesium source ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, synthetic seawater, or seawater from Inskip Point). The aluminate hydrotalcites have been characterised using XRD and thermal analysis. A pure aluminate hydrotalcite formed when prepared using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, pH 14, and an aluminate: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ volumetric ratio of 1:1. The DTG of Alum 1 was used to help identify the mass losses observed in hydrotalcites synthesised using seawater. Differences in the DTG curves were due to the different phases that formed for each of the hydrotalcite samples. The decomposition of the aluminate hydrotalcite structure occurs in two steps: (1) removal of interlayer water (230 °C) and (2) the simultaneous dehydroxylation and decarbonation (330 °C). The dehydration of bayerite is observed at 250 °C. Increasing the volumetric ratio of magnesium to aluminium resulted in a much more

disordered structure and as a result a smaller quantity of interlayer water was intercalated into the structure (Alum 8 and 9). Aluminate hydrotalcites synthesised using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ show less contamination of bayerite than those synthesised using seawater.

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