The effect of synthesis temperature on the formation of hydrotalcites in Bayer liquor–a vibrational spectroscopic analysis

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ABSTRACT

The seawater neutralisation process is currently used in the Alumina industry to reduce the pH and dissolved metal concentrations in bauxite refinery residues, through the precipitation of Mg, Al, and Ca hydroxide and carbonate minerals. This neutralisation method is very similar to the co-precipitation method used to synthesise hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$). This study looks at the effect of temperature on the type of precipitates that form from the seawater neutralisation process of Bayer liquor. The Bayer precipitates have been characterised by a variety of techniques, including X-ray diffraction, Raman spectroscopy and infrared spectroscopy. The mineralogical composition of Bayer precipitates largely includes hydrotalcite, hydromagnesite, and calcium carbonate species. XRD determined that Bayer hydrotalcites that are synthesised at 55 °C have a larger interlayer distance, indicating more anions are removed from Bayer liquor. Vibrational spectroscopic techniques have identified an increase in hydrogen bond strength for precipitates formed at 55 °C, suggesting the formation of a more stable Bayer hydrotalcite. Raman spectroscopy identified the intercalation of sulfate and carbonate anions into Bayer hydrotalcites using these synthesis conditions.

KEYWORDS: hydrotalcite, Bayer liquor, characterisation, spectroscopy

INTRODUCTION

The Bayer process produces large quantities of the highly alkaline bauxite refinery residue (red mud), which consist of a variety of hazardous anions. Red mud requires treatment before it can be safely discharged into the environment or stored. The seawater neutralisation of red mud reduces both the pH and dissolved metal concentrations of the residue, and has been employed in a number of refineries around the world. This is achieved through the precipitation of Mg, Ca, and Al hydroxide and carbonate minerals [1]. The formation of these compounds removes oxy-anions of transition metals through a combination of intercalation and adsorption mechanisms.

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 [2, 3]. The general formula for these structures is: $[M^{2+}_{1-x}\ M^{3+}_{x}(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, 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 resultant positive charge, caused by the substitution of Al, is neutralised through the intercalation and adsorption of anions. The affinity of anions for the interlayer region is based on charge density and size. Carbonate has a high affinity for the hydrotalcite interlayer, which limits the removal of other anions from solution if present in high concentrations.

Hydrotalcites have been synthesised using Bayer refinery liquors under seawater neutralisation (SWN) conditions. This investigation will enable the identification of the type of minerals that form during the SWN of bauxite refinery residues, and the mechanism of formation. This study is looking at determining the most stable precipitate that forms at different 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 assessed to see if there is any effect on the formation of Bayer hydrotalcite. The mechanism for the intercalation of different anions and the characterisation of the products of the seawater neutralisation of red mud have previous been investigated by the authors [5, 6].

EXPERIMENTAL

Supernatant liquor (SNL) from an Australian alumina refinery was neutralised with seawater (SW), collected from Inskip Point, QLD, Australia in October 2008. The chemical composition of SNL and seawater can be found in Table 1. The average initial pH value for SNL is 12.40, and a final pH value of around 9 was obtained once the SNL had been neutralised with seawater. Dependent on the desired synthesis temperature, the Bayer liquor was cooled using an ice water bath and heated on a hotplate to 0, 25, 55, and 75 °C before the addition of 4.5 times the volume of seawater to Bayer liquor. Seawater was added to the liquor at a rate of 5 mL a minute. The mixture was continuously stirred for 2 hours 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.

Characterisation of the precipitates included XRD, Raman spectrocopy, and infrared spectroscopy. 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). The Fourier Transform Raman spectroscopy (FT-Raman) analyses were performed on powder samples using a Perkin Elmer System 2000 Fourier transform spectrometer equipped with a Raman accessory comprising a Spectron Laser Systems SL301 Nd:YAG laser operating at a wavelength of 1064 nm. Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000-525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 m/s.

Spectral manipulation such as baseline correction, smoothing, and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA). For more information on the experimental and analysis techniques used, refer to previous work by the authors [6, 7].

RESULTS AND DISCUSSION

X-Ray Diffraction

The X-ray diffraction patterns of the precipitates and the corresponding reference patterns are given in Figure 1. The results show that multiple phases precipitate during the SWN process, in particular hydrotalcite-like structures, and calcium and magnesium carbonate species. The main peak at around 11° 2θ (d_{003} plane peak), is assigned to hydrotalcite (00-035-0965). The broadness of the hydrotalcite peaks indicates that poorly crystalline Bayer hydrotalcites are formed under these synthesis conditions. For more crystalline products, a slower addition rate is required along with a longer syntheis period. However, these studies are based on real scenarios in the Alumina industry. The crystallinity of these Bayer hydrotalcites decrease with increasing temperature, shown by the broadening of the 2 peaks at 60° 2θ. The d_{003} spacing of the synthesised Bayer hydrotalcites (BHT) from 0 °C to 75 °C are 7.71, 7.82, 7.93, and 7.79 Å, respectively. The d_{003} plane peak represents the interlayer distance between the hydroxyl layers of the hydrotalcite structure. The basal spacing for the Bayer hydrotalcites increased with increasing temperature, suggesting that the removal ability of hydrotalcites formed from the co-precipitation method increase up to 55 °C. Based on the results of this study, the synthesis of Bayer hydrotalcites formed at 55 °C appears to be the most effective in the removal of anions from Bayer liquors. 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. Therefore, for optimal removal of anions from Bayer liquors, it is suggested that temperatures between 25 and 55 °C should be used in the seawater neutralisation process.

The elemental composition (Energy dispersive X-ray spectroscopy - EDX) of the Bayer hydrotalcites indicates that the SWN process produces hydrotalcites with a Mg:Al ratio between 3 and 4, with the average value of 3.5, for the hydrotalcites prepared at 0, 25, and 55 °C. The Mg:Al ratios are 3.4, 3.8, and 3.4, respectively. The precipitate formed at 75 °C resulted in a Mg:Al ratio of 6.8. This large

increase in Mg:Al ratio is due to the precipitation of hydromagnesite, however, it is thought a Mg:Al ratio of around 3.5 is still obtained at 75 °C, due to minimal changes observed in other techniques used. The elements detected using EDX are Mg, Al, Ca, S, O, C, and Cl. No significant changes were observed in S concentrstions, therefore, the synthesis temperature does not appear to have an effect on the uptake of sulfate anions. Apart from carbonate, sulfate, and hydroxide, no other anions are thought to be adsorbed or intercalated into these structures.

Another predominant phase that formed during the SWN process is aragonite ($CaCO_3$ – orthorhombic crystal sturcture). This mineral phase appears to be more crystalline than hydrotalcite, and appears to form predominantly at 25 and 55 °C. The formation of aragonite is unfavourable at 75 °C, shown by a significant reduction in peak intensity. At this elevated temperature, the formation of a new specie; hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$)) becomes favourable. The formation of calcium carbonate hydrate (CCH), increases with increased synthesis temperatures, shown be the increasing peak intensity at around 20° 2θ. The formation of hydromagnesite and CCH reduces the concentration of available carbonate in solution, and therefore limits the formation of aragonite.

Vibrational spectroscopy

Hydroxyl stretching and bending vibrations.

The Raman spectra and infrared spectra of the OH stretching region of the Bayer precipitates are shown in Figure 2. Both Raman and infrared band profiles in the hydroxyl stretching region are broad, consisting of multiple overlapping bands. These bands include water in the interlayer between the hydroxyl layers, which may or may not form bridging-type bonds with interlayer anions, water adsorbed on the outer surface, and free water between layers. These broad bands are assigned to the stretching modes of hydroxyl groups in the hydroxyl layers and water molecules associated with the hydrotalcite structure. Band component

analysis was used to help identify the different hydroxyl species in both the Raman and infrared spectra.

The Raman bands in the 3800 to 3000 cm^{-1} region are attributed to the H-bonded stretching vibrations of the OH units of the brucite-like sheets, and stretching vibrations of water molecules. The low intensity bands at 3570 cm^{-1} and the higher intensity bands at 3440 cm^{-1} are assigned to the OH stretching vibrations of OH units in the brucite-like sheets. The Raman bands at 3570, 3565, 3574, and 3566 cm^{-1}, for the four precipitates in order of increasing temperature, are assigned to the OH stretching vibrations of –MgOH, while bands at 3445, 3451, 3438, and 3438 cm^{-1} are assigned to the OH stretching vibrations of –AlOH in hydrotalcite and to a small extent hydromagnesite for the 75 °C precipitate.

The bands in the infrared spectra are at slightly higher wavenumbers and include a couple of additional bands. The infrared spectra of BHT @ 25°C and BHT @ 55°C are quite similar in appearance, whereas, the spectrum for BHT @ 0°C has one less band, while BHT @ 75°C has two additional sharp small intensity bands. It is proposed that the absence of the additional band for BHT @ 0°C is due to the overlapping of the broad intense peaks, while the additional sharp peaks in BHT @ 75°C is due to two different kinds of OH groups in hydromagnesite. The band at 3519 cm^{-1} is believed to participate in hydrogen bonding, while the other band at 3648 cm^{-1} does not [8]. According to the results obtained by XRD, hydromagnesite only forms at 75 °C. Infrared bands at 3598, 3622, 3643, and 3637 cm^{-1} are assigned to the OH stretching vibrations of –MgOH, while bands at 3481, 3527, 3561, 3567 cm^{-1} are assigned to the OH stretching vibrations of –AlOH. There is a slight shift to slightly higher wavenumbers, indicating a weaking of the bonding. The other bands within the region 3600 to 3400 cm^{-1} are attributed to the stretching frequencies of hydroxyl groups bonded to Al, Mg or a combination of both.

The Raman and infrared bands in the region 3400 to 3200 cm^{-1} are assigned to the O-H stretching vibrations of water coordinated to the cations in the brucite-like layers. Bayer precipitates formed at 0 and 25 °C observe an additional Raman band at around 2950 cm^{-1}, assigned to water strongly hydrogen bonded to an anion

intercalated into the hydrotalcite interlayer. However, due to the high concentration of carbonate anions in Bayer liquor streams, the band at 2950 cm^{-1} is proposed to be carbonate bonded to water in the hydrotalcite interlayer. Generally these lower wavenumber bands are not observed in Raman spectra, due to water being a very weak Raman scatterer. Raman bands at 3120, 3097, 3185, and 3126 cm^{-1}, with increasing temperature, are also attributed to hydrogen bonded water molecules to interlayer anions. The corresponding infrared bands are more intense, due to a large change in dipole moment in water. BHT @ 0°C observed four bands in this lower wavenumber region, 3097, 2916, 2769, and 2596 cm^{-1}. The other Bayer precipitates observed three bands in this lower wavenumber region. Infrared bands at 3097 and 2916 cm^{-1} for BHT @ 0°C, 3034 and 2899 cm^{-1} for BHT @ 25°C, 3078 and 2932 cm^{-1} for BHT @ 55°C, and 3172 and 2950 cm^{-1} for BHT @ 75°C are believed to be attributed to water hydrogen bonded to interlayer anions in the hydrotalcite interlayer. Infrared bands at around 2700 and 2500 cm^{-1} are assigned to the calcium carbonate specie, aragonite and calcium carbonate hydrate. The infrared bands at 2769 and 2703 cm^{-1}, BHT @ 0°C and BHT @ 75°C respectively, are believed to be due to adsorbed water hydrogen bonded with carbonate associated with hydromagnesite, while bands at around 2550 cm^{-1} are assigned to water hydrogen bonded to carbonate, associated with aragonite. These assumptions are base on XRD results, which showed the presence of aragonite in all samples, and hydromagnesite in BHT @ 75°C.

The Raman spectrum of BHT @ 55°C appears to be more compact then the other three samples. It is suggested that a smaller quantity of water is associated with this sample, in particular interlayer water. The d_{003} spacing, found by XRD, showed this Bayer hydrotalcite had the largest interlayer distance, which would indicate a larger quantity of water and anions in the interlayer region. However, the absence of the water band at 2950 cm^{-1}, suggests that the increase in interlayer distance is an increase of intercalated anions rather than water.

The water deformation modes are observed in the infrared spectra at around 1650 cm^{-1}, Figure 3. The Bayer precipitates show water deformations modes at 1649, 1649, 1651, and 1657 cm^{-1}, with increasing temperature, attributed to interlayer water hydrogen bonded to interlayer anions. The position of this band

appears to shift to slightly higher wavenumbers for the precipitates formed at 55 and 75 °C, indicating a strengthening of the hydrogen bond. The position of these bands suggests that interlayer water is hydrogen bonded to carbonate and possibly sulfate [9].

Carbonate vibrational region.

The Raman spectra in the 1200 to 900 cm^{-1} region show multiple bands at around 1085 cm^{-1} attributed to the (CO_3^{2-}) symmetric stretching vibrations, Figure 4. Four normal modes of free carbonate exist: the ν_1 symmetric stretch of A_1 symmetry normally observed at 1063 cm^{-1}, the antisymmetric stretch of E' observed at 1415 cm^{-1}, the ν_2 out of plane bend at 680 cm^{-1} [8]. All modes are Raman and infrared active except for the ν_2 mode, which is infrared active only. The intercalation of carbonate anions into the hydrotalcite structure causes a shift towards lower wavenumbers, due to the interaction of carbonate with interlayer water molecules and/or hydroxyl groups from the brucite-like layer.

The Raman band profiles for the carbonate symmetric stretching vibrations clearly show the formation of calcite and aragonite at varying temperatures. The most simplistic profile is observed for BHT @ 25°C, with a sharp intense band at 1085 cm^{-1}, and a broad shoulder at around 1060 cm^{-1}. The sharp band at 1085 cm^{-1}, observed in all precipitates, is assigned to the symmetric stretching mode of carbonate in aragonite. The bands at around 1060 cm^{-1} are assigned to hydrotalcite and are due to the symmetric stretching mode of carbonate anions bonded to interlayer water. Raman bands at around 1090 and 1100 cm^{-1} for the three other precipitates are assigned to CCH. These values are in good agreement with literature [8]. The shift towards higher wavenumbers indicates stronger hydrogen bonding of the carbonate ion occurs at increased temperatures.

The overall band profile in the infrared spectra for the carbonate antisymmetric vibrational region, Figure 3, consists of two or three overlapping bands. Determination of these bands proved to be more difficult then those in the Raman spectra, however the following assignments have been made based on literature

and XRD results found in this study. Bands at around 1400 and 1360 cm^{-1} are assigned to carbonate incorporated into the hydrotalcite interlayer. BHT @ 75°C has a significantly different shape, due to the sharp peaks at around 1480 and 1420 cm^{-1}. These sharp bands are assigned to the carbonate antisymmetric stretching mode of hydromagnesite. Infrared bands around 1420 cm^{-1} are assigned to calcite [10]. The broader bands at 1477, 1477, 1486, and 1484 cm^{-1}, with increasing temperature, are assigned to aragonite, reported in literature to be situated at 1493-70 and 1450-30 cm^{-1} [10]. The shoulder at around 1520 cm^{-1} is also assigned to aragonite and possibly a minor contribution from carbonate in hydrotalcite. XRD results showed only a minor quantity of aragonite present in BHT @ 75°C, and the absence of the peak at 1520 cm^{-1} for this precipitate, indicates that this peak is predominantly due to the antisymmetric stretch of carbonate in aragonite and not hydrotalcite.

There appear to be two peaks in the 1000 to 900 cm^{-1} region for all four precipitates, proposed to be sulfate anions intercalated into the hydrotalcite structure. A tetrahedral ion, such as sulfate, has four modes of vibration when it retains its full (T_d) symmetry; these are the symmetric stretching (ν_1) modes observed at 983 cm^{-1}, the ν_2 bending mode observed at 450 cm^{-1}, the ν_3 mode at 1105 cm^{-1}, and the ν_4 mode at 611 cm^{-1}. The ν_1 and ν_2 modes are Raman active only, whereas the ν_3 and ν_4 modes are both infrared and Raman active. The Raman bands at 990 and 980 cm^{-1} are assigned to the ν_1 S-OH stretch of the sulfate anions in the hydrotalcite interlayer. The two different peaks suggest that sulfate anions exist in two different environments within the hydrotalcite interlayer. The band at 990 cm^{-1} is proposed to be sulfate anions bonding with the cationic surface of the brucite-like sheets, while the band at 980 $^{-1}$ is assigned to sulfate anions hydrogen bonded to interlayer water. The intercalation of other anionic specie is not identified in this study. There are a limited number of intercalation sites in the hydrotalcite interlayer, and the intense competition of the high affinity anions sulfate and carbonate limits the intercalation of other anions.

Cation OH deformation modes.

An intense Raman band at 550 cm^{-1} with a shoulder at 565 cm^{-1}, figure not shown, are assigned to the $Al(OH)_6$ unit in hydrotalcite due to the vibration of aluminium-oxygen bonds. No apparent changes are detectable in these bands, and therefore, it is proposed that the synthesis temperature has a minimal effect on the brucite-like sheets of the hydrotalcite structure. Raman bands at around 470 cm^{-1} are assigned to the Mg-O-Mg linkage bonds in hydrotalcite.

CONCLUSIONS

The seawater neutralisation of supernatant liquor resulted in the formation of a variety of mineralogical phases, including hydrotalcite-like structures, hydromagnesite, and two forms of calcium carbonate. XRD showed that the crystallinity of the Bayer hydrotalcite decreased with increasing temperature, shown by the broadening of the 60° 2θ peak and the reduction in peak intensities. Bayer hydrotalcites formed at 55 °C observed the largest basal spacing, indicating a larger concentration of anions and water are intercalated into BHT @ 55 °C. Therefore, the precipitation of Bayer hydrotalcites at 55 °C appears to be the most effective at removing dissolved anions from Bayer liquors via intercalation. Results show that Bayer hydrotalcites are formed at all temperatures investigated, with minor amounts of manasseite forming at higher temperatures. Raman spectroscopy showed a reduction in the amount of aragonite that forms 75 °C, whilst the formation of hydromagnesite and calcite increased.

The presence of bands at 3000 cm^{-1} in the Raman spectra, indicate Bayer hydrotalcites have large quantities of interlayer water. However, the absence of this peak in BHT @ 55°C and a large basal spacing, suggests that the interlayer region is composed of a smaller percentage of interlayer water and a higher percentage of interlayer anions. This characteristic is responsible for the removal of anions in Bayer liquor streams.

The position of the water deformation modes indicate that interlayer water is hydrogen bonded to carbonate and sulfate. The intercalation of sulfate anions is confirmed by the presence of Raman bands at around 990 and 980 cm^{-1}. The intercalation of other anionic species is not identified by the techniques used in this study.

ACKNOWLEDGEMENTS

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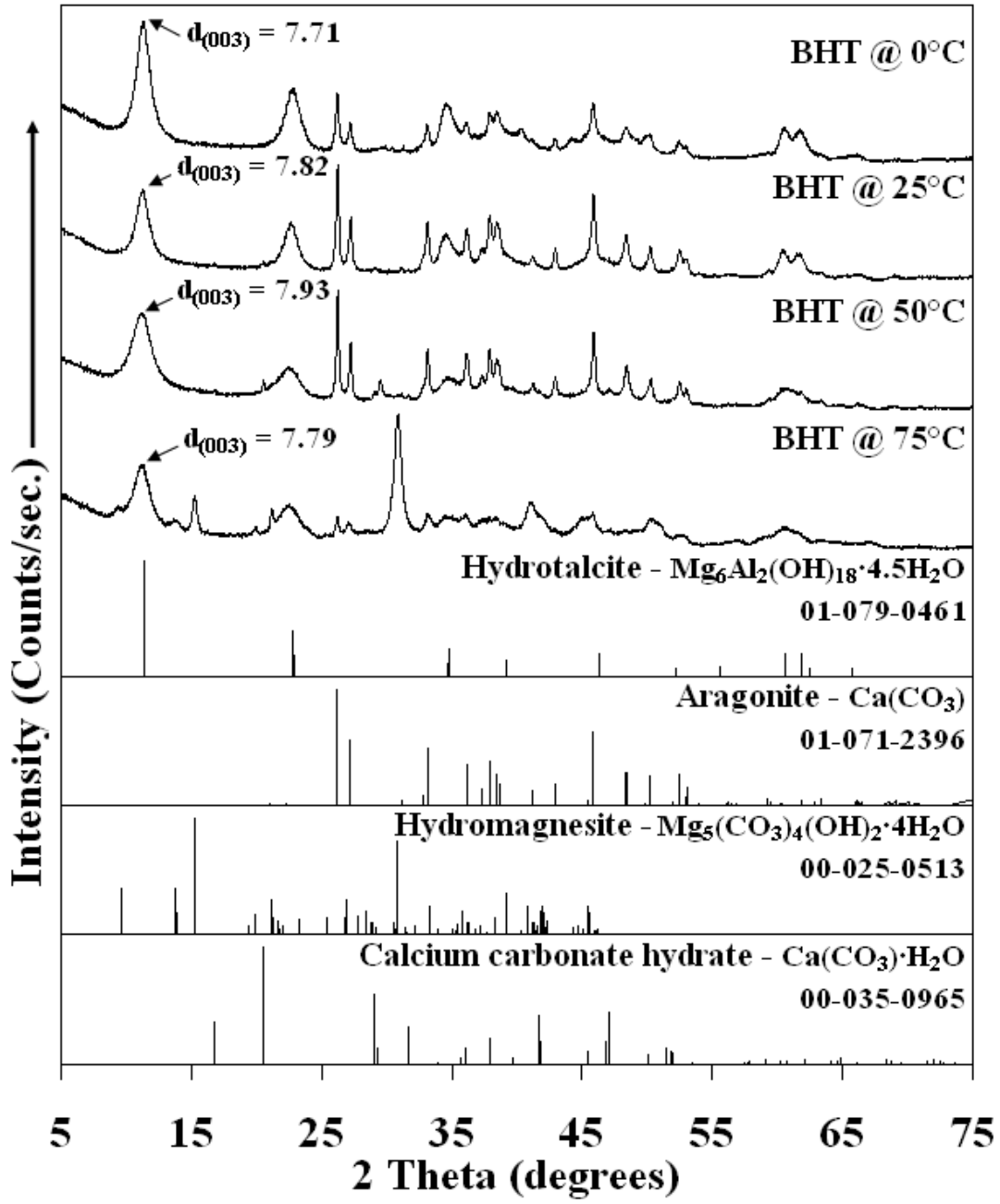
Table 1: Chemical composition of SNL and seawater.

Cation/Anion	Concentration
SNL	
Al^{3+}	**2.8 (g/L Al_2O_3)**
OH^-	**3.0 (g/L Na_2O)**
CO_3^{2-}	**9.9 (g/L Na_2O)**
Seawater	
Mg^{2+}	**1295 ppm**
Ca^{2+}	**416 ppm**
SO_4^{2-}	**2701 ppm**
HCO_3^-	**145 ppm**
Cl^-	**19345 ppm**

394 **FIGURES**



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396 Figure 1: XRD patterns of Bayer precipitates synthesised at different temperatures
397 via the SWN process.

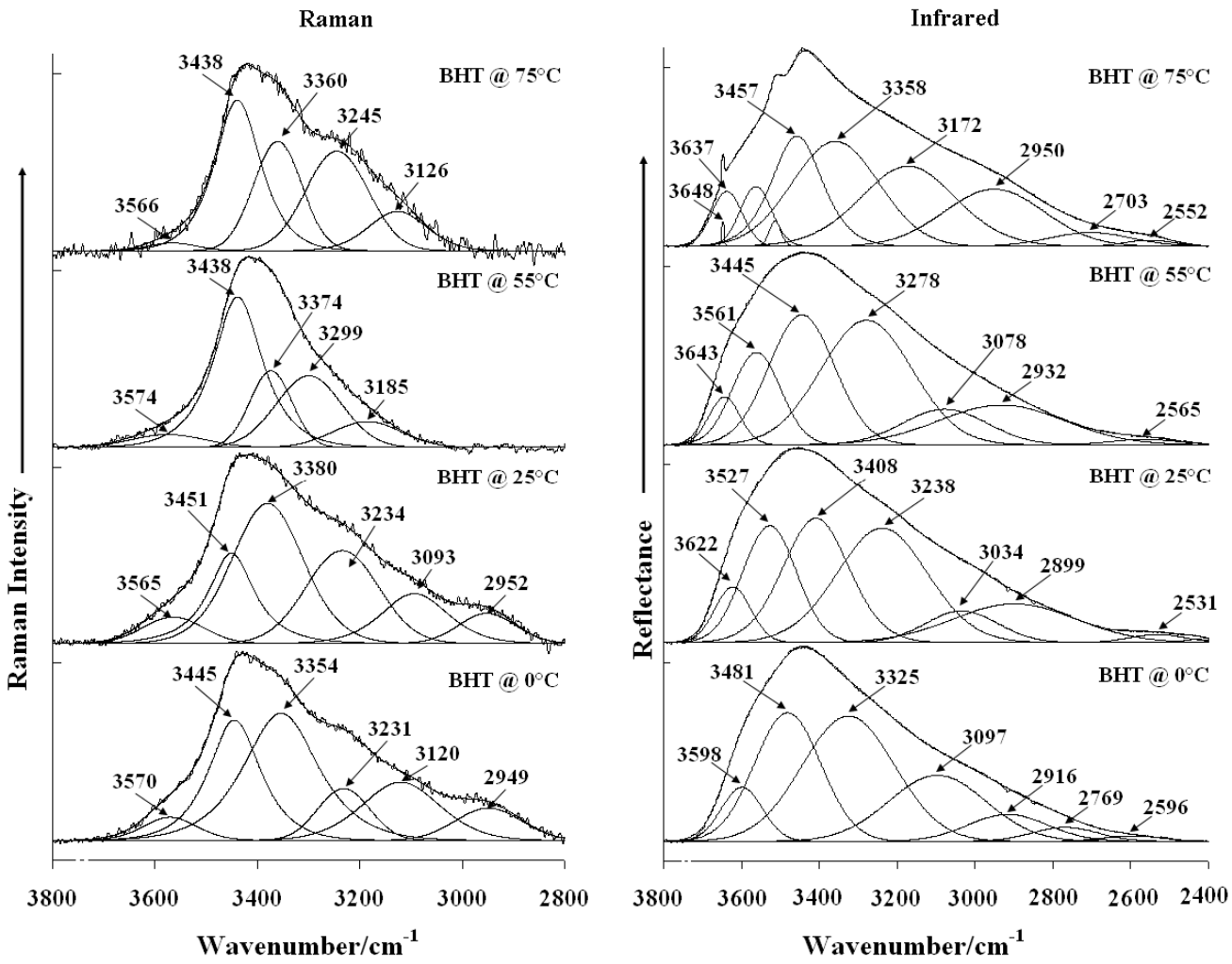


Figure 1: Raman and infrared spectra of Bayer precipitates in the hydroxyl stretching region.

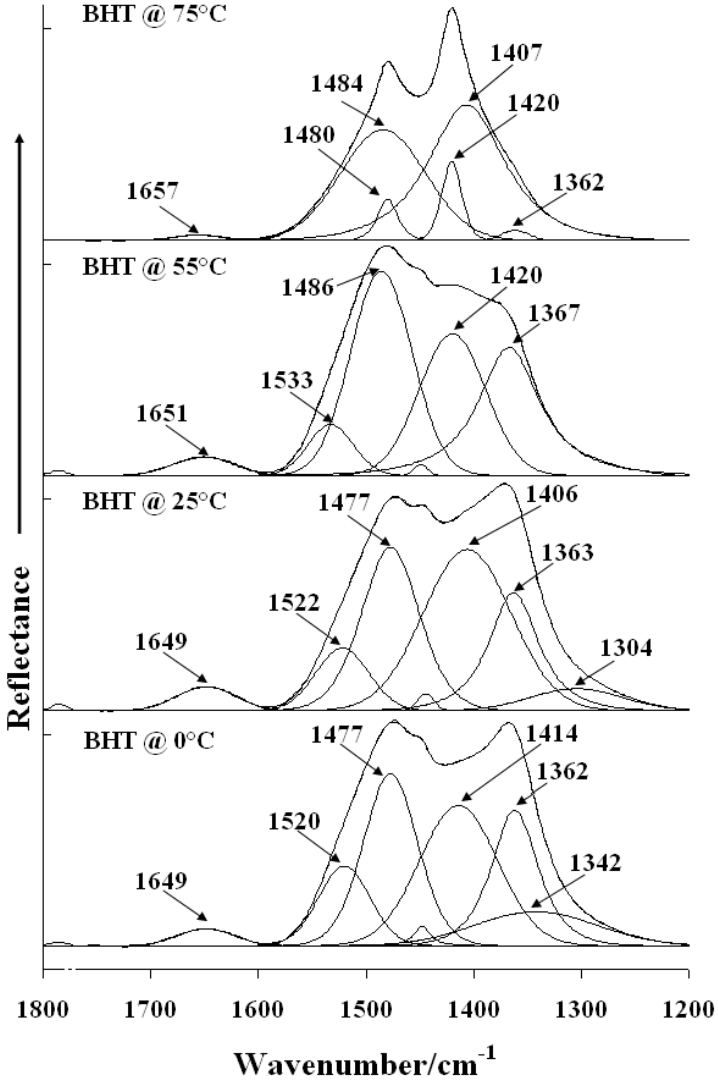
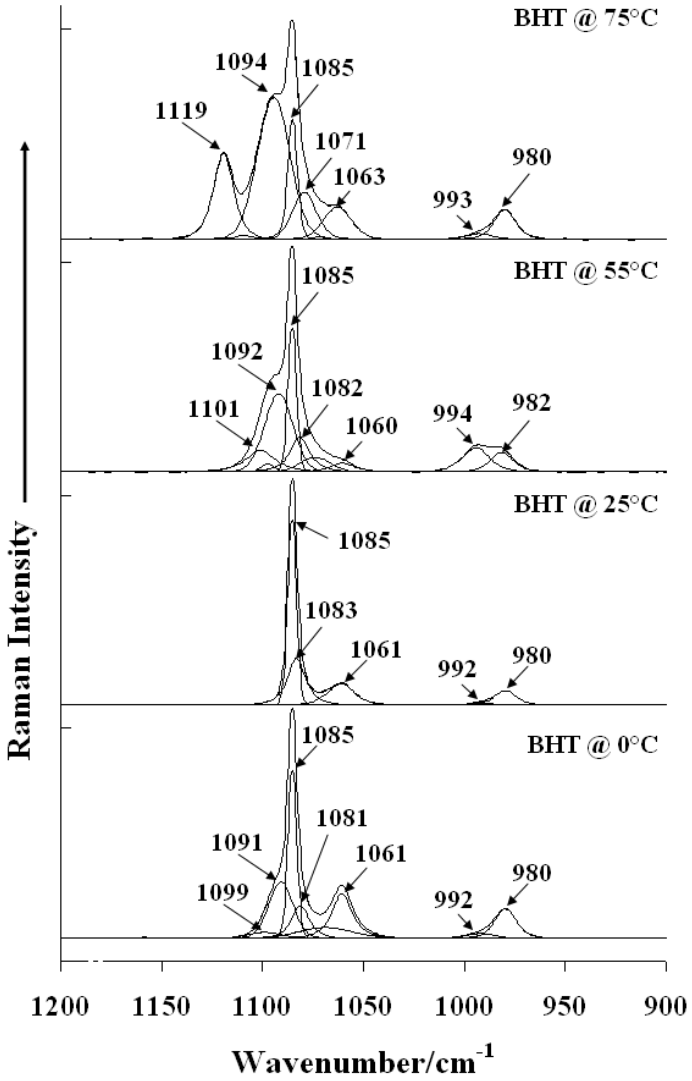


Figure 3: Infrared spectra of Bayer precipitates in the 1800 - 1200 cm^{-1} region.



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405 Figure 4: Raman spectra of Bayer precipitates in the 1200 - 900 cm^{-1} region.