Synthesis and characterisation of hydrotalcite from bauxite residue liquor and magnesium nitrate

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Introduction

The extraction of alumina from bauxite by the Bayer process produces a slurry by-product referred to as 'bauxite residue' or 'red mud'. The liquid component of the slurry is highly alkaline and requires neutralisation to render it environmentally benign. A common practice is neutralisation using Mg rich seawater, which results in the formation of the layered double hydroxide (LDH) mineral hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ (Johnston et al. 2010). Hydrotalcite consists of brucite-like sheets containing magnesium and aluminium co-ordinated with hydroxyl groups. The presence of aluminium imparts a positive charge which allows anions such as carbonate to be incorporated into the interlayer regions. Gillman and Noble (2001) and Tamagawa (2003) have explored the use of hydrotalcite as a slow release fertiliser by incorporating plant macronutrients P and N as anions PO_4^{3-} and NO_3^- into the interlayer region. The purpose of this investigation was to establish whether bauxite residue liquor could be used as a source of aluminate alkalinity to synthesise a nitrate-substituted hydrotalcite which might find use as a soil conditioner. The envisaged reaction with magnesium nitrate is as follows:

$$2[Al(OH)_4]^-_{(aq)} + 8OH^-_{(aq)} + 6Mg^{2+} + 2NO_3^-{}_{(aq)} \rightarrow Mg_6Al_2(NO_3)_2(OH)_{16}.4H_2O_{(s)}$$

Experimental

Synthesis

Hydrotalcite was synthesised by addition of uncarbonated bauxite residue liquor (ex Alcoa, Pinjarra refinery) to an equal part of 0.3 M magnesium nitrate. The liquor was added under a nitrogen atmosphere at 5.2 ml/min, with a start pH of 6.8 and a final pH of 9.4. The slurry was split and aged at both room temperature and 80°C for 24 h, washed of salts and then freeze-dried using the method of Perrott (1976). Hydrotalcite was similarly synthesised from sodium aluminate using 0.1 M sodium aluminate solution in place of bauxite residue liquor.

Characterisation

Powders were analysed on a Phillips X-ray diffractometer with a 1°2Θ/min scanning speed and Cu Kα radiation. Simultaneous TGA-DSC analyses were carried out with a Perkin Elmer STA 6000 thermal analyser in a nitrogen atmosphere at a heating rate of 10°C/min. Infrared spectra were recorded from 4000 to 450 cm^{-1} using pressed pellets of sample in KBr on a Perkin Elmer Spectrum One FTIR spectrometer. Chemical composition was determined by ICP-OES (Perkin Elmer Optima 5300 DV,) after dissolving 0.01 g powdered sample in 0.2 ml 10% HCl and diluting to 20 ml with water. Bauxite residue liquor and supernatant liquor following synthesis were also analysed by ICP-OES. Total organic carbon was determined by combustion using non-dispersive infrared spectroscopy on a Shimadzu TOC-5000A analyser. An Agilent Technologies 7890A gas chromatography system was used to determine oxalate, malonate, succinate and acetate while chloride was determined by capillary electrophoresis with a Hewlett Packard ^{3D}CE using a potassium dichromate electrolyte and sodium thiosulfate as internal standard.

Results and discussion

Hydrotalcite was confirmed by XRD as the reaction product of bauxite residue liquor and magnesium nitrate (Figure 1a). The reaction of sodium aluminate with magnesium nitrate gave hydrotalcite and gibbsite (Figure 1b).

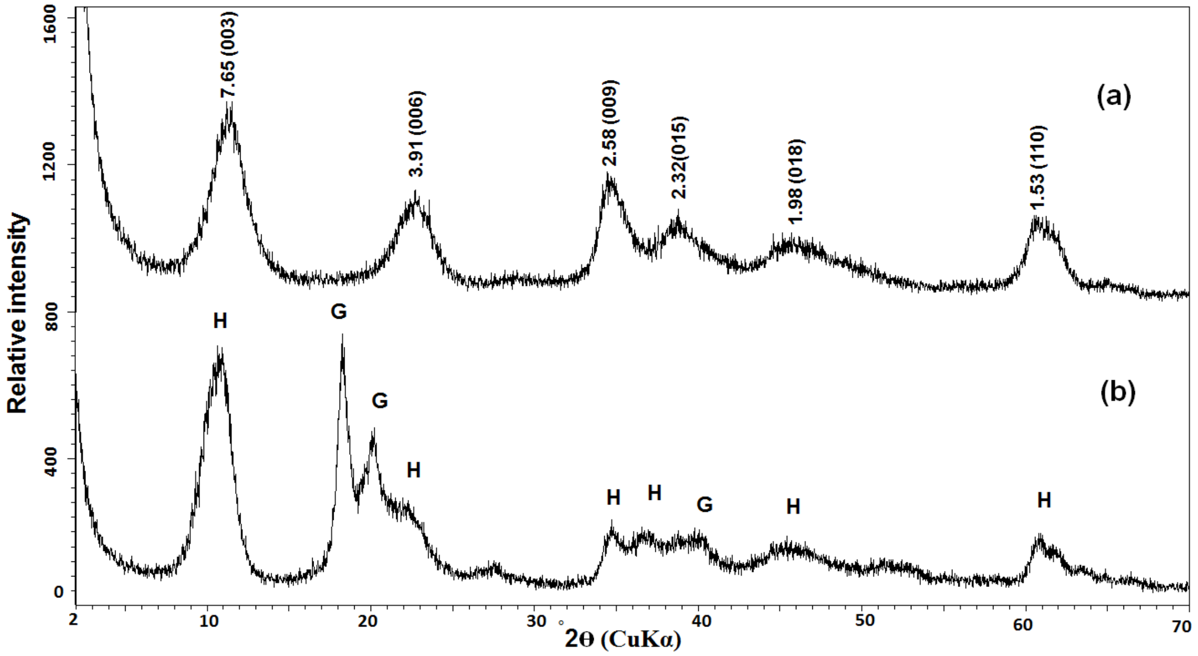

Fig 1. X-ray diffraction patterns for hydrotalcite. (a) Hydrotalcite synthesised from bauxite residue liquor and magnesium nitrate. Peaks are labelled with d-spacings and indices. (b) Hydrotalcite and an additional gibbsite phase synthesised from sodium aluminate and magnesium nitrate. H = hydrotalcite, G= gibbsite.

Hydrotalcite from sodium aluminate had sharper peaks and better resolved 110 and 113 planes than hydrotalcite from bauxite residue liquor. The lower crystallinity of the latter may be due to incorporation of additional anions. Thus Malherbe et al. (2000) found that hydrotalcite with ferricyanide was poorly crystalline compared to hydrotalcite with chloride and this was attributed to surface-adsorbed anions disturbing the stacking sequence. Palmer et al. (2011) also observed an aluminium hydroxide impurity forming in hydrotalcites synthesised from sodium aluminate.

The impurity was only absent at a synthesis pH of 14. A likely reason for absence of gibbsite alongside hydrotalcite synthesised from bauxite residue liquor is inhibition of crystal growth by organic anions as observed elsewhere (Friej et al. 2005; Lee et al. 1996; Paulaime et al. 2003).

The TGA curve (not shown) for BRL hydrotalcite indicated a total mass loss of 55.6% comprising removal of adsorbed water up to 100°C and structural water from 100 to 230°C then simultaneous dehydroxylation and decarbonation of the LDH sheets between 230 and 450°C (Palmer et al. 2009, Malherbe et al. 2000). Mass losses which take place 450–800°C are suggested in the literature to involve loss of other volatile interlayer anions. Calcination takes place at temperatures upward of 800°C. The IR spectrum (not shown) for the BRL hydrotalcite contained a large OH stretching band at 3465 cm^{-1}. A peak at 1585 cm^{-1} was attributed to interlayer water. Peaks at 1659, 1071 and 662 cm^{-1} were assigned respectively to asymmetric (v_3), symmetric (v_1) and planar (v_4) vibrational modes of intercalated carbonate.

The BRL hydrotalcite contained a 2.75:1 Mg to Al ratio, close to the target ratio 3:1. Sulfur was the main impurity detected (0.46%). Other elements in smaller amounts (mg/kg) were V (285), Fe (162), As (154), K (141), P (141) and Ca (123). Sulfur, V, As and P are interpreted to exist as intercalated oxy-anions, sulfate, vanadate, arsenate and hydrogen phosphate.

The hydrotalcite synthesised from bauxite residue liquor had only 0.20% N. Total organic C content was 4.05% and inorganic C (as CO_3^{2-}) was 1.6%. A comparison of the bauxite residue liquor with the spent supernatant revealed incorporated concentrations of oxalate (8.27), malonate (5.77) and succinate (0.585 $cmol_c$/kg). Since organic C makes up 4% of the structure other organic species of unknown charge such as humate are also likely to be present. Assuming that all the Al present is within hydrotalcite, the positive charge would be 350 $cmol_c$/kg. This is higher than the value of 320 $cmol_c$/kg calculated by Tamagawa (2003). If the charge present on other anions is subtracted from this value, the positive charge which organic carbon offsets can be estimated. A summary of intercalated/adsorbed anions and estimates of the charge they offset in the hydrotalcite structure is presented in Table 1.

Table 1. A summary of anions concentrations (cmol$_c$/kg) presumed to offset charge in the BRL hydrotalcite.

CO_3^{2-}	Organics*	SO_4^{2-}	NO_3^-	Cl^-	VO_4^{3-}	HPO_4^{2-}	AsO_4^{3-}	Total
266	36.6	28.7	14.3	1.95	0.288	1.65	0.103	350

**Oxalate, malonate, succinate and humate.*

Conclusions

Hydrotalcite synthesised from bauxite residue liquor and magnesium nitrate did not contain sufficient N to make it useful as a fertilizer. Impurities from the bauxite residue liquor were incorporated into the structure preferentially and mainly included carbonate, organic anions and sulfate. The organic anions in the bauxite residue liquor were likely to have prevented the crystallisation of gibbsite which was observed alongside hydrotalcite synthesised using sodium aluminate and magnesium nitrate.

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