DISSOLUTION OF SOLIDS IN PROCESS WASTE STREAMS

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Abstract

Solid wastes from the Bayer process include a variety of neutral and caustic solids. Some of the caustic compounds also contain aluminium, including solids in forms that are considered to be stable, such as desilication product and tricalcium aluminate (TCA). Caustic, aluminium and other components of waste solids are labile or soluble under various conditions. The conditions of dissolution, the identity of the source solids and rates of dissolution were explored in laboratory work.

A method for neutralising alkaline components of Bayer waste streams is the use of seawater as a neutralising agent. The current laboratory work concentrates on characterising the solid products of seawater neutralisation and evaluating the rate of dissolution of some of the red mud waste components, not detailed in previous work.

1. Introduction

Alumina is refined industrially from bauxite by the Bayer process, patented by Karl Josef Bayer in 1888. The valuable aluminium species are extracted from the ore by dissolution into sodium hydroxide solution in the digestion part of the process. Digestion produces a desired pregnant sodium aluminate solution and a by-product of undissolved impurities. These impurities are separated from the supersaturated sodium aluminate solution in a clarification process. The by-product stream is typically a characteristic red colour, commonly termed 'Red mud', containing iron oxides, titanium oxides, and silica and aluminium compounds. The stream can be highly alkaline due to the presence of residual caustic and other alkaline components. Dissolving alkaline solids and bound caustic contribute to the apparent alkalinity of the Red mud.

A method for reducing the alkalinity of Red mud is addition of seawater as a neutralising agent. The mechanism for seawater neutralisation of alkali components of Red mud relies on the presence of Mg^{2+} and Ca^{2+} ions in seawater. As such, this neutralisation differs from traditional acid-base type neutralisation. The magnesium and calcium cations react with alkali components to precipitate out solid products, reducing the caustic and soda in solution.
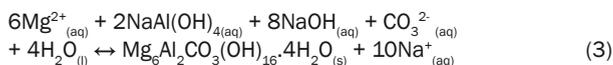
For example,

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightarrow Mg(OH)_{2(s)} \qquad (1)$$

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow CaCO_{3(s)} \qquad (2)$$

Combinations of fast and slow reactions occur during neutralisation of the Bayer red mud.

The dominant reaction occurring on neutralisation of Bayer waste products with seawater is the formation of hydrotalcite, $Mg_6Al_2CO_3(OH)_{16}.4H_2O$.

The formation of hydrotalcite can be described by the reaction:

$$6Mg^{2+}_{(aq)} + 2NaAl(OH)_{4(aq)} + 8NaOH_{(aq)} + CO_3^{2-}_{(aq)}$$
$$+ 4H_2O_{(l)} \leftrightarrow Mg_6Al_2CO_3(OH)_{16}.4H_2O_{(s)} + 10Na^+_{(aq)} \qquad (3)$$

Other reported products of the neutralisation of sodium aluminate solutions with seawater include calcites, aragonite, monohydrocalcite and magnesian calcites, (Smith & Parkinson 2005).

The hydrotalcite formed has low solubility and therefore forms a relatively stable precipitate, making its formation desirable for the neutralisation process.

Lime solids formed in the neutralisation process, as well as those present in the pre-neutralised waste streams may participate in competing silica reactions as described in Boynton, (Boynton 1966). In particular, TCA can form as an intermediate in certain reactions and is susceptible to reacting to form other compounds. Other largely insoluble calcium aluminates exhibit some potential to react. Laboratory simulation of seawater neutralisation of various constituents of the output to the waste treatment facility was used to characterise neutralisation kinetics and products.

2. Experimental

Samples of various waste streams were obtained from the plant in 250mL Nalgene bottles for laboratory neutralisation. The samples were centrifuged (2000rpm, 4min), the liquor component decanted, then the solid component was re-slurried with approximately 200mL of DI water and centrifuged (2000rpm, 4min). This process was repeated a further two times to ensure adequate washing of the solids. The solids were vacuum filtered using Buchner funnel and GFC and dried in an oven overnight at 80°C. Both liquor and solids components were titrated with plant seawater in a glass beaker with stirrer. The progression of the neutralisation was measured by monitoring of pH using a portable pH meter, TPS WP-80. 1mL aliquots of seawater were added and the pH recorded for each addition. Seawater was added at regular intervals until establishment of equilibrium, assessed by stabilisation of pH.

Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC) analysis were performed on liquor samples using an OIC 1010 liquor analyser. Elemental analysis was conducted on liquors and solids using ICP. XRD analysis was performed on solid neutralisation products. The solids were filtered from the supernatant, washed with DI water, dried at 60°C and ground to a fine powder using a mortar and pestle. The XRD pattern was obtained using a Siemens D5000 XRD with copper radiation at 40kV and 30mA with range 10 to 80°2θ, a step of 0.03 degrees and step time of 4 seconds. A graphite monochromator was used in the diffracted beam. Intermediate samples were obtained to further characterise the neutralisation products.

3. Results and Discussion

3.1 Liquors

After each seawater addition, the pH stabilised rapidly, see Figure 1. A loss of colour was detectable on reaction with the seawater, see Figure 2. Additionally, a visible increase in cloudiness of the sample indicated solid formation.

Samples of the solid neutralisation products were obtained for XRD analysis. Hydrotalcite was evident in the XRD analysis among other compounds, such as calcite, hematite, brucite, quartz and various magnesium aluminium hydroxides. No quantitative analysis was achievable from the XRD results.
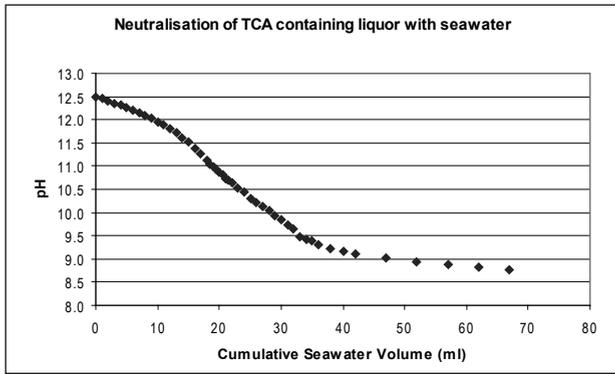
Figure 1. Typical neutralisation curve of liquor sample

Figure 2. Progressive neutralisation samples- filtered

3.2 Solids

The liquor component of the waste stream was expected to require significant seawater to neutralise the caustic and sodium carbonate present in it. The solids showed considerable seawater demand, distinct from this liquor component, see Figure 3. The solids neutralisation displayed a strong kinetic dependency. When the seawater was added at regular intervals (i.e. at 30sec intervals) the response was a predictable decrease in pH, similar to that experienced in the liquor titrations, see Figure 3. However, when the sample pH was left to equilibrate between seawater additions the pH initially decreased, but after a period of time began increasing until it reached a pH comparable to that observed pre-seawater addition, see Figure 4.
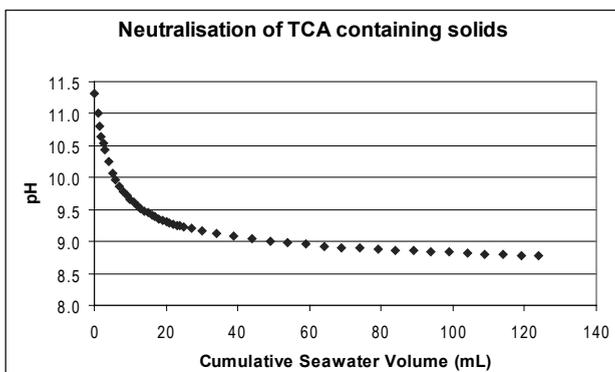

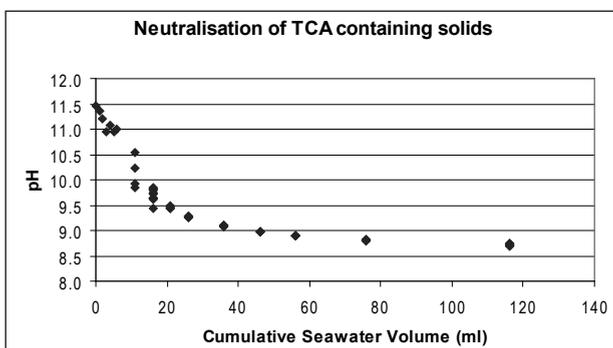Figure 3. Solids neutralisation (without kinetic effect)

Figure 4. Solids neutralisation showing kinetic effect

A possible cause of the solids neutralisation behaviour is residual caustic from the liquor remaining despite thorough washing of the solids. However, evidence of dissolution and fluctuating pH suggests the observed neutralisation behaviour is more complex than simply a consequence of residual caustic. The solids were much slower to react than their parent liquors. This was evident in the increased time required for the pH to stabilise after each seawater addition. This phenomenon is hypothesised to be the result of a stepwise process involved in dissolution and subsequent reaction of the solid components.

The pH instability observed is possibly a consequence of hydrotalcite being relatively insoluble. Reduced formation of hydrotalcite compared with calcium carbonate and calcium oxalate formation could cause an increase in dissolving species, resulting in the pH instability observed. The tendency for hydrotalcite to persist in the system is attributed to its reduced solubility in comparison with calcium compounds such as TCA and $CaCO_3$. Due to the dependency of reaction rate on concentration (the driving force for reaction), as magnesium is consumed, the rate of hydrotalcite formation slows. This allows the formation of other compounds to become more significant.

3.3 Neutralisation products

Consistency between aluminium content before and after neutralisation would provide evidence that no hydrotalcite has formed, as aluminium is not involved in formation of other neutralisation products and the seawater used for neutralisation contained <0.1mg/L dissolved aluminium. This was not found to be the case for a 50mL liquor sample prepared by filtering Filter-aid slurry. The aluminium in solution decreases post-neutralisation even after the 1.2:1 (volume seawater: volume sample) dilution is accounted for. The neutralisation curve of the liquor sample is shown in Figure 1. The decrease in aluminium suggests a compound containing aluminium precipitated as a neutralisation product and hydrotalcite may have formed, refer to Table 1.

Table 1. Elemental analysis of liquor sample

	Al (mg/L)	Ca (mg/L)	Mg (mg/L)	Si (mg/L)
Seawater	<0.1	452	1362	<0.1
PRE-neutralisation	590	0.28	0.06	0.12
POST- neutralisation	2.1	206	324	0.2

Alternatively, TCA may have formed as it requires a source of aluminium ions, which in the Bayer process is typically supplied by sodium aluminate liquor.

Additionally, the layered double hydroxide nature of hydrotalcites makes them susceptible to involvement in anionic exchange. The ability to perform ion exchange means hydrotalcite variants can be produced, and hydrotalcite-like compounds with differing structure and morphology may exist. Magnesium has ability to react with organics, or form hydroxides and carbonate compounds. Reduction in dissolved calcium concentration suggests calcium compounds are forming, including calcium carbonate and calcium oxalate. The exact nature of the products was uncertain and available XRD results were inconclusive.

3.4 Dissolution of solids during seawater neutralisation

The difficulty encountered in attempting to produce a smooth solids neutralisation curve was evidence of the complexity of neutralising solids and their kinetic dependence. The failure of the pH to stabilise over an extended period of time (1-2 hours) highlighted the difficulty in accurately estimating the seawater demand of the solids. Both inorganic and organic carbon reduced substantially during neutralisation. Similarly, dissolved aluminium decreased on neutralisation.

A number of samples displayed increased pH instability compared with other waste stream samples, see Figure 5. This is hypothesised to be a consequence of the calcium components in these streams. Tricalcium aluminate hexahydrate (TCAH) in particular, has high solubility and can transform to tricalcium aluminate silicate (TCAS) and $CaCO_3$ both of which are less soluble compounds than TCAH, (Ostap 1988). These compounds are hypothesised to be responsible for the larger seawater demand than expected for the initial pH.
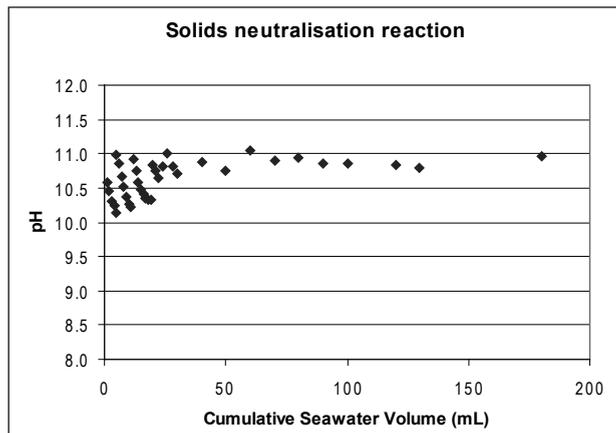

Figure 5. Solids neutralisation of calcium containing stream

The seawater demand of several streams was especially high. Conceivably, the caustic dominance in liquor streams disguises any interactions of neutralisation products, which may be causing an increased, long-term seawater demand.

The presence of silica in analytical results and the difference observed between pre and post neutralisation analysis indicates strong possibility of lime interactions contributing to the neutralisation behaviour.

3.5 Dissolution tests

A dissolution test was performed on a sample to further investigate the behaviour of neutralisation products. This was achieved by comparing the use of spent seawater and seawater as reagents over a 24-hr timeframe. It was anticipated that the lack of a fresh magnesium ion source in the depleted seawater would reveal any potential for solid samples to dissolve, liberating alkaline species into solution. The spent seawater represented a reagent that had been exhausted of supply of magnesium ions. The depleted seawater sample was prepared by neutralising alkaline liquor with seawater to pH 9, and retaining the resultant supernatant.

Initially, the pH of the seawater-mud sample was measured as 9.0±0.1 and after 24 hours increased to 9.2±0.1. This compared with the spent seawater-mud sample, which increased from 9.7±0.1 to 10.6±0.1. Pre-neutralisation the mud recorded a pH of 11.6±0.1, the seawater pH of 8.0±0.1 and spent seawater 9.0±0.1. The greater change in pH observed in the depleted seawater-mud sample provided evidence that there are alkaline components present either in the red mud samples or in neutralisation products which dissolve into solution over extended periods of time.

3.6 Solids dissolution in DI water

To further investigate the behaviour of dissolving solids, samples of washed solids were placed in DI water. Changes in pH were monitored until the pH stabilised. The pH rises and elemental analysis showed an increase in calcium and aluminium concentrations in the liquor, reflecting solids dissolution. Dissolution of aluminium was observed to be strongly pH dependent.
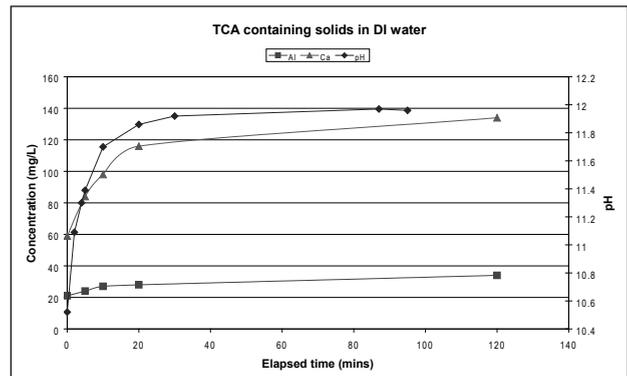

Figure 6. Kinetic effect of dissolution of solids in water

4. Conclusions and Recommendations

- Hydrotalcite was the primary neutralisation product, but there was strong evidence that other products were also formed
- The neutralisation of solids showed strong kinetic dependence and potential for dissolution, especially those containing tricalcium aluminate. Dissolution continued over extended periods of time
- The seawater demand and kinetic behaviour of waste solids should be considered in future planning and development of Bayer process waste areas

References

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