

# ALKALINITY AND ACID NEUTRALIZING CAPACITY (ANC) OF CONSTITUENTS IN BAYER REFINERY NEUTRALIZED WASTEWATER

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## Abstract

Alkalinity is considered one of the best indicators of Bayer liquor neutralization with seawater. For most aqueous systems, alkalinity is controlled by carbonate chemistry. However, there are non-carbonate contributors to alkalinity and acid neutralizing capacity (ANC); some of these are constituents in Bayer liquor and products of wastewater neutralization. The effects of vanadate, aluminate, hydrotalcite and organic anions on seawater alkalinity and ANC are presented in this paper.

The alkalinity and ANC of seawater was not affected by vanadate. This was also true for when 2.86 to 30.3  $\mu\text{g/L}$  Al was added to seawater. However, alkalinity decreased in the presence of 69.3  $\mu\text{g/L}$  Al. This may be attributed to hydrotalcite (HT) formation causing an increase in ANC. Alkalinity and ANC increased with 147  $\mu\text{g/L}$  Al.

Hydrotalcite greatly increased ANC. The results showed a linear correlation between HT and ANC. A slight increase in alkalinity was also observed, which was attributed to HT nanoparticles and release of loosely sorbed carbonate/noncarbonate contributors.

When present in high concentrations ( $\geq 1809\text{mg/L}$ ), oxalate greatly increased alkalinity. However, at lower concentrations ( $\leq 1206\text{mg/L}$ ), the effect of oxalate on seawater alkalinity was limited by the precipitation of non-titratable calcium oxalate; and did not contribute to ANC. Formation of non-titratable calcium oxalate was verified by experiments in deionized water, which also showed that alkalinity varied linearly with dissolved oxalate concentration.

Gran function plots of titrations down to pH 2.5 were used to determine alkalinity and ANC throughout this study. These were compared to those calculated using a set endpoint of pH 4.5. The results indicate that the endpoint method is adequate for typical seawater. However, the shortcomings of this method are revealed when HT and oxalate are present. In the case of HT, its incomplete dissolution at pH 4.5 results in an underestimation of ANC. However the contribution of oxalate to seawater alkalinity are completely undetected by titrations to pH 4.5, which is above the  $\text{pK}_a$  values of this organic anion.

## 1. Introduction

### 1.1 Alkalinity and acid neutralizing capacity

Alkalinity and acid neutralizing capacity (ANC) are measures of a water sample's ability to neutralize acid. Alkalinity is concerned with dissolved solutes in filtered water to neutralize acid, whereas ANC is the acid neutralizing capacity of both dissolved solutes and solid particulates in unfiltered water. In the absence of titratable solids, ANC is equivalent to alkalinity. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, for determining the efficiency of wastewater processes and the presence of contamination by anthropogenic wastes, and for maintaining ecosystem health (Rounds 2006). Measurements of these parameters have found applications in a number of industries. In the case of Rio Tinto Alcan Gove, ANC is considered one of the best indicators of Bayer liquor presence in and interaction with seawater discharges.

In many aqueous systems such as seawater, alkalinity is controlled by carbonate chemistry. However, any species that reacts with strong acids can contribute to alkalinity. Some important noncarbonate contributors include: hydroxide, ammonia, borate, silicate, aluminate, arsenate, phosphate and organic anions, e.g. acetate and propionate (Rounds 2006). A number of these species are present in significant concentrations in Bayer liquor and contribute to the elevated alkalinity. Bayer liquor derived noncarbonate species that persist in seawater neutralized wastewater are likely to increase seawater alkalinity. The formation of hydrotalcite (HT) and other titratable solid by-products in neutralized Bayer wastewater would elevate seawater ANC. The effects of vanadate, aluminate, HT and oxalate on seawater alkalinity and ANC are presented in this paper.

### 1.2 Gran function plot method

A few techniques are available for determining alkalinity and ANC. These include the inflection point titration (IPT) method, Gran function plot method and the fixed endpoint method (titration to pH 4.5). The latter is no longer recommended by the US Geological Survey as it is less accurate than IPT and Gran methods (Rounds 2006).

Alkalinity and ANC measurements in this study were determined using the Gran method, as it is recommended for samples with appreciable noncarbonate contributors and organic acids (Rounds 2006). Six Gran functions can be used to analyze potentiometric titration data. The use of a particular function depends on the pH range of interest. In this study the first Gran function ( $F_1$ ) was employed:

$$F_1 = (V_o + V_t)10^{-\text{pH}} \quad (1)$$

where  $V_o$  is the initial volume of the sample and  $V_t$  is the volume of acid titrant added.  $F_1$  is valid for the pH range below the bicarbonate equivalence point ( $\sim\text{pH}$  4.5). Hence contributions of organic acids to alkalinity can be determined if samples are titrated to pH 2.5 (Rounds 2006).

Figure 1a shows a normal titration curve for filtered seawater collected locally from Nightcliff (Darwin Harbour). This titration data can be expressed as  $F_1$  (Figure 1b). The non-zero linear portion of the Gran plot can be extrapolated back to the x-axis to determine a titre of 5.56 mL, which equates to an alkalinity of 2.22 meq/L or 111mg/L  $\text{CaCO}_3$  equivalent.

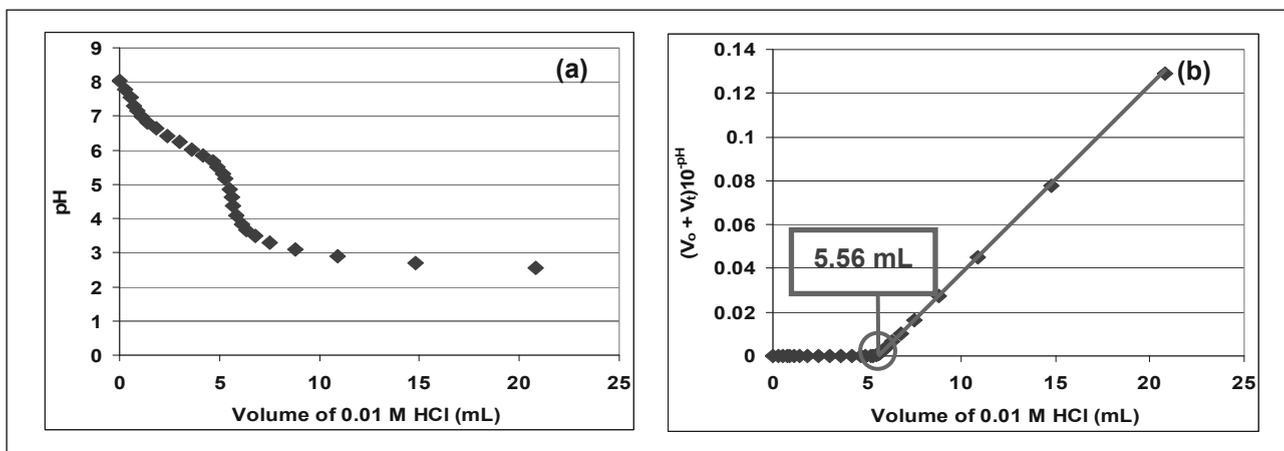


Figure 1. Nightcliff seawater (a) titration curve and (b) Gran function plot

## 2. Methodology

All chemicals used were analytical reagent grade. Alkaline solutions of aluminate and vanadate were prepared in deionized water ( $<0.5 \mu\text{S cm}^{-1}$ ) from 1000mg/L Al and V standard solutions and 0.1 M NaOH.

Experiments were performed in volumetric flasks or beakers with continuous stirring when equilibration was required. Filtered (0.45  $\mu\text{m}$ ) and unfiltered samples were collected for determination of alkalinity, ANC, oxalate and metals. However, filtration was not required for experiments involving vanadate due to the solubility of this species.

Filtered and unfiltered samples (25 mL) were analyzed by potentiometric titration with 0.01 M HCl to pH 2.5. A CyberScan pH 300 meter (Eutech Instruments) was used to monitor pH changes. Gran function plots of the titration data were used to determine alkalinity and ANC for filtered and unfiltered samples, respectively. Selected metals samples were measured by inductively coupled plasma-mass spectrometry (Agilent 7500ce ICP-MS) to support interpretation of alkalinity and ANC data when required. Oxalate analysis was performed by capillary electrophoresis at Rio Tinto Alcan Queensland Research and Development Centre (QRDC), Brisbane.

## 3. Results and discussion

### 3.1 Effect of vanadate on seawater alkalinity

Vanadium is one of the key indicators of Bayer liquor in seawater discharges from the refinery (Munksgaard and Parry 2006). In Bayer process wastewater, vanadium is likely to be a form of vanadate. Although vanadate was not considered a major contributor to alkalinity or ANC, the aspects mentioned above warranted its inclusion in this study. Aliquots of an alkaline vanadate solution (pH 8.72) were added to seawater. The resulting alkalinity was determined immediately and plotted against added V as shown in Figure 2; the inset illustrates V remains dissolved in seawater. The Gran results (filled diamonds) clearly show vanadate is not an important contributor to alkalinity, as values are within the range of background seawater alkalinity (Figure 2).

Although the fixed endpoint method was not used in this study, titration data from the Gran method was used to calculate alkalinity based on an endpoint of  $\sim\text{pH } 4.5$  for each V dosage. This data set is plotted in Figure 2 as unfilled diamonds, and would reflect ANC measured by the online meter at Rio Tinto Alcan Gove. Alkalinity values determined by the Gran and endpoint methods for vanadate solutions are in general agreement – a slight discrepancy of 0.3-3.4% was observed for corresponding alkalinities determined by the different methods. These results

indicate that the online meter is adequate for seawater with appreciable amounts of V.

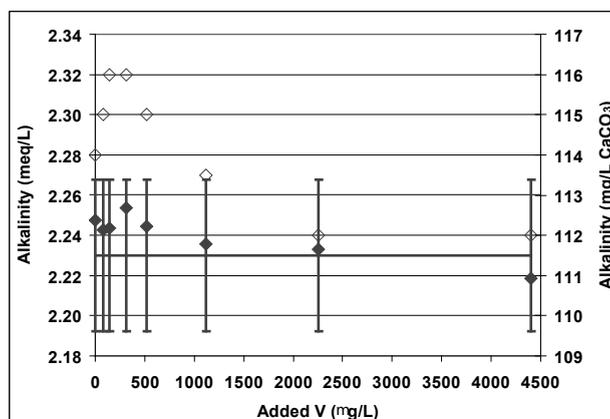
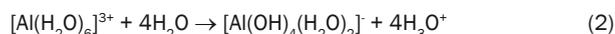


Figure 2. Effect of V on seawater alkalinity. Inset: Theoretical versus measured V in alkalinity experiments (horizontal line represents average background seawater alkalinity for this study; filled diamonds reflect Gran data; unfilled symbols denote simulated data based on  $\sim\text{pH } 4.5$  endpoint).

### 3.2 Effect of aluminate on seawater alkalinity and ANC

Neutralized wastewater from alumina production at Rio Tinto Alcan Gove contains higher concentrations of Al than background seawater. Hydrolysed Al species, including aluminate, can contribute to alkalinity (Reynolds and Neal 1987). This may partly explain the greater alkalinity of seawater at the outfall (median = 151mg/L  $\text{CaCO}_3$ ) compared to background (median = 128mg/L  $\text{CaCO}_3$ ).

To simulate discharge waters, Al was added to seawater experiments as aluminate, which was prepared by adjusting the pH of a 100mg/L Al solution to 10.76. Dissolved Al is converted to aluminate at  $\text{pH} > 10$  (Manahan, 1984):



Aliquots of the aluminate solution were added to seawater to yield a series of concentrations ranging from 2.86 to 147  $\mu\text{g/L}$  of added Al. These values are within the range of filtered (0.45  $\mu\text{m}$ ) Al measured at the Rio Tinto Alcan Gove outfall (Rio Tinto Alcan Gove Pty Limited 2006). To ensure Al was the only variable, deionized water with pH 10.55 was also added to experiments to conserve the added  $[\text{OH}^-]$  ( $6.91 \times 10^{-7} \text{ M}$ ). Solutions were allowed to equilibrate overnight before samples were removed for analyses. The alkalinity and ANC values determined by the Gran method are shown as filled symbols in Figure 3.

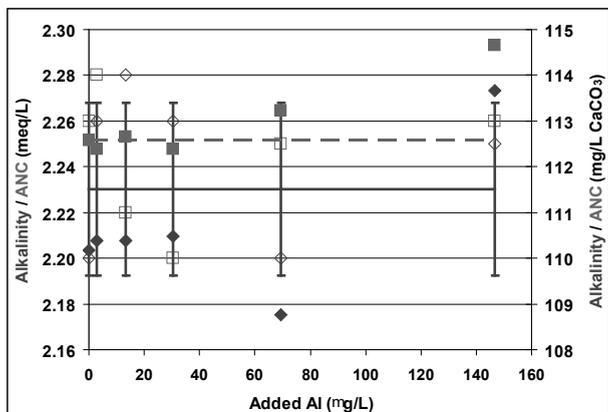


Figure 3. Effect of Al on seawater alkalinity (♦) and ANC (■) (solid and dashed horizontal line represents average background seawater alkalinity and ANC without added Al, respectively; filled symbols reflect Gran data; unfilled symbols denote simulated data based on ~pH 4.5 endpoint).

Local Nightcliff seawater, used for aluminate experiments, had a background alkalinity of ~2.23 meq/L (~111.5mg/L CaCO<sub>3</sub>). A slight increase in alkalinity was observed as the added Al increased from 2.86 to 30.3 µg/L (Figure 3), but this is considered negligible as values fall within the error of background alkalinity. Increasing the Al from 2.86 to 30.3 µg/L also had no effect on ANC values. Although ANC values for 0 to 30.3 µg/L of added Al are greater than corresponding alkalinities, both values fall within the range for average background alkalinity. This indicates the absence of titratable solids, such as HT, can greatly affect ANC and will be discussed later.

An increase in ANC was observed as the added Al increased to 69.3 µg/L. This also resulted in a corresponding decrease in alkalinity (Figure 3). It was initially believed these changes to ANC and alkalinity may be caused by the formation of hydrotalcite. However, Figure 4 clearly shows that very little, if any Al (for concentrations used in this study) precipitated out of solution as HT. This is supported by the corresponding ANC value for 69.3 µg/L added Al, which lies within the range of normal background alkalinity, indicating an absence or trace amounts of titratable solids. Further, the alkalinity only decreased by 2.5%, which is negligible. This means microparticles of HT are unlikely.

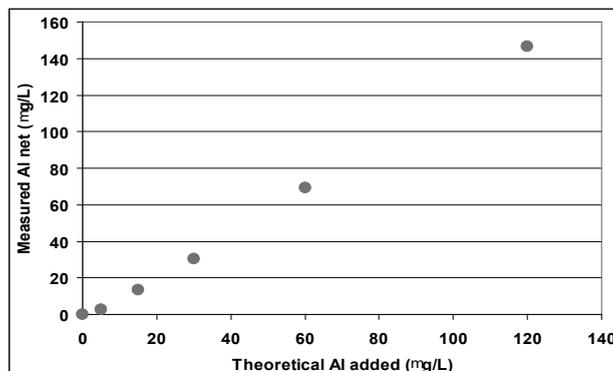


Figure 4: Theoretical and measured filtered (0.45 µm) Al in alkalinity experiments (Measured Al net: Background Al in seawater was subtracted from measured values)

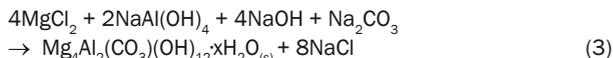
Increases in alkalinity and ANC are observed at the highest Al concentration studied. Although these changes to alkalinity and ANC are small (~2%), the results cannot rule out the possibility that dissolved Al at 147 µg/L contributes to alkalinity or indirectly to ANC by formation of HT. Reynolds and Neal (1987) reported a significant contribution of inorganic Al to fresh streamwater at concentrations similar to this study. However, Figure 3 clearly shows little or no effect of Al species on seawater alkalinity, which is outweighed by the bicarbonate buffering. It is conceivable that the effect of aluminate on alkalinity would increase at higher Al

concentrations. However, this was not pursued as any further increase in dissolved Al would likely cause the precipitation of HT from the seawater. The influence of HT on alkalinity and ANC is described below.

Alkalinities determined by the endpoint method compare well with Gran data (Figure 3). This is attributed to the large buffering contribution of bicarbonate. However, large differences in alkalinity values determined by the two techniques can occur (Reynolds and Neal 1987), depending on the abundance and nature of noncarbonate alkalinity contributors.

### 3.3 Effect of hydrotalcite on seawater alkalinity and ANC

Neutralization of Bayer process wastewater by seawater results in the precipitation of hydrotalcite (HT), which occurs when sodium aluminate reacts with magnesium chloride (Smith et al. 2005):



HT is known as a layered double hydroxide, which can intercalate carbonate (reaction 3). A large proportion of the HT is made up of hydroxide and carbonate, hence HT can be expected to greatly influence seawater ANC.

Natural HT from Rio Tinto Alcan Gove was used in this study without further treatment. It was added to seawater to yield concentrations ranging from 54.5 to 807mg/L. Gran titrations were performed on filtered and unfiltered samples to ascertain the effect of HT on the alkalinity and ANC of seawater. The results plotted in Figure 5 clearly show a large contribution of HT to seawater ANC. The linear relationship between seawater ANC and HT concentration indicates 53% of HT is made up of acid neutralizing components. It is noteworthy that hydroxide and carbonate represents 52.3% (by weight) for HT containing five water molecules of crystallization (x = 5, reaction 3). Further, the linear relationship between ANC and HT indicates ANC equals 105mg/L CaCO<sub>3</sub> in the absence of HT. This is equivalent to background alkalinity (horizontal line, Figure 5), which is to be expected when titratable solids are absent.

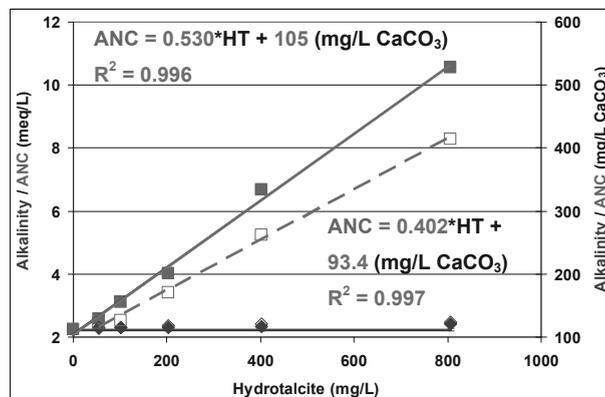


Figure 5. Effect of hydrotalcite on seawater alkalinity (♦) and ANC (■) (solid horizontal line represents average background seawater alkalinity; filled symbols reflect Gran data; unfilled symbols denote simulated data based on ~pH 4.5 endpoint).

Figure 5 shows a large discrepancy between ANC determined by the Gran method and values calculated with an endpoint of ~pH 4.5. This is attributed to complete dissolution of HT and thus complete buffering for Gran titrations, which are performed to pH 2.5. Hence incomplete dissolution of HT at pH 4.5 would result in the observed underestimation of seawater ANC by the endpoint method. The instability of HT precipitate at pH < 2.5 has been recognized by Smith et al. (2005).

HT has a negligible effect on seawater alkalinity compared to ANC (Figure 5). Nonetheless an increase in alkalinity was observed in

the presence of HT (Figure 6). This may be attributed to the release of loosely sorbed carbonate and/or non-carbonate contributors from the surface of HT. The increase in alkalinity with increasing HT concentration may support a desorption mechanism. It is also conceivable that HT nanoparticles that pass through the 0.45  $\mu\text{m}$  filter will contribute to alkalinity. Smith *et al.* (2005) reported discrete HT hexagonal plate-like crystals with dimensions of 50 nm by 20 nm.

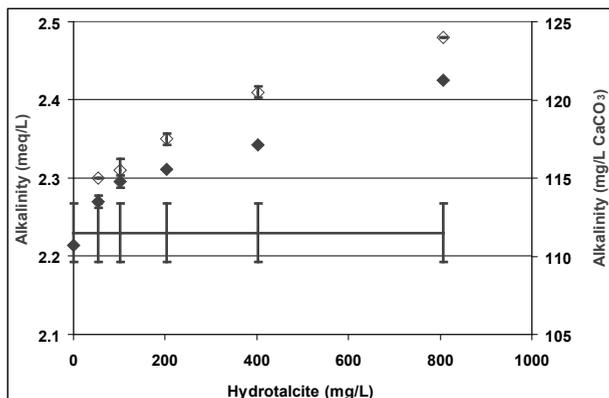


Figure 6: Effect of hydrotalcite on seawater alkalinity (solid horizontal line represents average background seawater alkalinity; filled diamonds reflect Gran data; unfilled symbols denote simulated data based on  $\sim\text{pH}$  4.5 endpoint).

In addition to carbonate, other anions present in Bayer process wastewater may be taken up by HT, including vanadate, molybdate and oxalate (Smith *et al.* 2005; Smith and Ramakrishna 2007). Desorption of these ions from HT would influence seawater alkalinity, some more than others. Release of molybdate and vanadate are expected to have little or no effect on seawater alkalinity based on results presented in sections 3.1 and 3.2. However, desorption of organic anions, such as oxalate, from HT are expected to have a greater contribution to alkalinity. The effect of oxalate on seawater alkalinity is presented below. Further, release of surface hydroxide ions from the untreated natural HT would also result in the observed increase in alkalinity (Figure 6).

Contrary to ANC results, alkalinity determined by titration to an endpoint of  $\sim\text{pH}$  4.5 results in an overestimation compared to values determined by the Gran method. This was also observed by Reynolds and Neal (1987) when they compared streamwater alkalinity determined by Gran and fixed endpoint methods. The inaccuracy of the fixed endpoint method compared to Gran titrations has also been recognized by the US Geological Survey (Rounds 2006).

### 3.4 Organic anions

Caustic digestion of organic material associated with bauxite gives rise to a suite of organic anions in Bayer process wastewater. These include low molecular weight anions such as oxalate, acetate, malonate, succinate, tartrate and formate (Baker *et al.* 1995; Breadmore *et al.* 2001; Chen *et al.* 2006; Haddad *et al.* 1995). Organic anions in neutralized Bayer process wastewater may contribute to seawater alkalinity. The effect of organic acids on the acid neutralizing capacity of natural waters has been reported (Mattsson *et al.* 1995). Oxalate, one of the principal organic degradation products from bauxite in the Bayer process (Chen *et al.* 2006), was used to demonstrate the effect of organic anions on seawater alkalinity.

#### 3.4.1 Effect of oxalate on seawater alkalinity and ANC

The effect of oxalate on seawater alkalinity is illustrated in Figure 7. The results clearly show alkalinity increases in the presence of oxalate, which was added to experiments as the ammonium

salt. The non-linear relationship between alkalinity and oxalate concentration is attributed to the precipitation of oxalate on addition to seawater. For ammonium oxalate dosages of 301.5, 603, 1206 mg/L, oxalate remaining in seawater was undetectable by capillary electrophoresis (Figure 8). However, the increase in alkalinity above background indicates that some oxalate remains in solution (Figure 7).

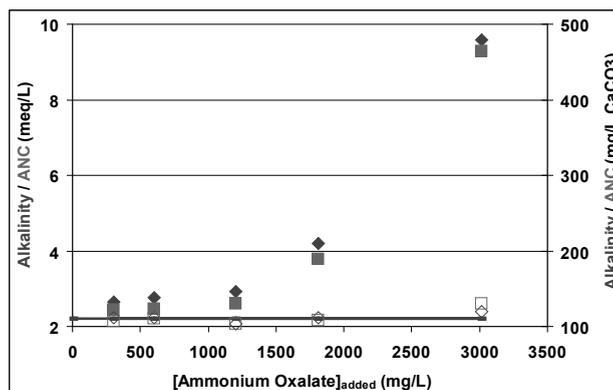


Figure 7: Effect of oxalate on seawater alkalinity ( $\blacklozenge$ ) and ANC ( $\blacksquare$ ) (solid horizontal line represents average background seawater alkalinity; filled symbols reflect Gran data; unfilled symbols denote simulated data based on  $\sim\text{pH}$  4.5 endpoint).

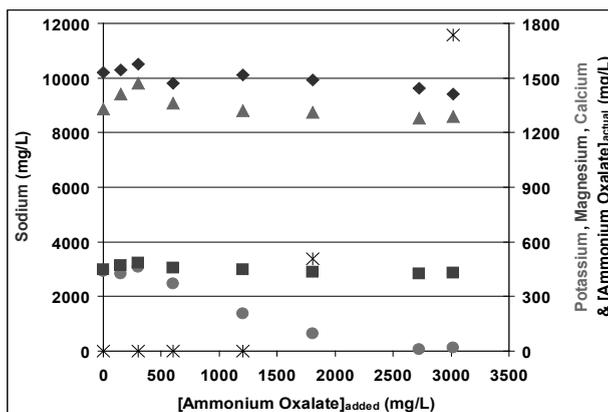


Figure 8: Effect of oxalate on seawater Na ( $\blacklozenge$ ), K ( $\blacktriangle$ ), Mg ( $\blacksquare$ ) and Ca ( $\bullet$ ) ( $[\text{Ammonium Oxalate}]_{\text{actual}}$  is denoted by  $*$ )

The concentration of  $\text{Ca}^{2+}$  in seawater decreases as the dosage of ammonium oxalate increases, whereas the other three cations remain relatively unchanged (Figure 8). This is in agreement with the order of solubility for oxalate salts:  $\text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} \gg \text{Ca}^{2+}$  (practically insoluble, Windholz 1983). The results in Figure 8 show  $\text{Ca}^{2+}$  is largely responsible for salting oxalate out of seawater – the other three cations may be involved but to a much lesser extent. Relatively little  $\text{Ca}^{2+}$  remains when the initial ammonium oxalate concentration is increased to 1809 mg/L and at 3015 mg/L,  $\text{Ca}^{2+}$  is almost undetectable (Figure 8). Consequently more dissolved oxalate is present (Figure 8), and thus a greater increase in alkalinity is observed (Figure 7).

Although major cations limit the effect of oxalate on seawater alkalinity, the resulting precipitate is not titratable and therefore will not contribute to ANC – unlike HT solids (section 3.3). This can be deduced from the similarity between alkalinity and ANC for each ammonium oxalate treatment (Figure 7).

Data determined by the fixed endpoint method also shows that seawater alkalinity is equivalent to ANC in the presence of oxalate (Figure 7). However, unlike the Gran method, the effect of oxalate on seawater alkalinity was undetectable by the fixed endpoint technique. This can be explained by considering the structure of oxalate, which has two sites of protonation (Figure 9). According to the  $\text{pK}_a$  values of oxalic acid (Table 1), the first carboxylate

group of oxalate protonates at pH 4.19 and the second site at pH 1.23. Hence neither functional group will be protonated during titrations to a fixed endpoint of pH 4.5. Consequently the buffering of oxalate and its contribution to alkalinity would be undetected as shown in Figure 7. Elevated alkalinity determined by the Gran method is attributed to buffering by one of the carboxylate groups as titrations were carried down to pH 2.5. At this pH, the second functional group of oxalate would be unprotonated as it has a  $pK_a$  of 1.23.

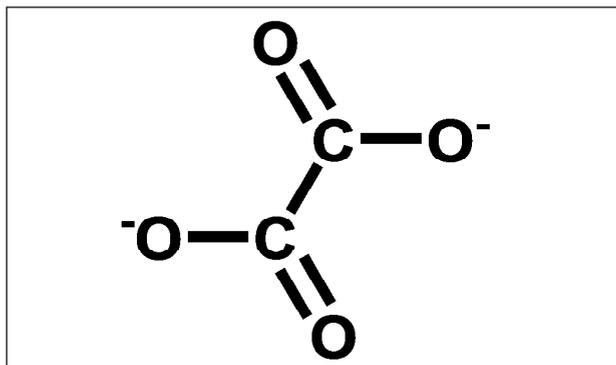


Figure 9. Molecular structure of oxalate.

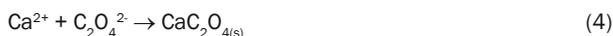
Table 1.  $pK_a$  values of some organic acids reported in Bayer process wastewater (ZirChrom 2008)

Organic acid	$pK_{a1}$	$pK_{a2}$
Oxalic	1.23	4.19
Malonic	2.83	5.69
Formic	3.75	-
Acetic	4.76	-
Succinic	4.16	5.61
Tartaric	2.98	4.34
Glutaric	4.31	5.41

### 3.4.2 Effect of $Ca^{2+}$ on oxalate alkalinity and ANC

A series of  $CaCl_2$  solutions: 0, 5, 10, 15, 20 mM were prepared in deionized water. These solutions also contained 21.3 mM ammonium oxalate. Oxalate was salted out of solution in the presence of  $Ca^{2+}$ , as was the case in seawater (section 3.4.1) which contains  $\sim 12.5$  mM  $Ca^{2+}$ . As the added  $Ca^{2+}$  ( $[Ca]_{added}$ ) increased so did the oxalate precipitation.

The  $Ca^{2+}$  measured in the control solution (without ammonium oxalate) was 16.9 mM – lower than the theoretically added amount of 20.1 mM. However, very little if any  $Ca^{2+}$  remained in solution when ammonium oxalate was added. Solid calcium oxalate is expected to form with a Ca to oxalate ratio of 1 to 1:



The theoretical amount of oxalate that did not react with  $Ca^{2+}$  ( $[Ammonium\ Oxalate]_{net}$ ) can be estimated by:

$$[Ammonium\ Oxalate]_{net} = [Ammonium\ Oxalate] - [Ca]_{added} = 21.3 - [Ca]_{added} \quad (5)$$

In the absence of added  $Ca^{2+}$ , the 21.3 mM Ammonium Oxalate solution has an alkalinity of 13.7 meq/L, which equates to  $\sim 690$ mg/L  $CaCO_3$  (Figure 10). This is a huge contribution to alkalinity considering that the alkalinity of the control  $CaCl_2$  solution is only 0.1 meq/L (3mg/L  $CaCO_3$ ). Further, the typical alkalinity of seawater is  $\sim 2.23$  meq/L (111.5mg/L  $CaCO_3$ ). It should be noted that oxalate contributions to alkalinity are better expressed in meq/L, rather than mg/L  $CaCO_3$  which is misleading.

As the added  $Ca^{2+}$  increases, the  $[Ammonium\ Oxalate]_{net}$  decreases and so too does the alkalinity (Figure 10). This is also observed for ANC. A comparison of corresponding alkalinity and ANC data shows the calcium oxalate precipitate is not titratable (Figure 10), and does not contribute to ANC as was observed for seawater experiments (section 3.4.1).

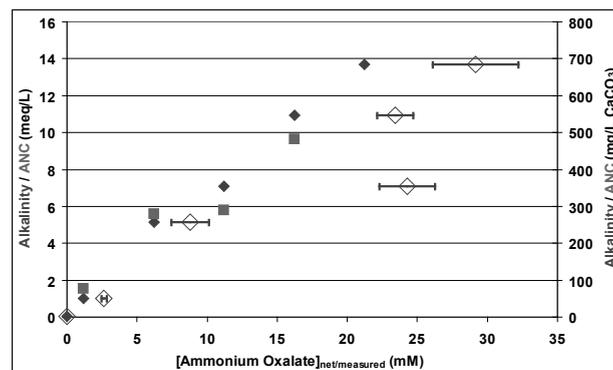


Figure 10: Alkalinity ( $\blacklozenge$ ) and ANC ( $\blacksquare$ ) of oxalate solutions in the presence of  $Ca^{2+}$ . Inset: Effect of added  $Ca^{2+}$  on  $[Ammonium\ Oxalate]_{net}$  ( $[Ammonium\ Oxalate]_{measured}$  is denoted by  $\diamond$ ).

Dissolved oxalate was measured using capillary electrophoresis and plotted in Figure 10 as unfilled diamond symbols against the corresponding alkalinity. The results show that alkalinity is generally proportional to the dissolved oxalate concentration, which was also observed for alkalinity plotted against  $[Ammonium\ Oxalate]_{net}$ . At concentrations less than 10 mM, the calculated  $[Ammonium\ Oxalate]_{net}$  is comparable to  $[Ammonium\ Oxalate]_{measured}$ . This gives credence to the assumption that calcium oxalate solids have a Ca:oxalate ratio of 1:1. The deviation of  $[Ammonium\ Oxalate]_{measured}$  from  $[Ammonium\ Oxalate]_{net}$  at dissolved oxalate concentrations greater than 10 mM may indicate lower precision of measured oxalate – as seen by the larger errors at higher concentrations.

## 4. Conclusions

Vanadium is present at a few milligrams per litre in Bayer liquor but is reduced to less than 200  $\mu\text{g/L}$  in discharge waters. Oxyanions of V are expected to persist in seawater but they would have very little if any contribution to seawater alkalinity.

Trace Al in seawater also had a negligible effect on seawater alkalinity. A marginal increase in alkalinity was observed at the highest Al concentration studied (147  $\mu\text{g/L}$ ). It is conceivable that higher concentrations of aluminate would outweigh the bicarbonate buffering in seawater and result in a detectable increase in alkalinity. However, this was not pursued as any further increase in added aluminate would also carry a greater hydroxide component that would influence alkalinity. Moreover, there would be the added complication of HT precipitation. An increase in ANC resulted when 147  $\mu\text{g/L}$  Al was added to seawater due to HT formation.

Natural HT from Rio Tinto Alcan Gove had a substantial effect on ANC, which varied linearly with HT concentration. The results indicated 53% of HT (by weight) was comprised of acid neutralizing components, which would most likely be hydroxide and carbonate. This translates to a possible molecular formula of  $Mg_4Al_2(CO_3)(OH)_{12} \cdot 5H_2O$  for the natural HT.

Hydrotalcite had a relatively negligible effect on seawater alkalinity. Nonetheless, an increase in alkalinity was observed in the presence of HT. This was attributed to release of loosely sorbed carbonate, hydroxide, transition metal anions and organic anions. The presence of HT nanoparticles may also contribute to the observed alkalinity increase.

Oxalate can greatly increase alkalinity. However, its effect would be limited in seawater due to the precipitation of calcium oxalate; which is non-titratable as it does not contribute to ANC – unlike HT.

A comparison between Gran and fixed endpoint methods show mixed alkalinity/ANC results depending on the acid neutralizing component being investigated. No difference between the two methods was noticed for experiments involving Al and V. However, titrations to a fixed endpoint of ~pH 4.5 would underestimate the ANC contribution of HT due to its incomplete dissolution; whereas an overestimation was observed for alkalinity. Nonetheless, it appears that the fixed endpoint method is capable of detecting HT contributions to ANC, albeit not absolute.

The limitation of the fixed endpoint method was noticed for oxalate experiments; where no change was observed despite significant increases in alkalinity for [Ammonium Oxalate]  $\geq$  1809mg/L. The Gran method was able to detect the oxalate contribution to alkalinity as titrations were performed to pH 2.5, which was able to protonate the carboxylate of oxalate that corresponds to a  $pK_a = 4.19$ . Titration to pH 4.5 would not protonate this functional group. Consequently buffering by oxalate cannot be detected by the fixed endpoint method. However, this method would be able to detect alkalinity contributions by other organic anions with  $pK_a > 4.5$ .

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