Hydrotalcite precipitation during neutralization of bauxite residue leachate with acidic saline drainage water

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Bauxite residue ('red mud') storage areas can produce an alkaline, saline drainage water, which is collected and presents a challenge for management after closure of residue deposit areas. Bauxite residue leachate (BRL) from residue storage areas is typically of pH 13, with Na⁺, Al(OH)₄⁻, OH⁻ and $SO_4^{2^-}$ as the dominant ions in solution (Table 1). The alkaline, saline-sodic nature of BRL limits opportunities for treatment or reuse. The treatment or reuse of acidic, saline drainage water (ASD) generated from deep drains installed in the Western Australian Wheatbelt to combat secondary salinity is similarly limited by its complex composition, high salinity, and unfavourably low pH (Table 1). This study investigated the potential to harness the undesirable pH and salinity of these waters by mixing them to achieve neutral pH, and decrease salinity by mineral precipitation.

Circumneutral pH values (8.0-8.5) were achieved with mixing ratios of 1:5 and 1:10 BRL:ASD, and pH of mixed solutions was significantly lower than expected at mixing ratios of 1:1, 1:5, and 1:10 BRL:ASD (Table 1). Although the electrical conductivity of the mixed solutions was still high (60-88 mS/cm), all except for the 1:10 ratio solution had lower EC than predicted in the case of simple mixing, indicating that mineral precipitation lowers solution salinity. Precipitation was observed immediately upon mixing of the solutions. X-ray diffraction patterns indicated that hydrotalcite was the only crystalline mineral in the precipitates (Fig. 1); and this was supported by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Fig. 2). The Mg/(Mg+Al) ratios in 1:10 and 1:5 BRL:ASD mixed solutions (Table 1) are close to the 0.7-0.8 range recommended by Mortland and Gastuche (1962) for precipitation of Mg-Al double hydroxides without the simultaneous formation of brucite or gibbsite; however, sharper hydrotalcite peaks were observed in XRD patterns from precipitates formed in 1:1, 5:1, and 10:1 BRL:ASD mixtures, without detectable brucite or gibbsite.

Salinity of mixed solutions was highest in 1:10 BRL:ASD, and decreased over the series of mixed solutions to lowest in 10:1 BRL:ASD, suggesting that the sequential increase in peak width and decrease in peak height in XRD patterns over the series BRL:ASD 1:10 to 10:1 is due to supersaturation conditions. The more supersaturated a solution, the faster the rate of nucleation compared to crystal growth, and therefore the finer and more numerous the crystals produced, resulting in an XRD pattern with increased peak width and decreased peak height (*e.g.* BA 1:10).



Fig. 1. X-ray diffraction patterns obtained for the five precipitates from different mixing ratios (bauxite residue leachate [B]:acidic saline drainage [A]). 'H' indicates the location of hydrotalcite peaks according to PDF Card No. 22-700, and the height of vertical lines indicates the relative intensities of hydrotalcite peaks.

Layered double hydroxides such as hydrotalcite are primarily used in industry as anion exchangers, and may find use as a slow release fertilizer for nutrients such as NO_3^- and PO_4^{-3-} (Komarneni *et al.*, 2004). Two locally available by-products, bauxite residue leachate and acidic saline drainage water, may therefore generate a locally useful product – a slow release anionic fertilizer for amelioration of nutrient-poor, sandy soils such as those commonly found in the Western Australian Wheatbelt. This would require modification of reaction conditions detailed in this paper but is theoretically possible. Beyond the implications of this study for possible co-disposal of bauxite residue leachate and acidic saline drainage water, the observation of hydrotalcite precipitation suggests that hydrotalcite may also form when acidic soils are amended with bauxite residue, and may account for some of the previously observed changes in leaching and nutrient retention behaviour.

Solution		рН 3.3	EC (dS/m) 89.1	Precipitate	AI	Са	Fe	K	Na	Mg	S	Si	Mg/Mg+A
					(mmol _c /L) ¹								(1101/2)
					10	24	1	18	1182	232	146	4	0.97
BRL		13.3	60.7		134	0.1	0.01	0.3	711	0.1	41	0.4	0.0004
		Removal by precipitation (%)											
	1:10	8.1	88.6	108	-100	-2	-88	-1	0	-18	-2	-99	0.85
BRL:ASD	1:5	8.5	81.5	314	-100	-10	-92	-1	0	-49	-9	-98	0.74
mixing	1:1	12.9	68.8	392	-56	-99	-100	0	2	-100	-2	-93	0.43
ratio	5:1	13.3	65.2	111	-21	-99	-98	-1	1	-100	1	-48	0.16
	10:1	13.3	60.3	51	-12	-98	-96	-4	2	-100	2	-24	0.08

Table 1. Chemical composition of initial and mixed solutions of acidic saline drainage (ASD) and bauxite residue leachate (BRL) at various mixing ratios, and precipitate yield. Observed values are the mean of three replicates, while values shown for percentage removal are based on expected values according to additive mixing, and calculated from the mean of observed concentrations in three replicates.



Fig. 2. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) curves for the five precipitates from different mixing ratios (bauxite residue leachate [B]:acidic saline drainage [A]). All samples were held at 30°C for 10 minutes, then heated to 1000°C at a rate of 30°C/min.

References

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