

CO-PRECIPITATION OF ORGANICS WITH HYDROTALCITE

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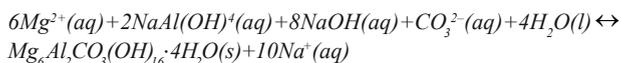
Abstract

Seawater was added to high oxalate Bayer liquor to evaluate the precipitation of organics, including oxalate solids. Laboratory trials have shown that coloured organic species may co-precipitate with hydrotalcite talcs formed upon addition of the seawater. The precipitates formed upon stepwise addition of seawater to plant liquors were analysed using a Cerium (IV) redox back titration to quantify the oxalate fraction. Results show that the coloured organics precipitate out early, during the initial formation of hydrotalcite talcs, while much of the oxalate precipitates out later, after formation of hydrotalcite. The species of oxalate changes throughout the course of liquor neutralisation and very little oxalate is removed through intercalation into hydrotalcite.

1. Introduction

Seawater neutralisation is the process of adding seawater to caustic waste streams, producing precipitates that remove alkali components (hydroxide and carbonate ions), resulting in a reduction in pH. Seawater contains relatively high concentrations of positively charged ionic species (Na^+ , Mg^{2+} , Ca^{2+}), which are capable of forming solids when added to Bayer liquor streams.

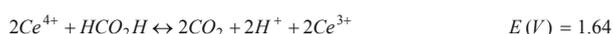
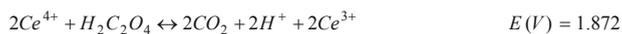
The formation of a fine, white precipitate, predominantly hydrotalcite, occurs when magnesium ions come into contact with Bayer liquor streams containing aluminium, hydroxide and carbonate as depicted by the following chemical formula (Smith and Parkinson, 2005).



Various other precipitates can also be formed which include calcite and aragonite (polymorphs of calcium carbonate), monohydrocalcite (mono hydrated calcium carbonate) and magnesian calcite (a magnesium rich calcium carbonate). Unlike other plant wastes, high oxalate Bayer liquor contains significant quantities of dissolved oxalate, which, upon treatment, precipitates as sodium and calcium oxalate. One previously-proposed mechanism for oxalate removal hypothesised that hydrotalcite would absorb oxalate from solution through anion-exchange (Lu & Zhu, 1999).

Other organics are present in plant liquor and these may precipitate during treatment, as well. Analysis of a Bayer liquor found the highest concentration low molecular weight organic compound was sodium acetate in the order of 6.4g/L (carbon equivalence) amounting to 25% of the TOC (Yamada *et al.*, 1981). Succinic acid, a low molecular weight compound, contributed approximately 9% to the TOC. High molecular weight organics present with molecular weights of 5000 – 10000 Da make-up approximately 26% of the TOC.

Since the focus of this study was to quantify oxalate in solids, the potential for cross-reaction with these other organics must be considered. Compounds with very similar redox potentials to oxalate would be expected to cross-react to some degree, though redox titrations tend to be more specific than most titrations. The standard reduction potential for oxalic acid is $E^\circ = -0.481$ V while formic acid is $E^\circ = -0.20$ V. The cell potentials for the two reactions with cerium (IV), shown below, indicate that both reactions are spontaneous with the preference for the oxalic acid to oxidise over the formic acid.



The chemical structure of acetic and succinic acid does not differ significantly from oxalic and formic acid, so it is logical

to assume that the standard reduction potentials could be similar between these compounds. Part of this study included quantifying the signal from non-oxalate sources that may end up in the neutralisation solids.

2. Experimental

2.1 Oxalate in solids

A method for quantifying oxalate from plant solids was developed at Queensland Alumina Limited (QAL), based on an analytical redox back titration of oxalate with cerium (IV) (Skoog *et al.*, 2004). The solid sample is dissolved in 50 % v/v sulphuric acid followed by the addition of cerium (IV) to oxidise the oxalic acid. Ferroin indicator is added and the unreacted cerium (IV) is back titrated with iron (II). This analytical method for determining oxalate in the solid phase has been used throughout this paper.

2.2 Solids from Seawater and High Oxalate Plant Bayer Liquor

Solids formed during seawater addition to high oxalate Bayer liquor were quantified for oxalate using the redox titration (above). Elements were quantified by Inductively Coupled Plasma (ICP), mineralogy was determined by X-Ray Diffraction (XRD), inorganic carbon was quantified from the carbon dioxide released upon acidification and organic carbon was determined using high temperature combustion.

All plant liquors were filtered through Whatman GF/C filters and analysed by Metrohm for aluminium, caustic and soda (A,C,S) along with elemental analysis by ICP. All solids formed were washed with MilliQ water and vacuum filtered through Whatman GF/C and 540 filters and dried at 80°C overnight prior to analysis. Where applicable, pH was monitored with a TPS model WP-80 portable pH meter and Metrohm electrode. Solids formed from actual and synthetic high oxalate Bayer liquor without organic contaminants were compared to clearly quantify oxalate precipitation. This was due to the fact that some organic species other than oxalate were found to cross-react in the redox titration, resulting in a small over-estimate of oxalate in solids when quantifying actual plant liquor. This general sample treatment procedure described here applies to the hydrotalcite addition and magnesium neutralisation described in the following sections.

2.3 Hydrotalcite for Removing Organics/Oxalate

2.3.1 Synthetic Hydrotalcite

Synthetic liquor was produced with the properties of the last washer underflow stream (LWUF). All reagents, including aluminium wire, sodium carbonate and sodium hydroxide pellets were analytical grade. The composition of the liquor was: caustic strength of 12g/L, A/C of 0.460 and a C/S of 0.900.

The synthetic LWUF liquor prepared above was used as the source of aluminium and carbonate for the formation of hydrotalcite. Analytical grade magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was added to drop the pH from 13.1 to 11.8. A pH around 12 was selected to ensure that side reactions which occur at lower pH values were not incorporated into the pure hydrotalcite solids formed. The solution was allowed to stir for a period of 1 hour and then filtered.

A sample of high oxalate Bayer plant liquor was separated into three separate portions (300 mL) to which pure hydrotalcite (prepared above) was added in varying quantities (0.5, 1.0 and 2.0 g). The samples were left to stir for 2 hrs before being filtered and dried.

2.3.2 In-situ Formation of Hydrotalcite in High Oxalate Synthetic Bayer Liquor

High oxalate synthetic Bayer liquor was prepared with reagents as above to yield: caustic 40g/L, A/C of 0.325 and C/S of 0.909. This solution also contained sodium oxalate (analytical grade reagent) to give an oxalate concentration of 9.0g/L expressed as the Na_2CO_3 equivalent.

This synthetic liquor was separated into three portions of 300 mL. Based on stoichiometric calculations, to form the equivalent mass of hydrotalcite used above (0.5, 1.0 and 2.0 g), analytical grade magnesium chloride hexahydrate was added (1.0, 2.0 and 4.0 g respectively). The samples were left to stir for 2 hrs before being filtered and dried.

2.3.3 In-situ Formation of Hydrotalcite in High Oxalate Plant Bayer Liquor

2.3.3.1 Using Magnesium Chloride

High oxalate plant Bayer liquor (TOC 49.7g/L and oxalate 8.7g/L expressed as Na_2CO_3) was separated into three portions of 300 mL and to this analytical grade magnesium chloride hexahydrate was added (1.0, 2.0 and 4.0 g) to replicate the experimental design with the synthetic liquor prepared above. The pH was monitored and the solution left to stir for approximately 2 hrs before being filtered and dried.

2.3.3.2 Using Magnesium Carbonate

High oxalate plant Bayer liquor (TOC 42.2g/L and oxalate 10.4g/L) was separated into three portions of 300 mL and the pH was monitored. A solution of 7 % w/v sulphuric acid was prepared by diluting 4 mL of concentrated sulphuric acid (analytical grade 98%) to a volume of 100 mL. Approximately 4.3 g of analytical grade magnesium carbonate (predominantly $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) was dissolved in this acidic solution. Volumes of 6.5, 13.0 and 26.0 mL were taken from the magnesium solution and added to the three portions of high oxalate Bayer Liquor. The volumes added provided the same quantity of magnesium to the plant liquor as the magnesium chloride experimental design thereby making the experiments comparable. The pH was monitored and the solutions were left to stir for approximately 2 hrs before being filtered and dried.

3. Results and Discussion

3.1 Oxalate Redox Titration Cross-reactant Analysis

The redox titration detects other organics in addition to oxalate (Figure 1). Only a small proportion of any compound was reported in the assay results. All the experiments were conducted with pure solids, therefore 100% signal interference corresponds to the total mass being quantified as oxalate. The mass of reactant tested was well in excess of what would be typically expected in solids precipitated during the neutralisation process. The cross-reactivity of larger molecules or more aromatic structures were not analysed in this experiment since they are not fully identified or characterised.

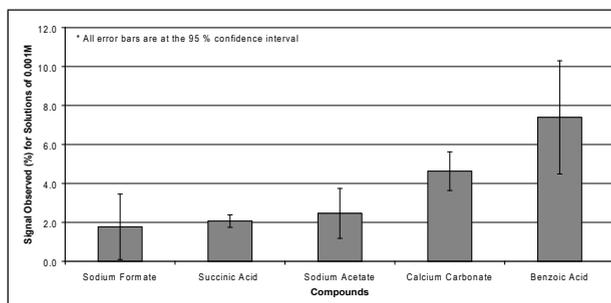


Figure 1. Analysis of Cross Reactivity during Oxalate Redox Titration

3.2 Seawater Neutralisation of High Oxalate Bayer Liquor

Figure 2 shows the pH as a function of cumulative seawater addition. Plotted on the secondary y-axis is the percent oxalate determined in the solid sample collected. Each point on the curve is where the solution was filtered; representing solids precipitated between the sample point and the preceding point. Duplicate redox titration results have been determined on different days with excellent reproducibility. The initial solids formed show slightly elevated oxalate concentrations when compared to samples at cumulative seawater volume of 500-1000 mL. After the apparent titration endpoint, where pH drops sharply, there is a rapid increase in the oxalate concentration in the solid sample to approximately 40%.

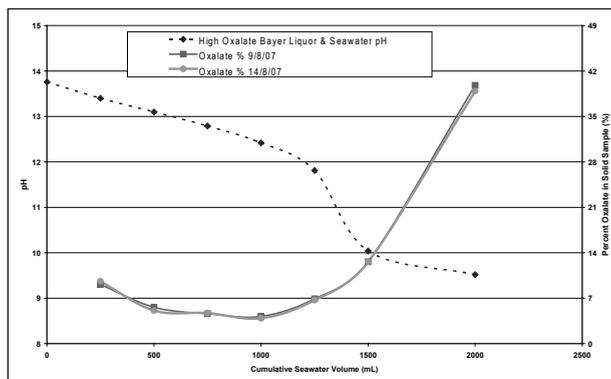


Figure 2. Step-Wise Addition of Seawater to High Oxalate Bayer Liquor with the Percent Oxalate in Solids at each Step

The amounts of solids formed at each point are not of equivalent mass, so in Figure 3 the percent oxalate is converted into the mass of oxalate actually extracted from the sample by multiplying mass of solids by percent oxalate. Based on the total mass of oxalate removed (~1.29g) the total percentage of oxalate removed from the liquor to this point in the neutralisation is approximately 70% of the available oxalate (~1.88g).

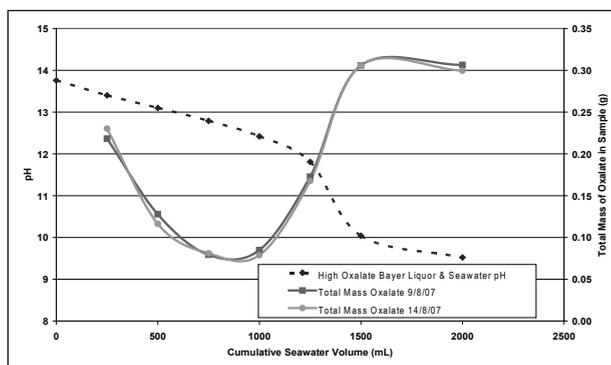


Figure 3. Step-Wise Addition of Seawater to High Oxalate Liquor with the Total Mass of Oxalate in the Sample at Each Step

At the beginning of the titration the total organic carbon is highest and the solid formed is of a dark brown colour. As the subsequent

titrations are performed, the solids become lighter (ranging from brown to yellow to white) as seen in Figure 4. The initial elevation in mass of oxalate detected in the solids produced may be due, in part, to cross-reaction with other organics precipitated out early in the titration.

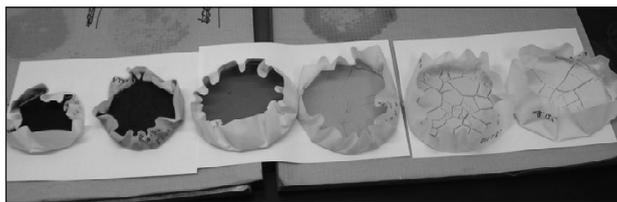


Figure 4. Solids Collected upon Step-Wise Addition of Seawater to high oxalate Bayer liquor (Photo by J. Gill)

Figure 5 shows the inorganic and organic carbon analysis of solids collected from the step-wise addition of seawater to high oxalate Bayer liquor. Oxalate would appear in the organic carbon content. The organic carbon results follow the pattern of the titration plots, Figures 2 and 3, above.

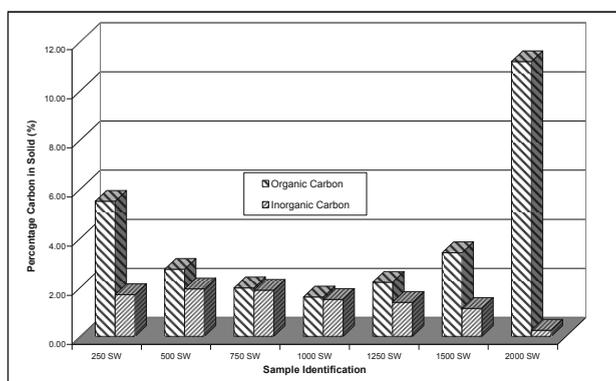


Figure 5. Carbon Analysis of High Oxalate Bayer Liquor and Seawater Samples

In the XRD scans of these solids (Figures 6 and 7), it was difficult to distinguish the magnesium aluminium hydroxide hydrate pattern due to broad and unresolved peaks over the characteristic angles (the XRD pattern for hydrotalcite has been included to highlight these regions not identified in the original scan).

The initial samples from 0 - 1000 mL of seawater displayed an unquantifiable amorphous content with possible trace of natroxalate ($\text{Na}_2\text{C}_2\text{O}_4$), weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and calcite (CaCO_3). XRD is not a quantitative technique, particularly in the presence of amorphous content, therefore the size of the peaks are not indicative of concentration. Natroxalate only appears to form at very high pH values early in the titration (Figure 6). The sample collected at pH 11.8 just prior to the end point of hydrotalcite showed trace components of weddellite with possible trace of the remaining compounds identified above. The sample collected at pH 10 contained a majority of weddellite and possible trace of whewellite (Figure 7). There was an absence of natroxalate and calcite in the pH 10 sample. There was insufficient sample collected at 2000 mL to perform an XRD.

ICP results for Mg, Ca, Al, and Na in the solids are presented in Table 1, along with pH, percent oxalate and total mass precipitated from 250 mL high oxalate Bayer liquor. All solid samples were rigorously cleaned and filtered, so it is interesting to note that the sodium percentage is so high, particularly in the early part of the titration. This is not linked to occluded sodium hydroxide or sodium carbonate because if these species were present they would be solubilised in the water wash step. Therefore the sodium has been attributed to a cold-water insoluble phase sodium compound, which has precipitated out of the liquor. This corroborates XRD evidence of sodium oxalate (natroxalate) in all solids except the 1500 mL and 2000 mL seawater samples. The 2000 SW sample displays a skewing of the elemental distribution possibly due to the large calcium oxalate solids dilution.

The magnesium and aluminium (major components of the neutralisation reaction) also trend together at a molar ratio of approximately 1.5:1.0 (Mg:Al). This is half the amount of magnesium expected for hydrotalcite, which could be caused by aluminium precipitating out in another form, possibly amorphous aluminium trihydroxide.

Presuming that all of the sodium in the solids exists as sodium oxalate, the percentage of oxalate associated entirely with sodium was plotted in Figure 8. The bar graph has been divided into two sections for each sample: the lower part is oxalate bound to the sodium (natroxalate) and the top part is the remaining organic carbon not related to natroxalate.

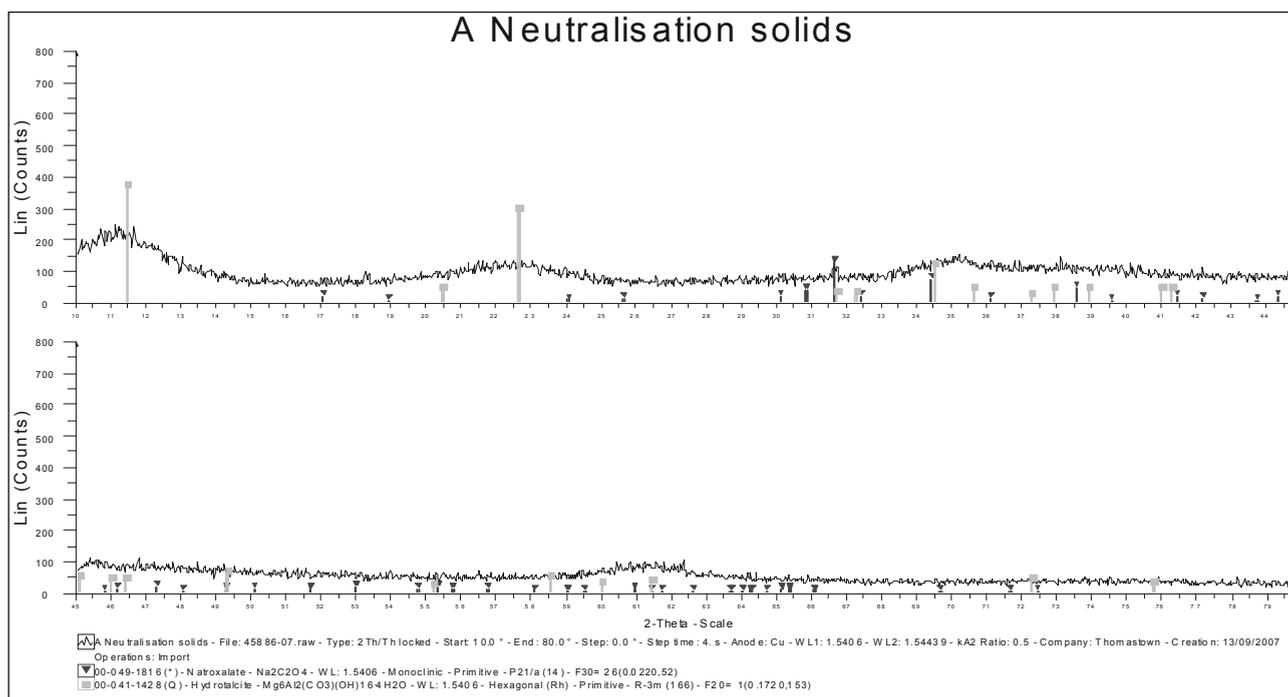


Figure 6. XRD Scan of Neutralisation Solid Collected After 250 mL Addition of Seawater

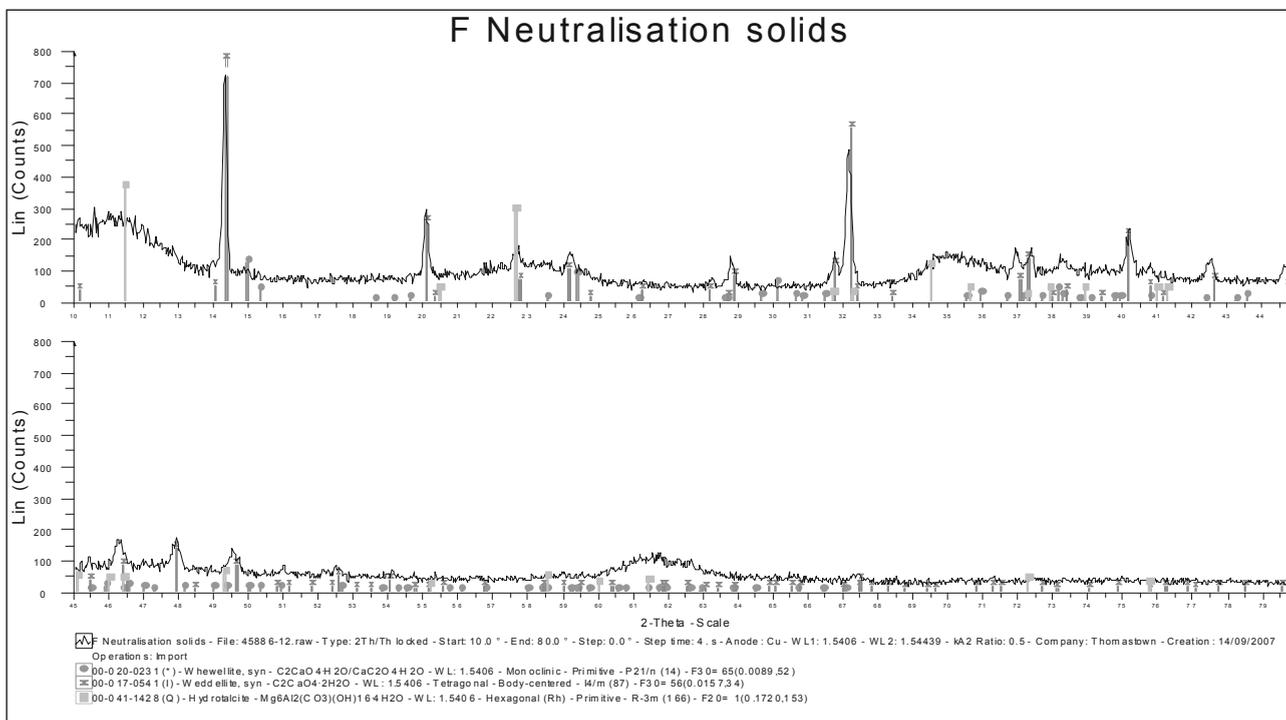


Figure 7. XRD Scan of Neutralisation Solid Collected After 1500 mL Addition of Seawater

Table 1. ICP, pH and Oxalate Analysis of Seawater Neutralisation solids

Seawater (mls)	Mg (%)	Ca (%)	Al (%)	Na (%)	pH	% Oxalate (Run 1)	% Oxalate (Run 2)	Mass Solid Formed (g)
250	12.9	3.8	9.4	7.3	13.4	9.1	9.6	2.3988
500	13.8	4.0	9.6	4.7	13.1	5.6	5.1	2.2800
750	14.2	4.0	9.6	4.1	12.8	4.6	4.7	1.7242
1000	14.2	3.9	9.5	4.1	12.4	4.2	3.9	2.0207
1250	14.0	4.1	9.2	2.9	11.8	6.9	6.7	2.5029
1500	13.5	4.4	10.0	0.4	10.0	12.6	12.6	2.4277
2000	4.5	16.5	3.4	1.0	9.5	39.8	38.9	0.7701

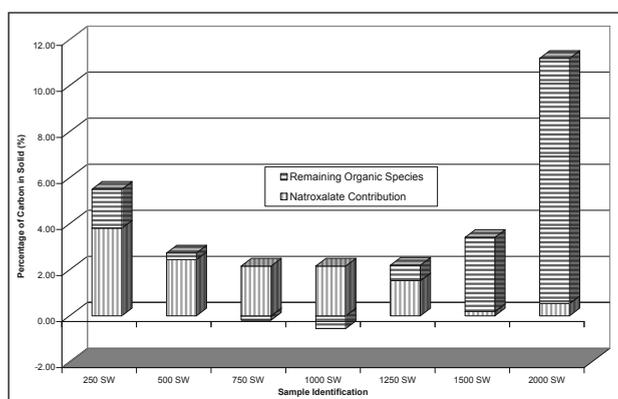


Figure 8. Organic Carbon in Solids, including Natroxalate Calculated from the Assumption that all Sodium Precipitates as the Natroxalate Species

Analytical error in the sodium or carbon determination may result in an over-prediction of oxalate associated with the sodium species in samples 750 and 1000 mL. Unless the sodium is precipitating out with some other organics, the oxalate as natroxalate is from 60 % to nearly all of the organic carbon prior to the titration endpoint.

The last two, post titration endpoint samples, have little sodium and the XRD reported only calcium oxalate species. The ICP results support this conclusion as seen by the high calcium

concentration (Table 1). Association of the calcium with carbonate would be minimal because, as the pH drops, the concentration of carbonate species is also depleted. This decrease in the inorganic carbon fraction over the course of the neutralisation is evidenced in Figure 5.

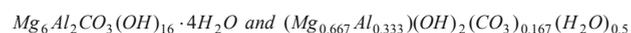
3.3 Hydrotalcite for Removing Organics/Oxalate

These experiments were designed to identify the uptake of oxalate from high oxalate Bayer liquor into the hydrotalcite clay structure. The two key experiments were:

1. Batch preparation of pure phase hydrotalcite and subsequent adsorption of organics from high oxalate Bayer liquor
2. Formation of hydrotalcite in-situ with concomitant adsorption of organics from synthetic and high oxalate plant Bayer liquor.

3.3.1 Synthetic Hydrotalcite

The pure hydrotalcite produced were analysed by XRD and the two hydrotalcite candidates were:



Adding this synthesised hydrotalcite to high oxalate Bayer liquor resulted in 3.3-3.5% oxalate in the solids collected (Figure 9, vertical bars) independent of whether 0.5, 1.0 or 2.0 grams were added. Although TOC was present in solution, the hydrotalcite did not become significantly discoloured. Pre-synthesised hydrotalcite

is a poor oxalate removal agent and probably a poor organics removals agent under the conditions of this experiment.

3.3.2 In Situ Formation of Hydrotalcite in Synthetic High Oxalate Liquor

Amounts of magnesium chloride were added to synthetic high oxalate Bayer liquor calculated to result in 0.5, 1.0 and 2.0 grams of hydrotalcite formed in situ, resulting in only 2.3-2.6% oxalate in the solids (Figure 9, horizontal bars). These results are lower than those for hydrotalcite added to high oxalate liquor, possibly due to the presence of TOC in the plant liquor that, if precipitated out, may cross-react in the oxalate assay. The concentration of oxalate added to this synthetic high oxalate liquor was similar to actual plant liquor at 9.0g/L (expressed as Na₂CO₃). The percent oxalate removed from solution is presented in the final column of Table 2. These results show a maximum of 1.5% oxalate removal from the liquor. It was shown earlier that, for the step-wise seawater addition, approximately 70% of the oxalate in solution is removed as various other solid oxalate forms.

Table 2. Oxalate Removal by Hydrotalcite Formed in situ from Synthetic High Oxalate Liquor

Theoretical Hydrotalcite Formed (g)	Solids Collected (g)	Average Oxalate in Solids (%)	Oxalate Removed from Solution (%)
0.5	0.3457	2.58	0.39
1.0	0.6439	2.34	0.66
2.0	1.5667	2.25	1.53

These results indicate that there is not a strong driving force for the oxalate in synthetic liquor to be intercalated into hydrotalcite, even when it forms in situ. The mass of solids collected is less than the mass of hydrotalcite expected to form, presumably due to incomplete dissolution and/or reaction of the magnesium and from losses during sample handling. Experiments reported here show that hydrotalcite is only a minor contribution to oxalate removal, though it may contribute to the removal of other organics present in actual plant liquors.

3.3.3 In-Situ Formation of Hydrotalcite in High Oxalate Plant Bayer Liquor

3.3.3.1 Using MgCl₂

The magnesium chloride did not undergo complete dissolution, at least when added in quantities to yield 1.0 and 2.0 grams of hydrotalcite. The 0.5 g sample showed a dark, fine powder indicative of hydrotalcite and organics, whereas the samples of 1.0 and 2.0 g hydrotalcite showed two separate solid forms: the dark solids observed in the 0.5 g sample and what appeared to be magnesium chloride crystals, slightly discoloured due to contact with the Bayer liquor. Based on these observations, it was hypothesised that the formation of hydrotalcite may be limited by the solubility of magnesium chloride in this basic media. Also, the Mg added may be precipitated out with non-oxalate organics rather than forming hydrotalcite. This would result in the percent oxalate observed in samples of 1.0 and 2.0 g hydrotalcite to be lower owing to less hydrotalcite formed and solids dilution Figure 9 (diagonal bars down to left).

3.3.3.2 Using MgCO₃

The magnesium carbonate was completely dissolved in sulphuric acid. The high oxalate Bayer liquor was nearly 20% higher in oxalate than that used in the MgCl₂ experiment. This, and the fact that all of the magnesium was in solution, may account for the slightly higher percent oxalate precipitated. The drop in % oxalate with increasing magnesium added was reduced compared to MgCl₂. Other precipitates of magnesium could also be forming causing the decrease in the percent oxalate as more magnesium is added.

The lowest pH of these experiments did not drop below 13. Therefore, as the pH was still high, there is the possibility that hydrotalcite formed in situ may contribute more to oxalate removal as the pH (and carbonate) are reduced.

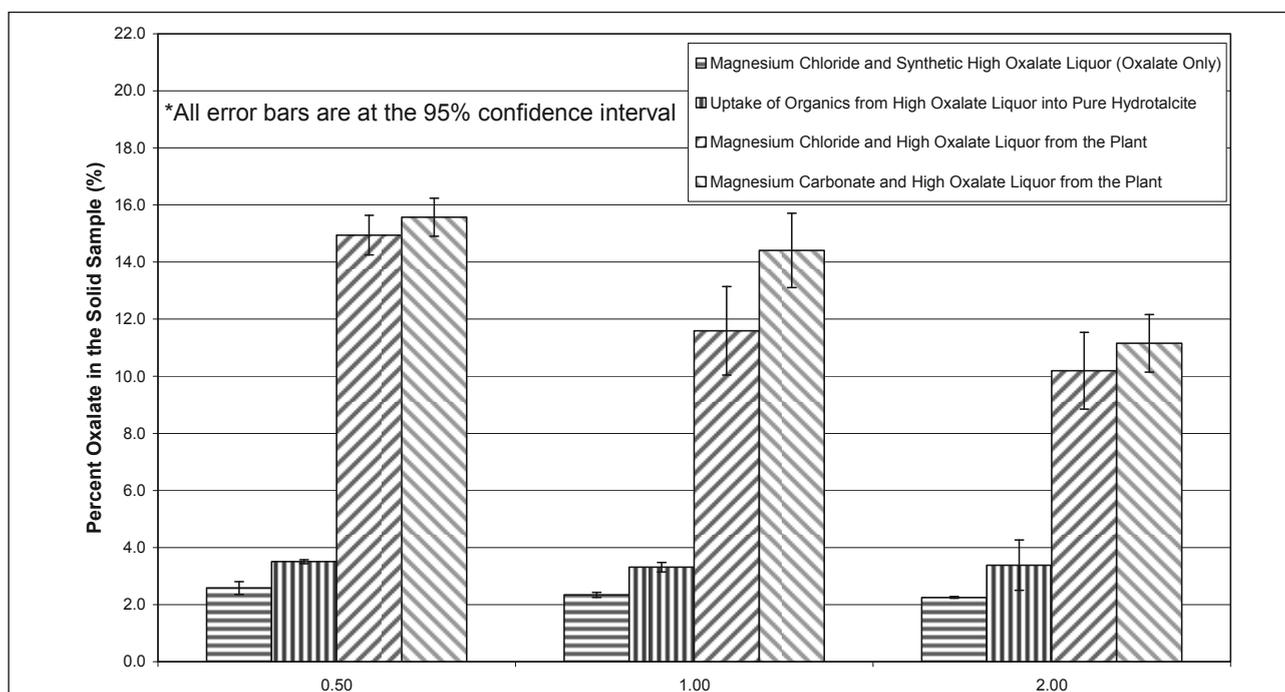


Figure 9. Oxalate Results for Hydrotalcite Solids Synthesised under Different Conditions

4. Conclusions

The experimental analysis showed that sodium oxalate or a similar oxalate salt was favoured at high pH values. As the pH drops upon neutralisation with seawater, calcium oxalate salts are the predominant solid species. Hydrotalcite was shown to be an insignificant contributor to oxalate removal.

Acknowledgements

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