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Thermal decomposition of Bayer precipitates formed at varying temperatures

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Abstract Bayer hydrotalcites prepared using the seawater neutralisation (SWN) process of Bayer liquors are characterised using X-ray diffraction and thermal analysis techniques. The Bayer hydrotalcites are synthesised at four different temperatures (0, 25, 55, and 75 °C) to determine the effect of synthesis temperature on the thermal stability of the Bayer hydrotalcite structures and the mineralogical phases that form. The interlayer distance increased with increasing synthesis temperature, up to 55 °C, and then decreased by 0.14 Å for Bayer hydrotalcites prepared at 75 °C. The three mineralogical phases identified in this investigation are; (1) Bayer hydrotalcite, (2), calcium carbonate species, and (3) hydromagnesite. The DTG curve can be separated into four decomposition steps; (1) the removal of adsorbed water and free interlayer water in hydrotalcite (30–230 °C), (2) the dehydroxylation of hydrotalcite and the decarbonation of hydrotalcite (250–400 °C), (3) the decarbonation of hydromagnesite (400–550 °C), and (4) the decarbonation of aragonite (550–650 °C).

Keywords Thermal analysis · Hydrotalcite · Bayer liquor · Seawater neutralisation

Introduction

The alumina industry produces large quantities of highly alkaline bauxite refinery residue (red mud), and therefore treatment is required before it can be safely discharged into the environment or stored. The seawater neutralisation of red mud is one particular method used to reduce both the pH and dissolved metal concentrations of the residue. This is achieved through the precipitation of Mg, Ca, and Al hydroxide and carbonate minerals [1]. The formation of these hydrotalcite-like compounds removes hydroxide ions and oxy-anions of transition metals through a combination of intercalation and adsorption mechanisms, while the carbonate concentration is reduced through the precipitation of calcium carbonate species.

Hydrotalcites consist of stacked layers of metal cations (M^{2+} and M^{3+}) similar to brucite ($Mg(OH)_2$). For hydrotalcite-like structures, the substitution of divalent cations for trivalent ones (of similar radii), gives rise to a positive charge on the brucite-like layers [2, 3]. The general formula for these structures are: $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]^{x+}A^{m-}_{x/m}\cdot nH_2O$, 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 $0.2 \leq x \leq 0.33$ [4]. The positively charged hydroxyl layers are neutralised through the intercalation and adsorption of anionic species, therefore stabilising the structure. Anions that are intercalated between the hydroxyl layers need to meet certain criteria, including having a high charge density and small anionic radius. Carbonate and sulfate have one of the highest affinities for the hydrotalcite interlayer, and reduces the removal of other anionic species from solution if present in high concentrations.

This study is looking at determining the most stable Bayer hydrotalcite that forms at these different synthesis temperatures. It is proposed that different precipitates will form depending on the temperature of the resultant solution during the SWN process. Therefore, any structural changes that result from increasing temperatures need to be

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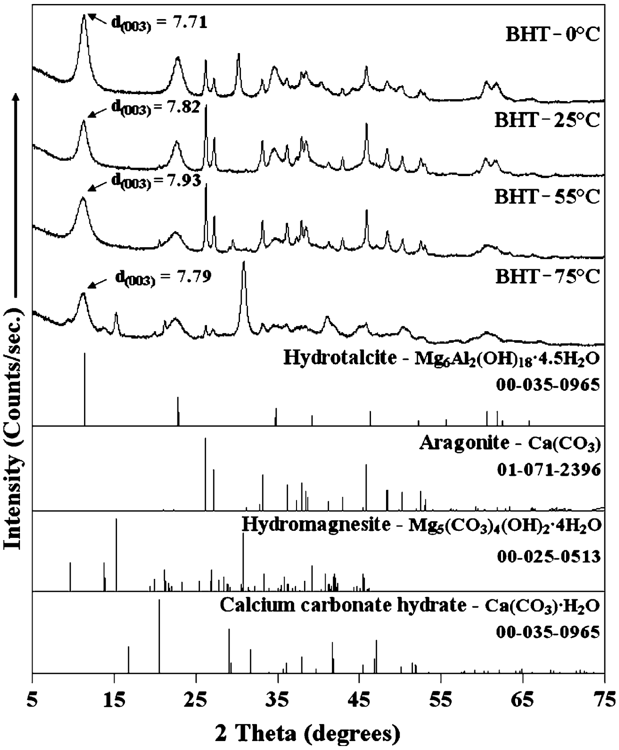

Fig. 1 X-ray diffraction patterns of the Bayer precipitates formed at varying temperatures

assessed to see if there is any effect on the removal abilities of Bayer hydrotalcites. The mechanism for intercalation of anionic species and the characterisation of the products of the seawater neutralisation of red mud have previously been investigated by the authors [5, 6].

Experimental

Synthesis of Bayer precipitates

Synthetic supernatant liquor (with the following concentrations: Al = 4.1 g/L Al_2O_3, caustic = 8.1 g/L Na_2O, and carbonate = 6.3 g/L Na_2O), was neutralised with seawater, collected from Inskip Point, QLD, Australia. Dependent on the desired synthesis temperature, the supernatant liquor was cooled using an ice water bath or heated on a hotplate to 0, 25, 55, and 75 °C before the addition of 4.5 times the volume of seawater to liquor, at a rate of 5 mL a minute. The mixture was continuously stirred for 2 h before being vacuum filtered and washed thoroughly with de-ionised water. The precipitate was dried in an oven (85 °C) overnight, to remove any surface water. The SWN of Bayer liquors is highly similar to the co-precipitation method used to prepare synthetic hydrotalcite structures.

Characterisation techniques

Thermal decomposition of approximately 50 mg of hydrotalcite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min), at a rate of 2.0 °C/min up to 1,000 °C. X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu Kα radiation (1.54052 Å). For more information on the experimental and analysis techniques used, refer to previous work by the authors [5–7].

Results and discussion

X-ray diffraction

The X-ray diffraction patterns of the precipitates and the corresponding reference patterns are given in Fig. 1. Multiple phases are detected and in different proportions for the four Bayer precipitates that formed. The most significant phase is hydrotalcite, reference pattern (00-035-0965), identifiable as the broader peaks in the pattern. The broadness of the hydrotalcite peaks indicates that poorly crystalline Bayer hydrotalcites formed under these synthesis conditions. The crystallinity of these Bayer hydrotalcites decrease with increasing temperature, cleary shown by the broadening and overlapping of the two peaks at 60° 2θ. The $d_{(003)}$ spacing of the synthesised Bayer hydrotalcites (BHT) from 0 to 75 °C are 7.71, 7.82, 7.93, and 7.79 Å, respectively.

The Bayer hydrotalcites that formed are believed to have a Mg:Al ratio between 3 and 4. Hydotalcite structures formed at high pH generally have a 2:1 Mg:Al ratio, while those formed between 8 and 10 have a Mg:Al ratio of 3:1. Hydrotalcites with a 4:1 Mg:Al ratio are also possible, however, the pH in the synthesis of these Bayer hydrotalcites did not reach values below 8. The Bayer hydrotalcites formed at pH 8.35, and therefore a Mg:Al ratio of around 3 is expected. Energy Dispersive X-ray spectroscopy (EDX) revealed that these Bayer hydrotalcites had an average Mg:Al ratio of 3.5:1.

The basal spacing for the Bayer hydrotalcites increased with increasing temperature up to 55 °C, suggesting that the removal ability increased. The predominate anions intercalated into the interlayer region are carbonate, sulfate, and water molecules. Carbonate and sulfate both have very high affinities for the hydrotalcite interlayer. The disorder of the hydrotalcite structures, as the temperature increased, may have caused this increase in interlayer distance. A disordered structure has hydroxyl layers that are slightly askew, which may allow for more anions and water molecules to be intercalated into the structure, compared to more crystalline structures that are aligned with finite interlayer distances. Therefore, it is proposed that the increase in basal spacing for Bayer hydrotalcites at 25 and 55 °C is due to an increase in interlayer anions and water molecules. Bayer hydrotalcites that formed at 75 °C, showed a reduction in interlayer distance. This reduction is believed to be due to the dehydration of the interlayer region of the hydrotalcite structure at these increased temperatures.

Another predominant phase that formed during the SWN process is aragonite ($CaCO_3$), which has an orthorhombic crystal system. Only a small quantity of aragonite formed at 75 °C, however, the formation of other carbonate species appear to be favoured at these elevated temperatures, hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) and calcium carbonate hydrated (CCH). Aragonite is more crystalline than hydrotalcite, and appears to form predominantly at 25 and 55 °C. Bayer liquors have high carbonate concentrations, and therefore it is not unexpected that a range of carbonate species formed. Minor quantities of CCH also formed, for all temperatures except at 0 °C. The concentration of CCH increased with increasing synthesis temperature, clearly shown by the sharp peak overlapping the $d_{(006)}$ peak of hydrotalcite at approximately 18° 2θ.

Thermal analysis—TG and DTG

Decomposition between 30 and 230 °C

The four precipitates, in increasing order of synthesis temperature, show a common broad band stretching from 30 to 175 °C, shown in Fig. 2. The broad band appears to be due to a number of overlapping bands, primarily situated at around 50 and 140 °C. The first band is assigned to the removal of adsorbed water to the external surfaces of the different precipitates that formed. The second band is believed to be due to the evolution of water originating from free interlayer water in Bayer hydrotalcite. The separation of the bands is most clearly seen in Fig. 2a, where a band assigned to adsorbed water is observed at 50 °C with a mass loss of 3.17%, while the second band observed at 156 °C, assigned to the removal of interlayer water, has a mass loss of 9.85%. The combined mass loss between 0 and 200 °C decreased with increasing synthesis temperature; 13.02%, 11.94%, 11.17%, and 9.09%, respectively. It is believed that at increasing temperature, less water is associated with these structures due to slight evaporation/dehydration. It is observed that the adsorbed water evolution temperature for these structures decrease with increasing synthesis temperatures. This suggests there is

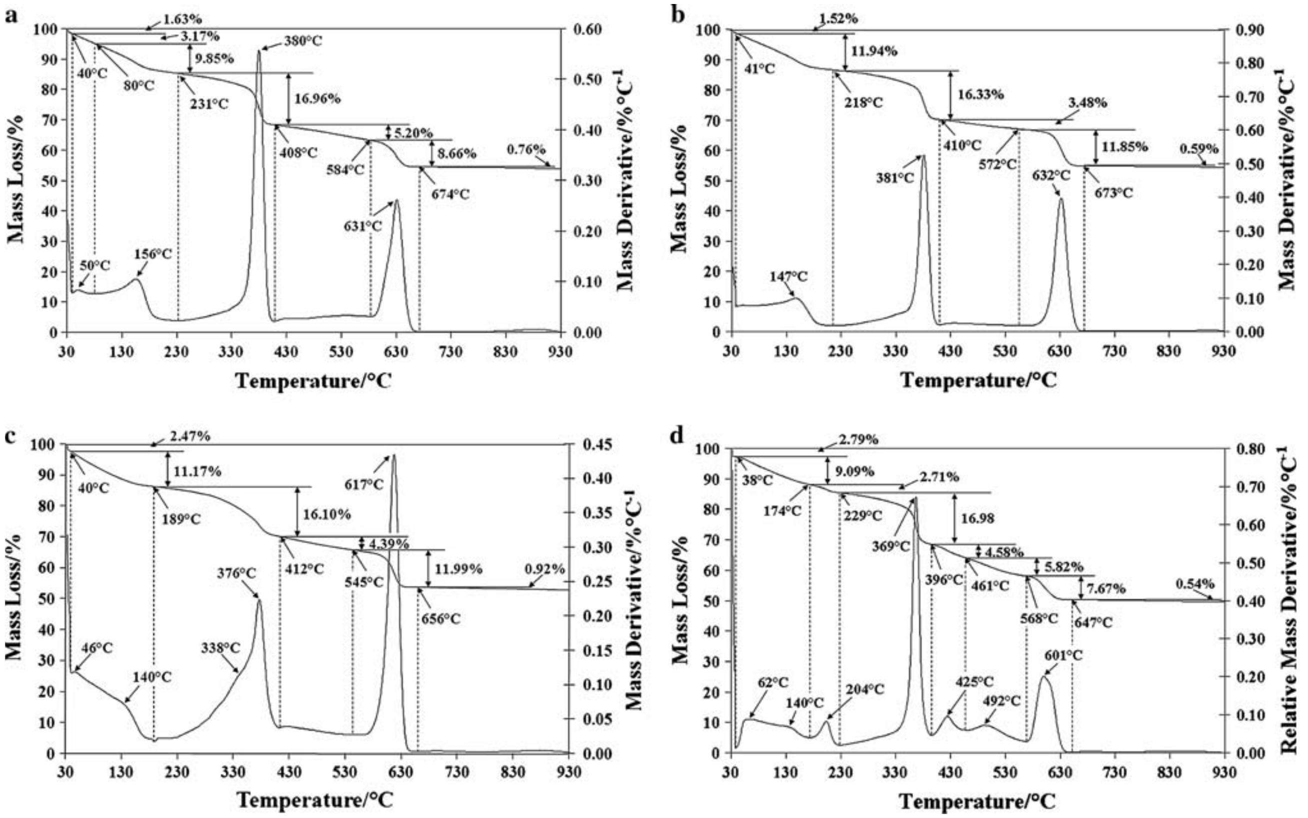

Fig. 2 Thermal analysis of Bayer precipitates formed at different temperatures

less hydrogen bonding, involved in Bayer hydrotalcites formed at elevated temperatures, and therefore, rendering them slightly less stable.

The molecular formula of the Bayer hydrotalcite that formed, is thought to be as follows; $Mg_7Al_2(OH)_{18}(CO_3^{2-},SO_4^{2-}) \cdot xH_2O$. The amount of interlayer water associated with these hydrotalcites is unknown, however, previous work by the authors (synthesis of hydrotalcites using SWN conditions) [5], suggests that there are 4–5 mol of water associated with these structures. The decomposition step for the removal of interlayer water is proposed to be as follows:

$$Mg_7Al_2(OH)_{18}(CO_3^{2-}, SO_4^{2-}) \cdot xH_2O_{(s)} \rightarrow Mg_7Al_2(OH)_{18}(CO_3^{2-}, SO_4^{2-})_{(s)} + xH_2O_{(g)}$$

The peak at around 204 °C, for the 75 °C precipitate, is believed to be due to the evolution of water vapour associated with the dehydration of hydromagnesite. The formula used to represent hydromagnesite is based on the reference formula identified by XRD. The dehydration of hydromagnesite is as follows:

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O_{(s)} \rightarrow Mg_5(CO_3)_4(OH)_{2(s)} + 4H_2O_{(g)}$$

Decomposition between 250 and 400 °C

Numerous studies on the decomposition of hydrotalcites report the dehydroxylation of the brucite-like layers and the decarbonation of the interlayer region occurring at temperatures generally between 300 and 400 °C. The possibility of organics, present in Bayer liquor, in the samples prevented mass spectroscopy data to be obtained on the evolved gases, therefore, assignments of the peaks in this work will be determined from previous work by the authors on synthetic hydrotalcites prepared using SWN conditions [5, 8]. The DTG curves of the Bayer precipitates are compared with pure and synthesised compounds, determine to be present in the precipitate by XRD, Fig. 3. This figure will be used in the analysis of the curves to determine the assignments of the mass losses observed for the Bayer hydrotalcites.

The decomposition temperature, between 250 and 400 °C, decreases with increased synthesis temperatures, 380, 381, 376, and 369 °C respectively. This decrease in decomposition temperature indicates that Bayer hydrotalcites formed at 0 and 25 °C are more stable than those formed at 55 and 75 °C. Synthetic hydrotalcite, with only carbonate intercalated into the structure has a decomposition temperature at around 350 °C [5, 8]. The Bayer hydrotalcites synthesised in this investigation all obtained much higher decomposition temperatures. This increase in stability is believed to be due to the intercalation of sulfate. The intercalation of sulfate increases the stability of the structure due to an increase in the number of hydroxyl groups involved in a network of hydrogen bonding between the sulfate anions and the cations in the brucite-like layers.

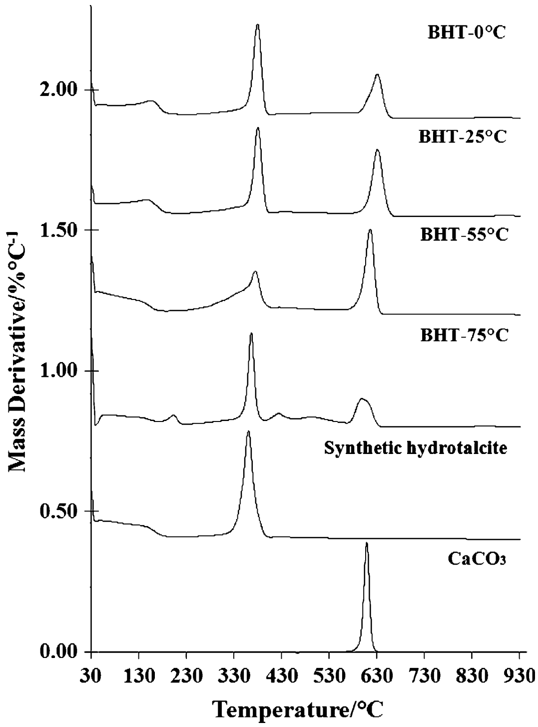

Fig. 3 Stacked DTG curves of the Bayer precipitates and the reference DTG curves

Raman bands situated at around 1,085 cm^{-1} are assigned to the ν_1 symmetric stretching modes of carbonate, while the smaller band at around 985 cm^{-1} is allocated to the ν_1 symmetric stretching modes of sulfate, figure not shown. Multiple bands in the same region are due to the carbonate/sulfate anions in different environments. The presence of these bands suggests that Bayer hydrotalcite predominantly contain carbonate and sulfate in the interlayer region.

The symmetric decomposition step at around 380 °C for Bayer hydrotalcites synthesised at 0 and 25 °C, and at 369 °C for the Bayer hydrotalcite synthesised at 75 °C, indicates the simultaneous dehydroxylation and decarbonation of these structures. The Bayer hydrotalcite synthesised at 55 °C, however, is asymmetric in shape. It is believed the existence of two types of interlamellar water molecules are present in this structure; (1) water molecules that are bonded to the cationic brucite-like surface (low 300 °C), and (2) water molecules that are solvating the intercalated anionic species (high 300 °C). The DTG curves of the four hydrotalcites have been peak fitted and stacked, Fig. 4, and shows that all four hydrotalcites have multiple bands.

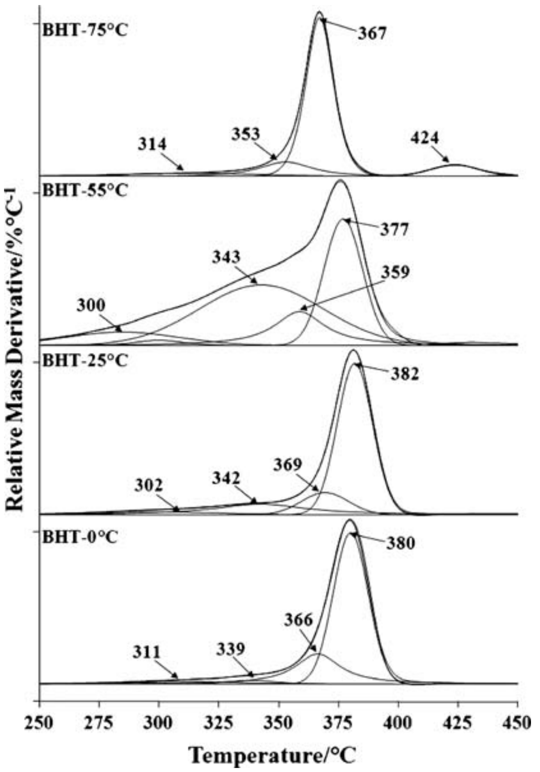

Fig. 4 Stacked DTG curves of the Bayer precipitates in the dehydroxylation/decarbonation region

Four bands are present for three of the precipitates; BHT-0 °C observed bands at 311, 339, 366, and 380 °C, BHT-25 °C observed bands at 302, 342, 369, and 382 °C, and for BHT-55 °C bands at 300, 343, 359, and 377 °C are observed. BHT-75 °C observed three bands at 314, 353, and 367 °C. The bands at lower decomposition temperatures, at around 300 °C, are assigned to the removal of weakly bonded interlayer water. The bands at around 340 °C are assigned to the initial dehydroxylation of the brucite-like layers of the Bayer hydrotalcite structures. There appears to be a slight delay in decomposition temperature as the synthesis temperature increased. This indicates that the hydroxyl layers of Bayer hydrotalcite become slightly more stable with increased synthesis conditions. The Bayer precipitate formed at 55 °C showed a very large broad band at 343 °C, compared to the other precipitates. Raman spectroscopy results indicate a smaller quantity of interlayer water is present in precipitates formed at 55 °C, shown by the absence of a band at 3,000 cm^{-1}, figure not shown. A reduction in the amount of interlayer water is suggested to make the dehydroxylation process easier, due to a reduction in the number of hydrogen bonds.

The bands situated at around 360 °C are believed to be due to the slight decarbonation of aragonite. Aragonite is thermally unstable at standard temperature and pressure, and transforms to calcite over time. It is thought that a small phase transition occurs, which results in a small mass loss. Aragonite is assigned to these bands based on; (1) XRD showed an increase in the amount of aragonite in the sample up to 55 °C and minimal amounts in the 75 °C precipitates, (2) an increase in intensity of the DTG peak at around 360 °C as synthesis temperature increased to 55 °C, and (3) the absence of a DTG band at 360 °C for the precipitate formed at 75 °C.

The final bands at 380, 382, 377, and 367 °C, are assigned to the simultaneous dehydroxylation and decarbonation of the Bayer hydrotalcites. The removal of interlayer sulfate anions is also removed during this decomposition step. The presence of sulfate anions is believed to have increased the stability of the hydrotalcite structures, through a highly complex network of strong hydrogen bonds between the interlayer anions, water, and the cationic surface of the brucite-like layers. The decrease in thermal stability of the hydrotalcite formed at 75 °C is believed to be due to the dehydration of the interlayer region during synthesis, which is supported by the decrease in interlayer distance of this hydrotalcite found by XRD techniques. A reduction in the number of interlayer anions that form complex networks of hydrogen bonding renders the structure more thermally unstable. The full dehydroxylation and decarbonation decomposition steps of Bayer hydrotalcite are as follows:

$$\begin{aligned}&\mathrm{Mg_7Al_2(OH)_{18}\left(CO_3{}^{2-},SO_4{}^{2-}\right)_{(s)}}\\&\quad\rightarrow \mathrm{MgAl_2O_{4(s)}} + 6\mathrm{MgO_{(s)}} + \mathrm{\left(CO_2,SO_2\right)_{(g)}} + 9\mathrm{H_2O_{(g)}}\\&\qquad + \mathrm{O_{2(g)}}\end{aligned}$$

The additional band observed at 424 °C, in the 75 °C precipitate, is due to the dehydroxylation of hydromagnesite, shown below. The dehydroxylation of synthetic hydromagnesite has been reported to occur between 375 and 450 °C [9, 10].

$$\mathrm{Mg_5(CO_3)_4(OH)_{2(s)}} \rightarrow 4\mathrm{MgCO_{3(s)}} + \mathrm{MgO} + \mathrm{H_2O_{(g)}}$$

Decomposition between 400 and 650 °C

This temperature region can be separated into two sections; (1) between 400 and 550 °C, and (2) between 550 and 650 °C. The first region is assigned to the decomposition of $\mathrm{MgCO_3}$ (final decomposition step of hydromagnesite): $4\mathrm{MgCO_{3(s)}} \rightarrow 4\mathrm{MgO_{(s)}} + 4\mathrm{CO_{2(g)}}$. The peaks are observed at 425 and 492 °C, and are only present in the 75 °C precipitate, confirming the observations obtained for XRD.

The sharp intense peak at around 600 °C is assigned to the decarbonation of aragonite. The mass loss step and peak maxima are as follows; BHT-0 °C peak maximum at 631 °C and a mass loss of 8.66%, BHT-25 °C peak maximum at 632 °C and a mass loss of 11.85%, BHT-55 °C peak maximum at 617 °C and a mass loss of 11.99%, and BHT-75 °C peak maximum at 601 °C and a mass loss of 7.67%. The stability of aragonite appears to decrease at elevated temperatures. The decarbonation of aragonite is as follows:

$$\mathrm{Ca(CO_3)_{(s)}} \rightarrow \mathrm{CaO_{(s)}} + \mathrm{CO_{2(g)}}$$

Conclusions

X-ray diffraction identified three mineralogical phases that form due to the SWN of supernatant liquor. The variation in synthesis temperature caused the formation of some of the phases to become more favourable at elevated temperatures, for example hydromagnesite. The formation of aragonite is favourable at temperatures between 25 and 55 °C. The synthesis temperature did not appear to affect the quantity of Bayer hydrotalcite that formed, however, the interlayer distance did change with temperature. The interlayer distance of Bayer hydrotalcite increased up to 55 °C, maximum of 7.93 Å, and then decreased to 7.79 Å at 75 °C. This reduction in interlayer distance is believed to be due to the dehydration of the structure during synthesis. It is proposed Bayer hydrotalcites formed at 55 °C are the most effective in removing anions from supernatant liquors.

The thermal analysis of Bayer precipitates showed four decomposition steps. The initial decomposition step (30–230 °C) involved the evolution of adsorbed water to the external surfaces of the precipitates (30–100 °C), and the removal of free interlayer water in Bayer hydrotalcites (100–200 °C). The second major mass loss included multiple decomposition steps including: (1) the removal of weakly bonded interlayer water in the hydrotalcite structures (~300 °C), (2) the partial dehydroxylation of the hydrotalcite structures (~340 °C), (3) the slight decarbonation of aragonite, and (4) the simultaneous dehydroxylation and decarbonation of the remaining hydrotalcite structure (~375 °C). The Bayer hydrotalcite formed at 55 °C showed a much larger partial dehydroxylation at 343 °C, believed to be due to a smaller amount of interlayer water in the structure, thus making the dehydroxylation process easier. The high decomposition temperatures for the full dehydroxylation and decarbonation processes are believed to be due to substantial network of hydrogen bonding between the cationic surface of the layers and solvated intercalated anions, such as sulfate and carbonate. The third decomposition stage involved the decarbonation of hydromagnesite, while the final decomposition stage at 600 °C, involved the decarbonation of aragonite and CCH.

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