

IMPLICATION OF CALCIUM HYDROXIDE IN THE SEAWATER NEUTRALISATION OF BAUXITE REFINERY LIQUORS

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Abstract

Tricalcium aluminate, hydrocalumite and residual lime have been identified as reversion contributing compounds after the seawater neutralisation of bauxite refinery residues. The formation of these compounds during the neutralisation process is dependent on the concentration of residual lime, pH and aluminate concentrations in the residue slurry. Therefore, the effect of calcium hydroxide (Ca(OH)₂) in bauxite refinery liquors was analysed and the degree of reversion monitored. This investigation found that the dissolution of tricalcium aluminate, hydrocalumite and Ca(OH)₂ caused reversion and continued to increase the pH of the neutralised residue until a state of equilibrium was reached at a solution pH of 10.5. The dissolution mechanism for each compound has been described and used to demonstrate the implications that this has on reversion in seawater neutralised Bayer liquor. This investigation describes the limiting factors for the dissolution and formation of these trigger compounds as well as confirming the formation of Bayer hydrotalcite (mixture of Mg₆Al₂(OH)₁₆(CO₃²⁻, SO₄²⁻)·xH₂O and Mg₈Al₂(OH)₁₂(CO₃²⁻, SO₄²⁻)·xH₂O) as the primary mechanism for reducing reversion during the neutralisation process. This knowledge then allowed for a simple but effective method (addition of magnesium chloride or increased seawater to Bayer liquor ratio) to be devised to reduce reversion occurring after the neutralisation of Bayer liquors. Both methods utilise the formation of Bayer hydrotalcite to permanently (stable in neutralised residue) remove hydroxyl (OH⁻) and aluminate (Al(OH)₄⁻) ions from solution.

1. Introduction

Bauxite refinery residues are derived from the Bayer process by the digestion of crushed bauxite in concentrated caustic (NaOH) at elevated temperatures and pressures. The process results in the dissolution of gibbsite (Al(OH)₃) and boehmite (Al(O)OH) to form a solution of sodium aluminate ions, while the insoluble residue red mud (45% liquor and 55% solid mud) is separated by means of flocculation and decantation.¹⁻³ The composition of bauxite refinery residue is complex, with the concentration of compounds varying with the type of bauxite and refinery process used. The supernatant liquor (SNL) from this residue is strongly alkaline⁴⁻⁵ and requires neutralisation to a pH below 8.9, with an optimum pH value of 8.5 to 8.9,⁶ before environmental discharge can be considered. The aim of the neutralisation process is to add sufficient seawater to permanently reduce the pH below 8.9, however, an increase in pH after the neutralisation point (i.e. after all the seawater has been added) can occur and this is referred to as "pH reversion". The solid residue consists of a variety of compounds including calcium aluminate species, organic material, and various oxides of iron, titanium, and silica. The most common type of calcium aluminate formed in the Bayer process is tricalcium aluminate (TCA - Ca₃Al₂(OH)₁₂). TCA is formed via the reaction of calcium hydroxide (Ca(OH)₂), sodium aluminate (NaAl(OH)₄) and sodium hydroxide (NaOH).⁷⁻⁸ The addition of lime (CaO-burnt lime or Ca(OH)₂-slaked lime) at various stages of the Bayer process provides numerous benefits to the process including: 1) improving the dissolution of boehmite and diasporite during digestion, 2) helps to reduce liquor impurities, 3) assists in phosphate control in pregnant liquor, and 4) reduces soda losses in red mud.⁷

The seawater neutralisation method has been found to be very successful in the reduction of both the pH and dissolved metal concentrations of the bauxite refinery residue, through the precipitation of Mg, Ca and Al hydroxide and carbonate minerals.⁶

The formation of these hydrotalcite (HT)-like compounds (Mg₆Al₂(OH)₁₆(CO₃²⁻, SO₄²⁻)·xH₂O) also removes oxy-anions of transition metals through a combination of intercalation and adsorption mechanisms. The general formula for these structures is: [M²⁺_{1-x}M³⁺_x(OH)₂]^{x+}A^{m-}_{x/m}·nH₂O, where M²⁺ is a divalent cation, M³⁺ is trivalent cation, and A an interlamellar anion with charge m⁻. LDH phases exist for 0.2 ≤ x ≤ 0.33.⁹⁻¹¹ Hydrotalcite that forms during the neutralisation of Bayer liquors will be known as 'Bayer' hydrotalcite. However, reversion threatens to increase the pH and aluminium levels above environmental specifications after the seawater neutralisation process.¹² Therefore, the aim of this investigation is to establish that the formation of hydrotalcite permanently removes OH⁻ and Al(OH)₄⁻ from solution and to identify the compounds responsible for reversion.

Due to refineries striving to become more environmentally accountable and sustainable, an increase in bauxite residue management practises are being investigated and employed.¹³⁻¹⁵ A major objective for research in this particular field is understanding residue behaviour before and after various treatments. Carter et al., who looked at characterising bauxite residue using pH leaching tests and geochemical modelling methods have done a good example of this.¹⁶ A large amount of research has been published on Ca(OH)₂ in the Bayer industry,⁷⁻⁸ however, little focus has been placed on the effects of high concentrations of Ca(OH)₂ in residue liquors neutralised by seawater. Therefore, this investigation focuses on the effects of high Ca(OH)₂ concentrations in residue liquor on the neutralisation process, and the dissolution of Ca(OH)₂, hydrocalumite (Ca₂Al(OH)₆Cl·2H₂O) and tricalcium aluminate (Ca₃Al₂(OH)₁₂) in regards to pH and aluminium reversion. The aim of this investigation is to 1) verify tricalcium aluminate, calcium hydroxide and hydrocalumite cause an increase in pH and aluminium concentration after neutralisation, and 2) that hydrotalcite that forms from the neutralisation process permanently removes hydroxide and aluminium.

2. Materials and methods

2.1 Preparation of synthetic materials

Due to the complexity of red mud residues synthetic version of the waste material were synthesised in the laboratory using AR grade materials. TCA used in this work was provided by an Australian bauxite refinery plant. The effectiveness of using larger volumes of seawater and the addition of magnesium chloride to seawater was conducted using synthetic liquors and red mud slurry from an alumina refinery.

Synthetic seawater was prepared, using AR grade materials and concentrations specified by Heslop and Robinson.¹⁷ The concentration of salts used should represent seawater to 99.9 %.

Synthetic supernatant evaporate liquor (SEL) was prepared by the addition of 35 g/L of sodium carbonate (Na_2CO_3) to a concentrated NaOH (4 M) solution. The solution was stirred for 10 minutes before 1-2 grams of aluminium metal was added to the caustic solution, and allowed to dissolve completely before the addition of another 1-2 grams of aluminium metal. This process continued until all aluminium metal had been dissolved (31 g/L), which took around 6 hours to complete. Synthetic SNL was prepared by the dilution of SEL by a factor of 16. The synthetic supernatant liquor (SNL) composition was 3.2 g/L alumina (Al_2O_3), 6.5 g/L caustic (Na_2O), and 6.3 g/L of carbonate (Na_2O).

Hydrocalumite was synthesised by the addition of two solutions, where solution 1 contained 2M NaOH and a combination of Na_2CO_3 to give a concentration of 0.2M, while solution 2 contained 0.66M Ca^{2+} ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.33M Al^{3+} ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). Solution 2 was added drop wise to solution 1 under vigorous stirring. The precipitated compound was then thoroughly washed to remove any residual salts and dried overnight in an oven (85 °C).

2.2 SWN of synthetic SNL spiked with calcium hydroxide and hydrocalumite

The experiments involved the addition of different concentrations of calcium hydroxide (0.05-1M) or hydrocalumite (0.01-0.5M) to 60 mL of synthetic SNL, whilst being stirred for 5 minutes. The initial pH of SNL was maintained at around 12. The concentration of $\text{Ca}(\text{OH})_2$ used for each test and the theoretical concentration of solid $\text{Ca}(\text{OH})_2$ left in solution is given in Table 1. For 0.05 and 0.10M the complete dissolution of $\text{Ca}(\text{OH})_2$ occurs. After 5 minutes, synthetic seawater (270 mL) was added to SNL at around 120 mL a minute, and was left to stir for a further 2 hours. Samples (20 mL) were taken every 30 minutes to monitor the ions in solution, and the concentration of phases in the precipitate. Each sample was vacuum and syringe filtered (0.45 μm filters) for ICP analysis, while the precipitate was washed (after aqueous sample had been removed) and place in an oven (85 °C) overnight to dry. The pH of the solution was monitored at 15 second intervals for a total of 2 hours using a TPS-40 pH meter and general laboratory pH probe. The pH probe was calibrated using buffers 7 and 10.

2.3 SWN of synthetic SNL with tricalcium aluminate

The experiment involves the addition of different masses of tricalcium aluminate (TCA), Table 1, to synthetic SNL (60 mL). After 5 minutes of stirring, synthetic seawater (270 mL) was added to the SNL mixture (rate of 120 mL/min), and was left to stir for a further 2 hours. Sample collection is described in section 2.2.

Table 1: Concentration and mass of $\text{Ca}(\text{OH})_2$ and TCA in 60 mL of synthetic SNL.

Concentration (M)	Mass of $\text{Ca}(\text{OH})_2$ (g)	Mass of TCA (g)
0.005	-	-
0.010	-	0.1598 g
0.030	-	0.4793 g
0.050	0.2226g	0.7988 g
0.075	-	1.1982 g
0.100	0.4446g	1.5976 g
0.300	1.3338g	-
0.400	1.7784g	-
0.500	2.2230g	-
1.000	4.4472g	-

2.3.1 Addition of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

The experiment involves the addition of different concentrations of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, (50, 100, 150, 200, 250, 500 ppm) to synthetic seawater in order to increase the magnesium concentration. The spiked synthetic seawater (270 mL) was then added to synthetic SNL (60 mL) with TCA (1.6 g). The solution was left to stir for 75 minutes, whilst samples (20 mL) were taken every 30 minutes to monitor the ions in solution.

2.4 Characterisation techniques

Samples of the initial synthetic SNL and resulting solution after the SWN process were analysed using a Varian Inductively coupled plasma optical emission spectrometer (ICP-OES). Standards containing aluminium, magnesium, and calcium were prepared to establish a calibration curve. Results were obtained using an integration time of 3 seconds with 3 replications. The relative amounts of each element was recorded on the Varian Liberty 2000 ICP-OES at wavelengths of 394.400, 279.553 and 393.366 for aluminium, magnesium and calcium, respectively.

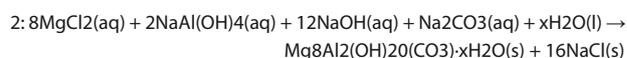
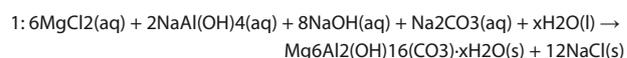
3. Results and discussion

3.1 Synthetic SNL with $\text{Ca}(\text{OH})_2$

Different amounts of $\text{Ca}(\text{OH})_2$ were mixed (5 minutes) with the same volume of SNL before the same volume of seawater was added. The solution pH was monitored at 15 second intervals for a 2 hour period.

All concentrations of $\text{Ca}(\text{OH})_2$ investigated observed an increase in pH after the addition of synthetic seawater, Figure 1. The required seawater volumes to neutralise Bayer residue is dictated by the dissolved levels of caustic and alumina in the liquor. Therefore, the presence of solid-phase compounds that can increase this neutralisation requirement, such as $\text{Ca}(\text{OH})_2$, will increase the seawater requirement. In the presence of $\text{Ca}(\text{OH})_2$, pH reversion occurs almost instantaneously after the final volume of seawater is added to SNL. At low concentrations (0.05 and 0.10M) an increase of less than 0.5 pH units occurs. An increase in the neutralisation point is due to the dissolution of $\text{Ca}(\text{OH})_2$ during the addition of seawater.

The primary mechanism for the removal of OH^- ions from solution is through the formation of a mixture of hydrotalcite structures:



The formation of hydrotalcite is pH dependent and as such a mixture of 3:1 and 4:1 hydrotalcite structures form during the SWN process.¹⁹

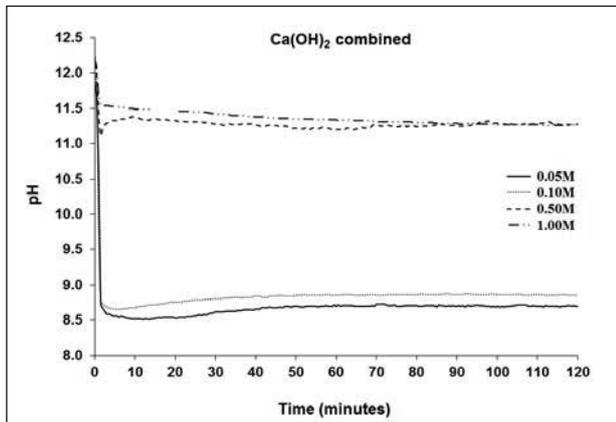
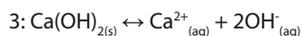


Figure 1: pH plots for the SWN of synthetic SW and SNL with varying concentrations of Ca(OH)_2 .

High concentrations of Ca(OH)_2 (0.50 and 1.00 M) showed a small reduction in pH but essentially remained at pH values greater than 11. The small reduction is due to the formation of hydrotalcite, hydrocalumite ($\text{Ca}_2\text{Al(OH)}_6\text{Cl}\cdot 2\text{H}_2\text{O}$), and brucite (Mg(OH)_2). A significant reduction in pH is not observed due to an influx of OH^- ions caused by the dissolution of Ca(OH)_2 . As hydrotalcite, hydrocalumite and brucite form, and the pH begins to fall the dissolution of Ca(OH)_2 is facilitated until insufficient amounts of magnesium, aluminium, and calcium remain in solution. A state of equilibrium for Ca(OH)_2 occurred between pH 11 and 11.5:



There are three shifts in equilibrium observed for the dissolution of Ca(OH)_2 during the seawater neutralisation process:

1. At low pH, the equilibrium reaction shifts to the right (dissolution of Ca(OH)_2) due to the use of OH^- ions in the formation of hydrotalcite.
2. The use of Ca^{2+} in the formation of CaCO_3 and CaCl_2 shifts the equilibrium to the right.
3. At high concentrations of Ca(OH)_2 , the release of OH^- ions is readily used up in the formation of brucite, hydrotalcite and hydrocalumite.

The solubility of Ca(OH)_2 in pure water is 1.26 g/L at 50 °C.²⁰ It should be noted that the solubility of Ca(OH)_2 increases at lower temperatures. Therefore, the presence of Ca(OH)_2 in the residue (disposed of in tailings dam) will show a continual pH increase as the residue cools.

The Mg^{2+} ion concentration decreases significantly with increased Ca(OH)_2 concentrations. The increase in OH^- ions in solution, due to Ca(OH)_2 dissociating, results in the additional formation of hydrotalcite and brucite. At 0.05 and 0.10M, the pH of solution is below pH 9, not favourable for brucite formation, and thus the removal of Mg^{2+} is dependent on the concentration of Al^{3+} (Al(OH)_3) ions for the formation of hydrotalcite. Excess Mg^{2+} ions remain in solution for Ca(OH)_2 concentrations of 0.05 and 0.10M as hydrotalcite is unable to form due to the lack of Al^{3+} ions. The absence of Al^{3+} ions at low pH allows for pH reversion to occur as hydrotalcite formation is the primary mechanism for the removal of OH^- ions during neutralisation.

3.2 Synthetic SNL with hydrocalumite

Reversion (pH) is observed when the concentration of hydrocalumite in SNL is greater than 0.10M, Figure 2. At concentrations below this, the final pH remains between 8.0 and 8.5. At low concentrations (0.10M and less), the release of OH^- ions from the dissolution of hydrocalumite (Eq. 4) is used up by the formation of hydrotalcite, thus preventing the pH to increase. Reversion only occurs when the concentration of Mg^{2+} ions in solution is negligible, and hydrotalcite is unable to form.

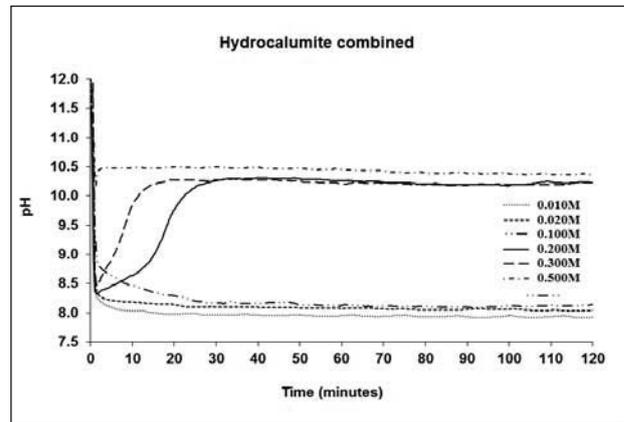
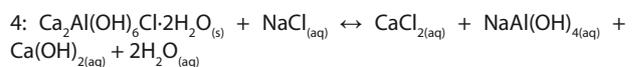


Figure 2: pH plots for SWN synthetic SW and SNL with varying concentrations of hydrocalumite.

Increasing the concentration of hydrocalumite causes the pH to rise at a faster rate until a state of equilibrium is reached at pH 10.5.²¹ The following equilibrium reaction is proposed:



As the pH falls below 10.5 during neutralisation, the dissolution of hydrocalumite becomes favoured and thus releases aluminate (Al(OH)_4^-) and hydroxyl ions into solution causing both pH and aluminium reversion. In this high pH range, the remaining hydrocalumite in solution is in equilibrium, and therefore dissolution of hydrocalumite is no longer favoured.

ICP analysis confirmed that Al^{3+} reversion occurred for hydrocalumite when present in concentrations above 0.10M, Figure 3. There is an inverse relationship between Al^{3+} and Mg^{2+} (Figure 4) concentrations in solution. It can be clearly seen from these charts that Al^{3+} reversion is prevalent when Mg^{2+} ions are absent from solution. The concentration of Mg^{2+} steadily decreases after the SWN process due to the simultaneous dissolution of hydrocalumite and formation of hydrotalcite. The formation of hydrotalcite results in the reduction in Al(OH)_3 , Mg^{2+} ions and pH.

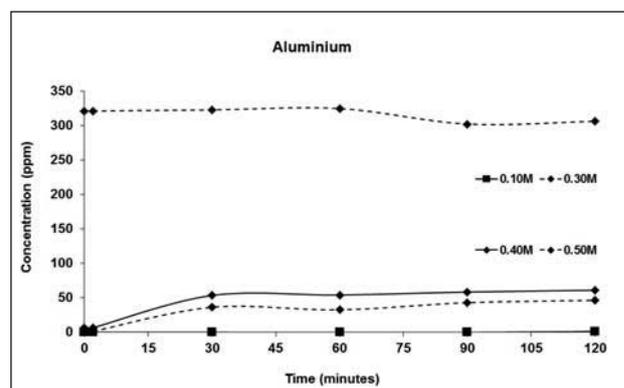


Figure 3: Mg^{2+} concentrations after the SWN of SNL with varying concentrations of hydrocalumite.

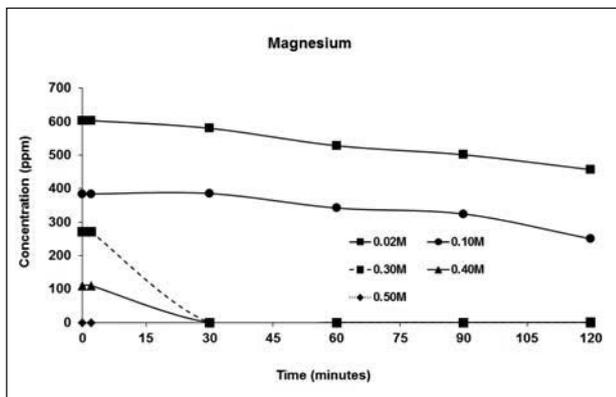


Figure 4: Mg²⁺ concentrations after the SWN of SNL with varying concentrations of hydrocalumite.

3.3 Reversion of tricalcium aluminate solutions

The neutralisation of SNL containing TCA increases the pH (reversion) after the addition of seawater, Figure 5. The extent of reversion is dependent on the concentration of TCA, where reversion occurs for concentrations above 0.03M. It is also observed that small quantities of TCA, up to 0.05M, cause the neutralisation point (minimum pH value) to decrease. This is due to the slight dissolution of TCA, which increases the concentration of soluble aluminium in solution, and therefore allows for a larger concentration of hydrotalcite to form. The formation of additional hydrotalcite removes OH⁻ ions from solution, thus causing the neutralisation point to decrease. However, the pH increases for high concentrations of TCA due to a lack of magnesium ions required for the formation of hydrotalcite. The dissolution of TCA continues until all TCA has been dissolved or until the pH increases above 10.5 where TCA is in a state of equilibrium. Therefore, if there is a shortage of magnesium ions, the release of hydroxide, aluminium and calcium ions are uncontrolled and reversion is significant.

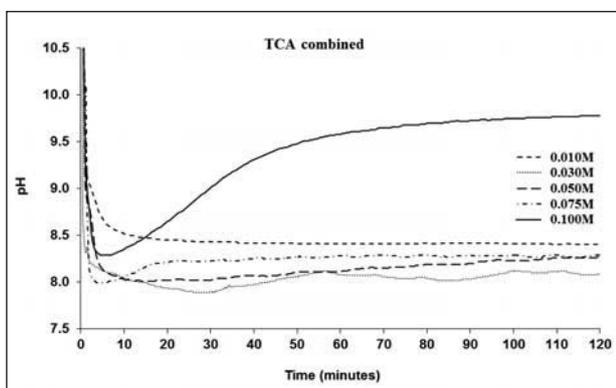
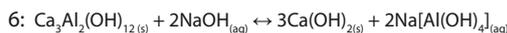


Figure 5: pH plots for the SWN of synthetic SW and SNL with varying concentrations of TCA.

The increase in aluminium ions, after the seawater neutralisation point, is only just observed at concentrations of TCA greater than 0.05M TCA. It is proposed that a higher concentration of aluminium is released into solution, however, the continual formation of Bayer hydrotalcite removes the majority of soluble aluminium from solution. It is not until all magnesium is removed from solution that the increase in aluminium is clearly observed. This is seen for 0.10M TCA, where the concentration of magnesium in solution is 0 ppm, whilst the aluminium concentration has risen to 145 ppm. Therefore, once all available magnesium is removed from solution via the formation of hydrotalcite, there does not appear to be another mechanism for the removal of aluminium.

3.3.1 Mechanism for TCA dissolution

Based on the works by Whittingto et al., Blenkinsop et al., and Alekseev et al.,^{8,22-24} two predominant reactions are involved in pH and aluminium reversion. It is thought a combination of the following reactions, involving NaOH and Na₂CO₃, participate in forming soluble Al(OH)₄⁻ ions from TCA (Ca₃Al₂(OH)₁₂). It is proposed that the initial dissolution step of TCA involves a combination of these reactions occurring simultaneously. Equation 5 releases NaOH into solution until the Na₂CO₃ concentration is depleted and because 4 moles of NaOH is released the pH of solution increases. However, the consumption of 2 moles of NaOH in equation 6 reduces the rate at which the pH increases.



It is also believed that the dissolution of Ca(OH)₂, formed in equation 6, causes an increase in OH⁻ ions. The dissolution of Ca(OH)₂ occurs once the majority of NaOH has been removed by the dissolution of TCA. The increased concentration of OH⁻ ions in solution is then believed to cause the further dissolution of TCA, removing OH⁻ ions by the formation Ca(OH)₂. It is not until the majority of TCA is removed from solution that the dissolution of Ca(OH)₂ becomes predominate. With no reactions removing OH⁻ ions from solution, the pH increases significantly until a state of equilibrium is reached.

3.4 Minimisation / prevention of pH and aluminium reversion

Aluminium and pH reversion are caused by TCA and hydrocalumite dissolution and can be reduced through the formation of hydrotalcite, as long as excess magnesium ions are in solution.

3.4.1 Neutralisation ratio

Red mud slurry (RMS) neutralised with a seawater neutralisation volumetric ratio (SWNR) of 4 clearly shows pH reversion, Figure 6. Increasing the volumetric seawater neutralisation ratio not only reduced the pH but appears to have eliminated any signs of reversion. The increased magnesium concentration at ratios greater than 5 is shown to significantly reduce the extent of reversion, with volumetric ratios greater than 8 showing no reversion. The mechanism for the removal of aluminium from solution is due to the formation of hydrotalcite.

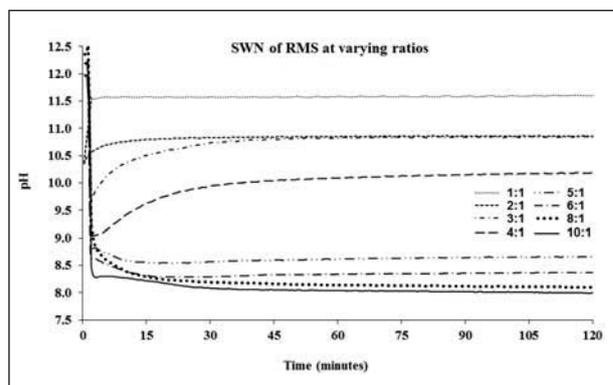


Figure 6: SWN of red mud slurry at variable seawater ratios.

3.4.2 Addition of MgCl₂·6H₂O to synthetic supernatant liquor

Red mud slurry containing 8 g/L of TCA will result in an increase in pH and soluble aluminium after neutralisation. The addition of different concentrations of magnesium chloride to seawater has been proven to reduce the pH and aluminium concentration in synthetic SNL solutions containing 0.10M TCA (Figure 7). For a SWNR of 4.5 the pH increased by 1 pH unit, while the aluminium concentration increased by 25 ppm. The addition of 100 ppm

MgCl₂ had a minimal effect on reducing the pH and aluminium concentration of the synthetic liquor, however, when the concentration of MgCl₂ is 200 ppm a slight reduction in pH and aluminium concentration (Figure 8) are observed. The continued increase in MgCl₂ in seawater, up to 500 ppm, showed a continual reduction in both pH and aluminium reversion. Using 500 ppm MgCl₂ in seawater resulted in a pH rise of less than 0.1 units, while the aluminium concentration remained below 3 ppm.

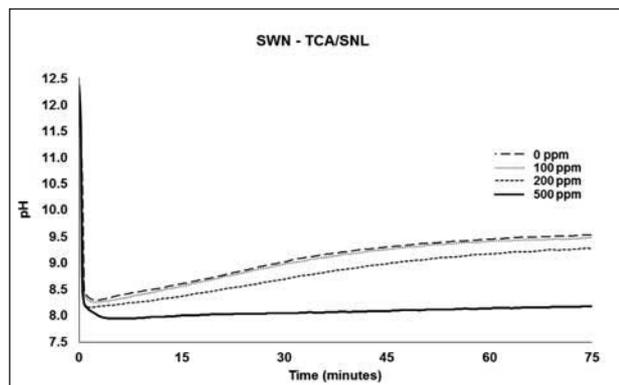


Figure 7: pH curves for the addition of MgCl₂·6H₂O to seawater and the SWN of synthetic SNL containing 0.10M TCA.

At low concentrations of MgCl₂ (0-200 ppm), the magnesium concentration (Figure 9) in solution decreases significantly (0-5 ppm left in solution after 1 hour). It is not until the aluminium concentration in solution is depleted (dissolution of TCA ceases) that the magnesium concentration increases due to a lack of hydrotalcite formation. This is clearly observed for 500 ppm MgCl₂, where the magnesium concentration after 75 mins is approximately 200 ppm, whilst the aluminium concentration is approximately 3 ppm. It is not until magnesium is in excess that the concentration of aluminium in solution is negligible and reversion is minimised.

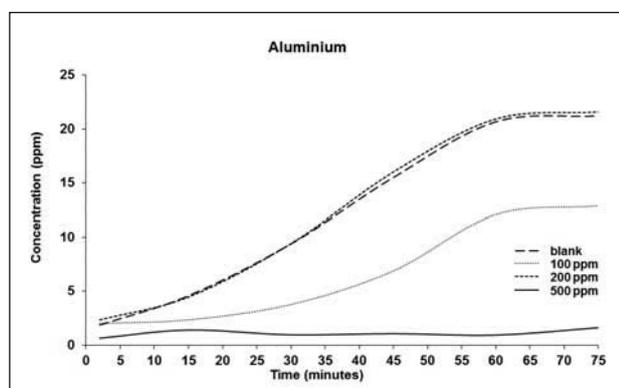


Figure 8: Aluminium concentration for SWN synthetic SNL containing 0.10M TCA with MgCl₂·6H₂O.

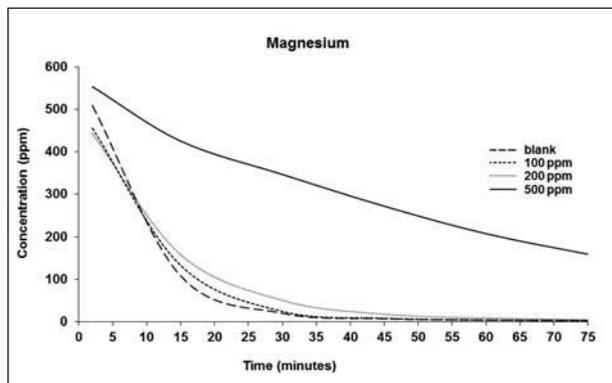


Figure 9: Magnesium concentration for SWN synthetic SNL containing 0.10M TCA with MgCl₂·6H₂O.

4. Conclusions

This investigation has shown that the presence of solid calcium hydroxide in supernatant liquor results in a pH rise after seawater neutralisation. It is believed this pH increase is due to:

1. the dissolution of Ca(OH)₂ and,
2. the dissolution of hydrocalumite.

The dissolution of Ca(OH)₂ in the solution continued until a pH above 11 is obtained. At this pH value, a state of equilibrium is reached. The presence of carbonate also promoted calcium hydroxide dissolution, through the precipitation of calcite, resulting in the additional release of hydroxide ions into solution. The presence of Ca(OH)₂ in the liquor promotes the formation of hydrocalumite. Hydrocalumite forms during the seawater neutralisation process (reaction of Ca²⁺ ions in seawater and Al(OH)₄⁻ ions in liquor), however it is unstable at pH values below 10.5. The dissolution of hydrocalumite not only causes pH reversion, but also Al³⁺ reversion. Therefore, the concentration of calcium hydroxide impacts the efficiency of the seawater neutralisation process for alumina refinery residues both directly and indirectly.

The pH plot of seawater neutralised bauxite refinery residues show a common trend: 1) rapid decrease in pH, 2) neutralisation point, 3) a rapid increase in pH, and 4) plateau of the pH. The rapid increase in pH is due to the dissolution of TCA and hydrocalumite, triggers for aluminium and pH reversion. The pH does not continue to increase above 10.5 because equilibrium reactions are stable in this pH range. It has been proven that Bayer hydrotalcite does not cause reversion, as previously speculated. A number of reactions are proposed to be involved in the dissolution of TCA, however, the two major reactions involve: 1) sodium carbonate, and 2) sodium hydroxide.

This investigation has identified two methods for the minimisation of pH and aluminium reversion: 1) increasing the seawater neutralisation volumetric ratio, and 2) addition of magnesium chloride to seawater. Both methods utilise the formation of hydrotalcite to remove both hydroxide and aluminium ions from solution permanently. By ensuring that there is always an excess of magnesium ions in solution, reversion can be prevented.

5. Acknowledgements

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