FINAL REPORT

# Lake Rotorua Alum Application Study

Alumina concentration trials mixed at 300 rpm

*Prepared for*

**Bay of Plenty Regional Council**

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BY

ENVIROMEX NZ

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Project Manager:

P G Browne

… ..

Peter Browne
Environmental Engineer

Author:
(Optional)

**ENVIROMEX NZ LTD**
31 Cornwallis Road
WAITAKERE CITY
Ph : 64 9 950 4463
Fax: 64 9 811 8033

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# Executive Summary

The aim of this report is to examine performance of various alum products to control phosphorus within Lake Rotorua and to understand in more detail the effect on lakewater alkalinity and quantity of buffer products needed to maintain alkalinity. This report details a benchtop study of tests designed to investigate these aspects using lakewater extracted from the normal Bay of Plenty Regional Council (BoPRC) sample location in deep water south of Mokoia Island.

Two sets of lakewater samples were tested. The first lakewater samples were found to have reactive phosphorus levels less than the detectable limit. Algae had consumed all the available phosphorus. Coagulation tests resulted in separation of algae from the water column, however a comparative evaluation of solid alum and liquid alum to lock phosphorus was not practicable from the first samples. A second set of lakewater samples were spiked using potassium phosphate to achieve a phosphorus concentration similar to lakewater during hypolimnion conditions. These samples were used to demonstrate phosphorus locking capability.

Findings of this work are explained in more detail in the conclusions of Section 5. The main points are summarised below:

1. Kibbled alum and liquid alum exhibited similar phosphorus locking properties, achieving identical DRP reduction for the same concentrations of aluminum.

2. Kibbled alum has some attractive handling properties. It also has a rapid settling velocity and reasonably rapid dissolution, which have benefit to treat phosphorus within the water column and at depth, particularly when hypolimnion conditions exist. The rate of alum dissolution during settling was not determined.

3. Alum effectiveness to control phosphorus by coagulation of algae could not be demonstrated, i.e. coagulation of algae is possible and well understood, but uptake of phosphorus by alum from decaying algae is not proved by this study.

4. To maximise success of the project, application of alum must target periods when locking of reactive phosphorus can be optimised, i.e. algae activity is low. Refer also to item D of the conclusions in Section 5.

5. The spiked water control sample gave total phosphorus (TP) of 0.083 mg P/L and Dissolved Reactive Phosphorus (DRP) of 0.043 mg P/L. This difference demonstrated rapid uptake of reactive phosphorus despite the sample for analysis being placed on ice and held in a covered chilli-bin. DRP uptake would be substantially due to algal activity.

6. An aluminium dose of 0.3 mg $Al^{3+}$/L (6:1, $Al^{3+}$:DRP) was sufficient to lock all detectable DRP, whereas an aluminium dose of 0.1mg $Al^{3+}$/L (2:1, $Al^{3+}$:P) had little effect. Therefore the molar dose of aluminum needed to lock reactive phosphorus is greater than predicted by molar stoichiometry, i.e. 1:1, as per the following equation:-

   $Al_2(SO_4)_3 14H_2 0 + 2PO_4^{3-} \rightarrow 2AlPO_4 + 3SO_4^{2-} + 14H_2 0$

Higher stoichiometric ratios are to be expected for a very low phosphorus concentration such as is typical of Lake Rotorua water.

7. Costs for supply of liquid alum compared to kibbled alum in terms of equivalent performance are:-

| | | |
|---|---|---|
| (a) | Liquid alum | \$7.87/kg$Al^{3+}$ OR (\$1575/ha at 1mg/L$Al^{3+}$ & 20m deep) |
| (b) | Kibbled alum | \$5.50/kg $Al^{3+}$ OR (\$1100/ha at 1mg/L$Al^{3+}$ & 20m deep) |

8. It is recommended that a buffer be used where lakewater alkalinity is affected. Some options to consider are:-
   - Restrict alkalinity loss to no more than 35 percent of the initial value, or
   - 1 pH unit of start value, or
   - Maintain pH above 6.1 and not greater than 7.7.

9. A 35 percent reduction in alkalinity corresponded to liquid alum addition of 0.5 mg$Al^{3+}$/L, OR, 6.67g alum/$m^3$, OR, 8.81 L 47%w/w liquid alum/1000 $m^3$ lakewater, OR pH 6.1 and alkalinity of 6g/$m^3$ (as $CaCO_3$).

10. Test results of alkalinity buffers of calcium carbonate ($CaCO_3$ powder, i.e. calcite, from McDonalds Lime) and sodium carbonate ($Na_2CO_3$ crystal from Damar Industries) produced:-

| | | |
|---|---|---|
| (a) | $CaCO_3$ | \$0.36/kg liquid alum, (based on supply at \$163/T) |
| (b) | $Na_2CO_3$ | \$0.22/kg liquid alum, (based on supply at \$645/T) |

The assessment of $CaCO_3$ can be considered as approximate due to the difficulty of handling a rapidly settling suspension that is formed when added to water. In comparison, $Na_2CO_3$ forms a uniform and clear solution that can be accurately added to water samples. However an attractive property of calcite is that it virtually impossible to over correct pH, regardless of the amount of excess calcite.

11. Powdered alumina ($Al_2O_3$) and sodium silicate ($Na_2SiO_3$) were trialled as nucleation sites to promote settling of aluminum hydroxide. Tests with alumina/alum showed no apparent improvement. Sodium silicate has the additional favourable properties of itself forming a floc and could buffer against alum due to it's inherent alkalinity. However, it proved ineffective to enhance reduction of DRP either when used alone or in combination with alum. In fact, a reduction in phosphorus locking capacity of alum was noted. Consequently, $Na_2SiO_3$ cannot be used for phosphorus locking.

12. On the basis of these findings, it is recommended that kibbled alum be progressed to the next stage of trials in conjunction with calcite and/or soda ash in accord with project aims.

NB: The terms 'lakewater' in the context of this report refers solely to Lake Rotorua water.

## Acknowledgements

Thanks to the following organisations:-

BOPRC for liquid alum and access to the Utuhina facility.

Daymar Industries for the generously providing kibbled alum and soda ash.

McDonalds Lime for providing calcium carbonate powder

Lochmoigh for assisting with setup of facilities and completing tests.

Hill Laboratories completed analyses.

## 1.1 Brief

A brief was submitted to BPRC on 10th August. It included the following:-

BPRC advised the following brief; testing of an alum application to a lake with an alkalinity provider, it would be good to test

1. a mixture of alum and calcium carbonate applied as a slurry
2. alum and calcium carbonate applied separately
3. alum and hydrated lime (calcium hydroxide) applied as a slurry
4. alum and calcium hydroxide applied separately
5. alum and soda ash applied separately
6. other alternatives e.g. sodium aluminate

In addition, verbal communications confirmed there is to be less emphasis on lake sediment capping and more focus on lesser applications of phosphorus locking agents targeting seasonal bloom precursors.

Note: Bench trials did not include calcium hydroxide due to the volume of tests required and the ability to convert between soda ash and calcium hydroxide using alkali neutralisation graph[1]. Sodium aluminate was not trialled due it being a class 8 hazard product (highly corrosive pH 14)[4]. The products of sodium aluminate and water alkalinity are aluminum hydroxide and calcium carbonate, hence the results of alum and calcium carbonate should be comparable. Alumina in the form of $Al_2O_3$ was trialled.

## 1.2 Aims

The following aims are to be covered in this study:-

- confirm the range of alum application rate to achieve phosphorus locking is expected to be in the range of 0.3 to 1.0 ppm $Al^{3+}$,
- confirm if the desired application rate will result in some, little or no sediment cap potential,
- check availability and solubility of solid alum forms and mixing requirements to achieve same as liquid alum,
- check behaviour of alum in relation to various alkalinity stabilising substances,
- check availability and cost of non-alkalinity adjusting $Al^{3+}$ coagulants,
- gain an understanding of logistics of ‘at point of use’ solid alum mixing requirements compared with liquid alum application by assessing preliminary costs for likely contracted options.

## 1.3 Report Structure

Sections 3 to 5 of this report are focused on reporting outcomes of the trials. Greater description of how the work was completed can be found in Appendices A and B. Only an overview of the method statement is given Section 2.

## 2.1 Method Introduction

Refer Appendix A for the test program used for this study and Appendix B for greater detail of methods used for benchtop work completed for this project. Gangstirrer, Imhoff and settling column tests were completed as described.

Samples of products used in the trial were sourced as follows:-

| | |
|---|---|
| BPRC | Alum solution taken from bulk alum tank at Utuhina |
| McDonalds lime Ltd | Calcium carbonate powder (calcite or limestone) |
| Darmar Industries, Rotorua | Flake alum, sodium silicate and sodium carbonate (soda ash) |
| Poolquip | Kibbled aluminum sulphate |

A temporary test facility was established at the Utuhina phosphorus locking plant at Depot Street, Rotorua. Benchtop trials were completed using lake samples extracted from 2 metres depth at coordinates that are consistent with in-lake monitoring done by Bay of Plenty Regional Council. 60 litres of water were kept in the cool atmosphere of the Utuhina facility while tests were completed. Representatives from Enviromex Ltd (Peter Browne) and Lochmoigh Ltd (John McIntosh) attended temporary facilities for the duration of on-site trials.

***Figure 2-1 Alkalinity measurement and correction equipment***

| | |
|---|---|
|  | Samples collected during the trial were placed into 250mL sample bottles for analysis by Hill Laboratories in Hamilton. As the intention is to examine the effect of prolonged contact of aluminum with phosphorus, samples were kept for three days before sending to Hill laboratories. In the case of alumina, instructions were specified for Hills to hold these samples for a further week before analysis. This was expected to allow locking of phosphorus onto low concentrations of alumina to occur to completion. |

## 2.2 Assumptions

Tests utilised 3x20 litre lakewater samples taken from 2 metres depth on Wednesday 21st September at the BPRC monitoring position approximately 0.8 km south of Mokoia Island, Lake Rotorua. Retest samples were collected from a more southerly position on Friday 11th November.

Analytical results found the initial samples contained dissolved reactive phosphorus at or below the detection limit. This required a second sample to be spiked using sodium phosphate to achieve a phosphorus concentration in the range of 0.06 to 0.09mg/L.

The tests do not account for effects such as the possibility of lakewater exhibiting differing chemistry throughout the lake body, either spatially (transport of alum causing areas of lower concentration) or chronologically (lakewater characteristic and constituent changes) and do not account for benthic effects, changes in stream inputs or atmospheric influences.

Chemical suppliers generally rely on information from others for concentration of active ingredients and trace contaminants. Independent tests have been done to validate supplied information.

The results are:

a) 62w/v liquid alum is advised to contain 4.3% aluminum. Laboratory analysis of a grab sample gave 70.3 g/m$^3$ aluminium, which equates to 5.3% aluminum.

b) Kibbled alum is reported to contain 9% aluminum. Laboratory analysis of a grab sample gave 10.3% aluminum.

Up to 20 percent more active ingredient is implied by the grab samples.

Alkalinity adjustments were sensitive to the amounts of buffer reagents added. In particular, calcite ($CaCO_3$) has low solubility compared to other reagents tested. When mixed with water it produces a little dissolved product and mostly suspended fines that do not dissolve until dissolved products are utilised. The suspended fines settle rapidly which makes it difficult to accurately assess true calcite concentrations while completing benchtop tests.

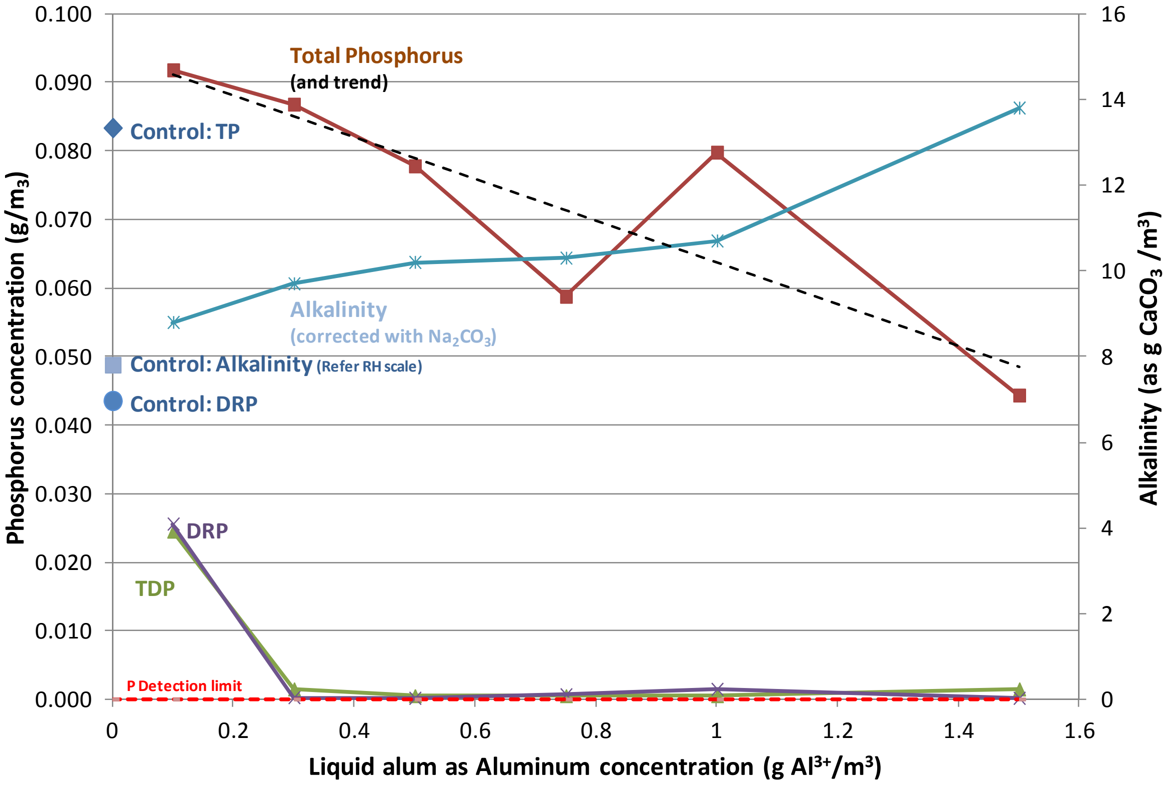
Hydrated lime and calcite are local supply. Soda ash requires indent with (for the purposes of this report) an exchange rate of 0.76 as advised by Damar Ltd.

## 3.1 Liquid Alum

### 3.1.1 Liquid alum phosphorus reduction

Figure 3-1 shows $Na_2CO_3$ alkali adjusted gang stirrer contact tests of liquid alum uptake of phosphorus. A target pH for adding alkalinity was set by the control sample ( raw water) that had a pH value of 6.53. These results clearly show that an aluminum dose of 0.3 mg/L is sufficient to lock all detectable DRP in lakewater. Higher dose rates are needed to precipitate total phosphorus. Most literature reviewed during this study agrees that an aluminum dose greater or equal to 2 mg/L is needed to significantly remove total phosphorus from the water column by precipitation. This is consistent with an extrapolation of Figure 3-1.

***Figure 3-1 Liquid alum uptake of DRP***



The large difference between total phosphorus and dissolved phosphorus before alum is added shows the effect of algae uptake of DRP. Also, uptake of DRP by algae occurred in the control sample. If algae were not present, then DRP in the above figure would have the same value as total phosphorus. It would therefore be better to target available phosphorus during conditions where microorganism activity is low. Refer Section 7.3.2 of Appendix B for more detail on this topic. Avoiding periods of high biomass (algae) will ensure phosphorus is directly bound to aluminum and locked.

### 3.1.2 Alkalinity and precipitate

Figure 3-2 shows alkalinity declining with increased alum dose. Lake Rotorua water is low in alkalinity compared to other central north island lakes and streams. Both control samples exhibited lakewater alkalinity less than 10mg $CaCO_3$/L.

Points highlighted by Figure 3-2 are:

a) There is only enough alkalinity to buffer the acid effect of 0.1 mg/L aluminum, thereafter alkalinity steadily declines to be substantially consumed by 1.25 mg/L aluminum. Therefore, on the basis of the sample tested, any greater dose than around 0.5 mg/L aluminum (i.e. 8.8 litres of 47%w/w alum in 1000 $m^3$) would result in a significant change in lakewater alkalinity.

b) Filtered aluminum steadily increases with dose rates above 0.5g $Al^{3+}/m^3$. Low alkalinity is responsible and suggests that it be supplemented thereafter.

c) Settleable floc was produced by all samples above 0.75 ppm $Al^{3+}$. Fine suspended (pinhead) floc was visible in all samples in gang stirrer tests, though no settled floc occurred at, or below 0.5 ppm $Al^{3+}$. (Refer section 3.1.5 for comparison of this with settling cylinder tests).

d) Most floc sank, but a visible proportion floated. Conditions that promote floating floc are not well understood, but may be associated with algae responding to the aluminum. Filtered aluminum residuals are most likely hydroxides in the colloidal range.

e) The effect of greater contact time was investigated by mixing overnight low concentrations samples from 0.05ppm to 0.5 ppm$Al^{3+}$. These are shown in Figure 3-2 and a photo in Figure 3-3. Overnight tests generated floating floc from 0.3 ppm$Al^{3+}$ and above. Tests containing less than 0.1 ppm$Al^{3+}$ did not produce visible floc.

f) At 0.5 ppm $Al^{3+}$ the strongest floating floc was produced and at 1.5 ppm $Al^{3+}$ the second strongest floating floc. These tests have corresponding lower total aluminum results, presumably more was consumed in the formation of floc.

g) The fraction of aluminum between total and filtered will be suspended floc. It was noted that water samples had a slight greenish tinge and floc also exhibited this. Therefore it is can be expected that some alum will be consumed forming precipitates that attached to algae as floc.

h) A condition to be avoided is excessive consumption of lakewater alkalinity by added reagents. This will inhibit hydrolysing of some alum to aluminum hydroxide resulting in free ions of aluminum. To avoid this, lakewater will require a buffer to be added where alkalinity of lakewater is significantly reduced, say by 30 percent or pH falls below 6.1, or pH falls by greater than 1 pH unit. It is therefore proposed that a margin be established to ensure lakewater alkalinity is preserved.

Figure 3-2 Liquid alum alkalinity demand

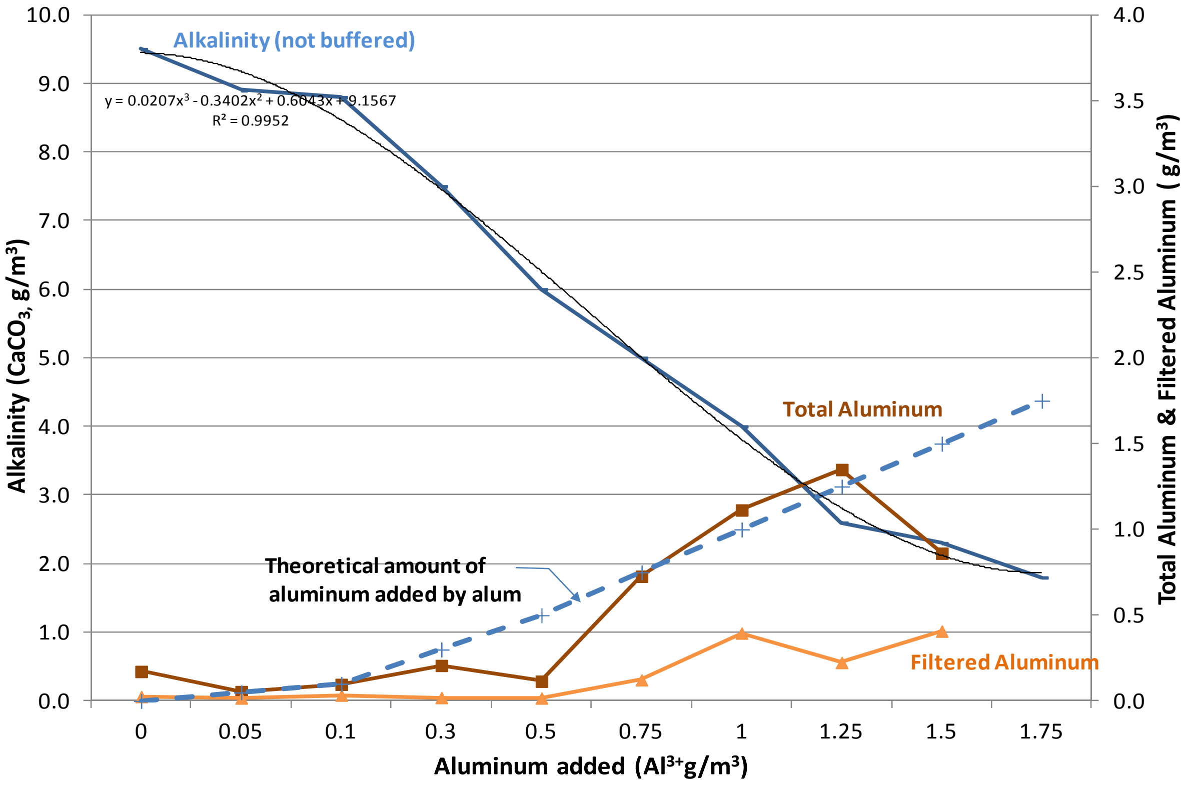


Figure 3-3 Floating floc produced by liquid alum

Plate A: 0.75 ppm$Al^{3+}$ floc just visible on surface of water in photo, but very obvious in the lab. Short contact time.

Plate B: 0.5 ppm $Al^{3+}$ generated strong floc, some of which can be seen floating in this sample. Overnight contact time.

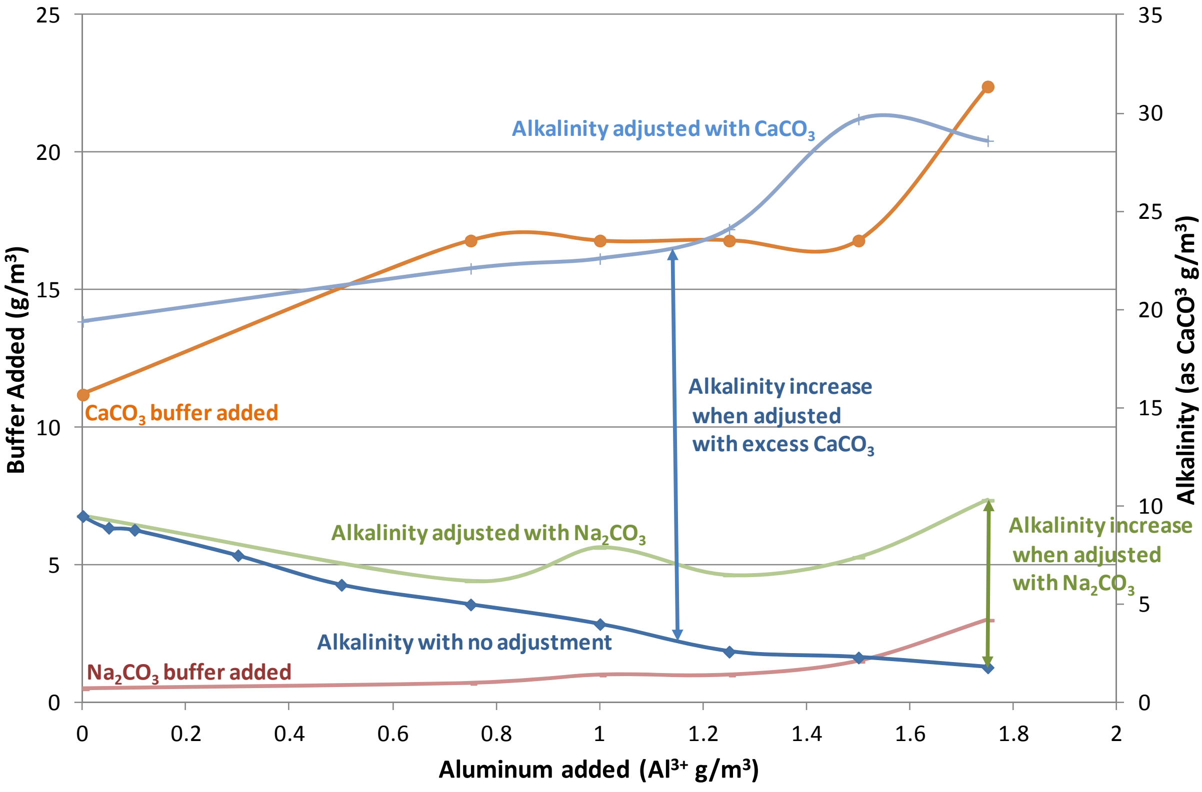
### 3.1.3 Liquid alum buffers

One percent solutions of calcium carbonate ($CaCO_3$ powder of low solubility) and sodium carbonate (highly soluble $Na_2CO_3$) were prepared to correct sample alkalinity. Recorded pH values for 1% buffer solutions were 8.0 for $CaCO_3$ and 11.5 for $Na_2CO_3$. Sodium carbonate was considered a better choice in benchtop tests for the purpose of correcting pH and alkalinity. It is a fully soluble buffer, whereas calcite is only partially dissolved, meaning it will continue to meet alkalinity demand as it's soluble fraction is utilised. The choice of buffer depends on it's intended purpose, i.e. to provide a one-off adjustment to maintain the status-quo, OR to provide prolonged alkalinity adjustment. A strong advantage of $CaCO_3$ is that it is virtually impossible to overcorrect pH, even in excess.

Figure 3-4 shows alkalinity adjustments made on 200mL lakewater samples already treated with liquid alum. Adjustments made with calcite will be somewhere in the range of 0.3 to 0.7% solution instead of 1.0% due to incomplete suspension of calcite particles. Larger fractions of calcite sink rapidly and are difficult to keep in suspension. Excessive adjustment of alkalinity can easily occur, compared to natural lakewater at 9.5mg/L as $CaCO_3$.

Alkalinity adjustments with $Na_2CO_3$ were easier to control as this buffer fully dissolves at concentrations likely to be used. The resulting increase in accuracy can be seen below as start alkalinity was maintained reasonably consistently with $Na_2CO_3$.

***Figure 3-4 Alkalinity adjusted using buffers***



A useful parameter is the amount of buffer required to maintain alkalinity of lakewater per unit measure of liquid alum. A number of results that were used to produce Figure 3-4 have been averaged to give:-

1. 2* to 5 kg $CaCO_3$ per litre of 47%w/w liquid alum,
2. 0.44 kg $Na_2CO_3$ per litre of 47%w/w liquid alum.

* 2.8 kg $CaCO_3$ is a more realistic value, although 4 kg $CaCO_3$ is the calculated value based on results from the 1% suspension used in the tests and a 20 litre trial. However subsequent benchtop tests have confirmed liquid alum is neutralised at lower doses. 2.8 kg $CaCO_3$ is adopted for this report. All $CaCO_3$ tests produced a settled solids layers.

Hydrated lime (calcium hydroxide) was also considered although not specifically tested. By review of the alkali comparison chart in Appendix D it is noted that hydrated lime powder is more active than sodium carbonate by a proportion as follows:-

1kg $Ca(OH)_2$ is equivalent to 1.45 kg $Na_2CO_3$

The following shows the activity of products to adjust pH:-

$$Ca(OH)_2 > Na_2CO_3 >> CaCO_3$$

However, in terms of solubility:-

$$Na_2CO_3 >> Ca(OH)_2 > CaCO_3$$

$Ca(OH)_2$ solubility at 25°C is 1.64 g/L, forms a slurry **suspension** when mixed at 20% conc.

$CaCO_3$ solubility at 25°C is 0.014 g/L, forms a slurry **suspension** when mixed at 20% conc.

$Na_2CO_3$ solubility at 25°C is 220 g/L , forms a clear **solution** when mixed at 20% conc.

Hence, while hydrated lime has greater alkalinity than all other products, it also has greater risk of increasing lakewater pH beyond the desirable range if unintentionally added in excess. Only sodium carbonate forms a clear solution at reasonable concentrations and does not colour water when applied.

### 3.1.4 Alkali buffers mixed directly with 47w/v alum

Some work was done to consider the merit of adding a buffer directly to liquid alum in a batching plant to apply immediately before application to the lake since aluminum is prevented from forming a hydroxide solid by low pH conditions, it was found that liquid alum rapidly forms a solid when concentrated alkali is used to achieve a pH similar to lakewater. This is demonstrated in Appendix B. Refer also to Section 3.5.4 for other comments when alum is mixed directly with buffer products.

### 3.1.5 Liquid and kibble alum settling cylinder test comparison

Figure 3-5 shows a short term settling cylinder comparison of alkalinity adjusted liquid and solid kibbled alum. Pre-calculated amounts of alkali (1mL of 1% soln. $Na_2CO_3$) were added to two cylinders that then had the water column pre-rotated at 120rpm for 2 minutes. Each cylinder was dosed with alum to achieve 1 mg/L $Al^{3+}$, one with liquid alum (7.5mL@1%) and one hour later the other cylinder with a 1% solution prepared from kibbled alum (7.8mL@1%). One hour after this, a further liquid alum sample was prepared without alkali addition and dosed with liquid alum to achieve 0.3mg/L $Al^{3+}$ (2.3mL@1%). Both liquid and kibbled alum were made into 1% solutions to aid the accuracy of dosing each product.

It was noted that:

a) both 1ppm $Al^{3+}$ tests of liquid and kibbled alum formed turbid water soon after addition.

b) 1ppm liquid alum column cleared with precipitated algae appearing to settle more rapidly than kibbled alum.

c) Settled material formed by liquid alum had a slightly more compact form than kibbled alum. However, this could also have been due to the cylinder having a slightly different residual static charge, although they were fully discharged before completing the tests (made of acrylic).

d) After overnight settling it was observed that liquid and kibble alum settled mass was similar and even the 0.3mg/L $Al^{3+}$ test had a small amount of settled solids.

***Figure 3-5 Comparison of liquid and kibble alum application***

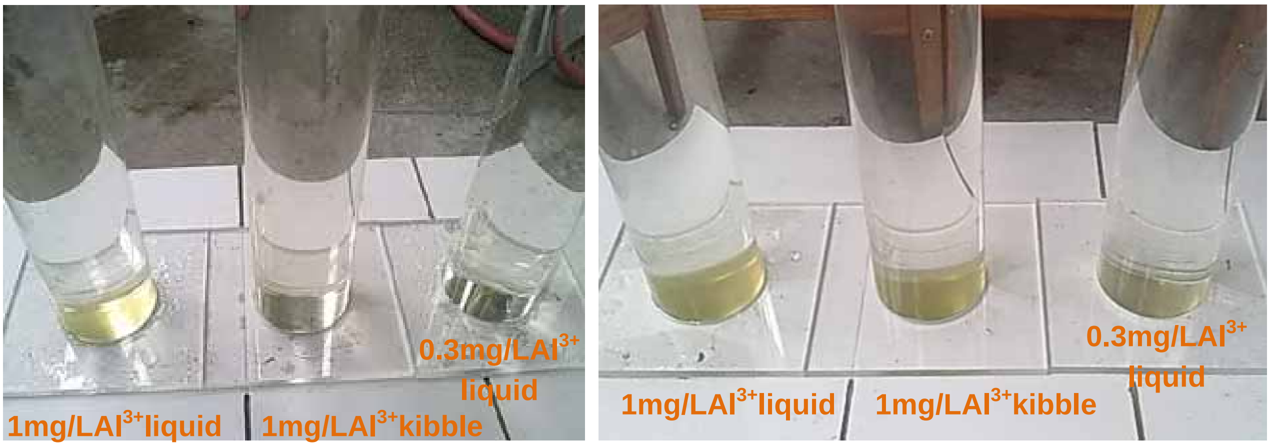


Plate A: Liquid and kibbled alum after a few hours (1 hour staggered start). No settled solids for kibble or 0.3mg/L liquid alum tests at this stage. Some settled solids 1 mg/L $Al^{3+}$ of liquid alum.

Plate B: Liquid and kibbled alum after overnight settling. All tests have settled solids, 1mg/L $Al^{3+}$ samples look similar. Few settled solids for 0.3mg/L $Al^{3+}$ liquid alum.

Table 1 indicates that liquid alum has a greater alkalinity demand than kibbled alum. Pre-addition of a small amount of buffer had little effect on the acid residual in liquid alum, but almost entirely compensated for acid effects of kibbled alum. However, alkalinity readjustment of kibbled alum tests show liquid and kibbled alum are closer than indicated in Table 1. (Refer section 3.5.3 where alkalinity demand is investigated further). Total phosphorus results confirm gang stirrer tests that kibble and liquid alum produce similar results. In this test liquid alum exhibited a high filtered aluminum value due to inadequate alkalinity.

***Table 1 Settling column results***

| **Column Test** | **pH** | **Alkalinity** | **TP** | **DRP** | **$Al_{total}$** | **$Al_{filtered}$** |
|---|---|---|---|---|---|---|
| | Units | mg/L$CaCO_3$ | mg/L | mg/L | mg/L | mg/L |
| 1mg/L $Al^{3+}$ liquid* | 6.12 | 2.3 | <0.004 | <0.004 | 0.38 | 0.13 |
| 1mg/L $Al^{3+}$ kibble* | 6.50 | 6.1 | 0.004 | <0.004 | 0.39 | 0.017 |
| 0.3mg/L $Al^{3+}$ liquid | 6.46 | 5.3 | 0.005 | <0.004 | 0.24 | 0.023 |

* 1 mL of 1% $Na_2CO_3$ added prior to adding alum (Note: 0.3mg/L column was not alkalinity adjusted).

## 3.2 Settling Rates

Settling rates were studied to determine if kibbled alum would reach to lake depths or fully dissolve in surface waters. The tests were completed in duplicate using 980 mm deep settling columns with average results recorded in Table 2. Values are expressed as *minutes* for a product to settle through *10 metres* of water column. 'Rapid settling fractions' are larger particles, 'average settling fraction' is a visual approximation of when half the settled material has occurred and 'slow settling fraction' was gauged to be when most settleable solids have fallen to the columns' base.

An interpretation of results in Table 2 follows:-

It will take 2 minutes for larger particles of kibbled alum to reach the deepest parts of Lake Rotorua. After 5 minutes, only smaller rapidly dissolved particles will be left in the water column. Most of that material will dissolve into solution and react to form aluminum hydroxide attracting any reactive substances. If the added quantity of fine material achieves a concentration of greater than 0.3mg/L $Al^{3+}$ a settleable precipitate will form and eventually settle to accumulate over bottom sediments. Lake current will most likely hold fine precipitates in suspension until calmer conditions prevail that allow it to settle. The rapid settling larger particles of kibbled alum form a light gelatinous-like solution within the soft top sediment layer. Buffer product will assist to stabilise this layer as aluminum hydroxide.

Alumina will formed a white haze of powdered material that will linger for a few hours and be transported (invisibly?) by lake currents for some time. However, other tests suggest alumina will be not improve alum performance. It's ability to stabilise floc remains unproven.

*Table 2 Settling rates for Kibbled Alum and Alumina Powder*

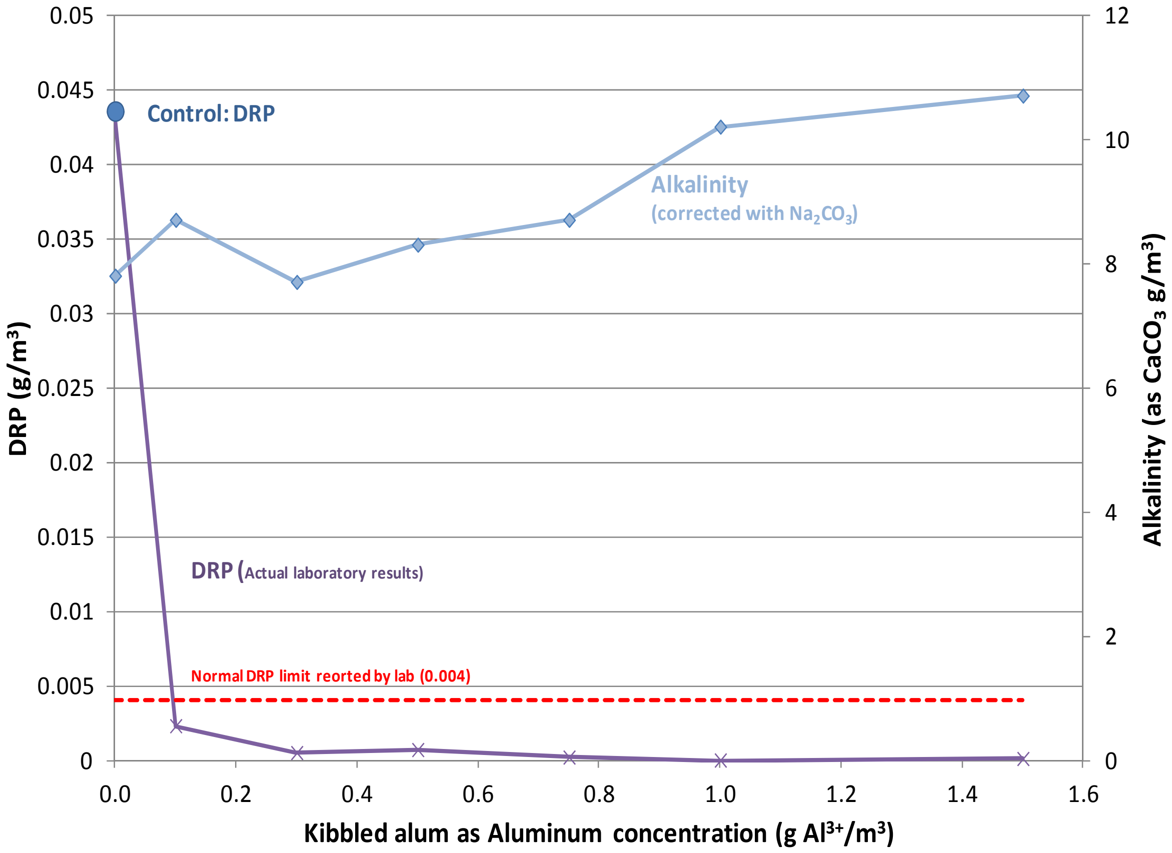
| Description | Unit | Kibbled Alum | Alumina |
|---|---|---|---|
| Rapid rate fraction | Min/10m | 1.0 | 7.3 |
| Average rate fraction | Min/10m | 1.7 | 10.2 |
| Slow rate fraction | Min/10m | 3.6 | 15.3 |

## 3.3 Kibbled Alum

### 3.3.1 Kibble alum phosphorus reduction

Kibbled alum tests to lock phosphorus are based on a lakewater sample spiked with phosphorus to overcome a DRP deficit (<0.004 mg/L P at the time of testing). Figure 3-6 shows DRP reducing with increase in aluminum. The rapid initial drop includes some uptake by algae, which is thought to be in the order of 50% by the time samples were analysed. Alkalinity is supplemented in these trials to retain pH within the range of 6.5 to 6.8 (start pH was 6.67).

*Figure 3-6 Kibbled alum phosphorus treatment results*



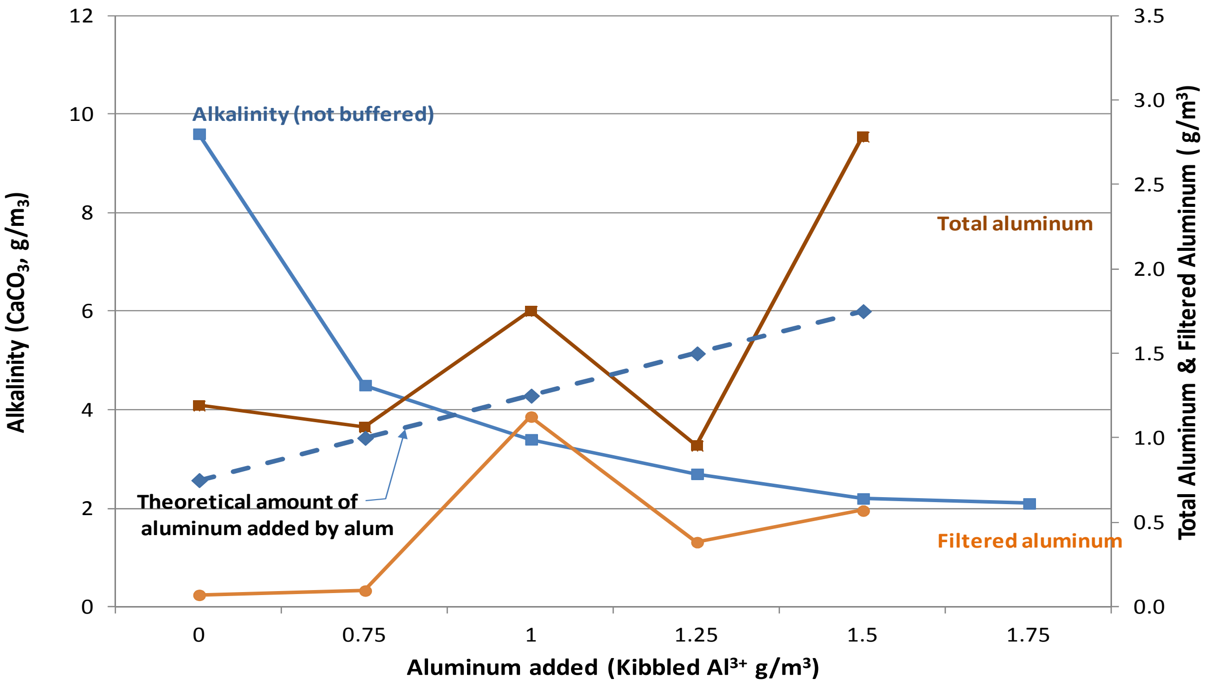
### 3.3.2 Alkalinity and precipitate

Figure 3-7 shows kibbled alum exerts a slightly lesser demand on lakewater alkalinity to that of liquid alum (Refer also to Figure 3-2 and Figure 3-12).

Also similar to liquid alum, kibbled alum shows an increase in filtered aluminum when lakewater alkalinity is substantially consumed. This occurs at an alkalinity value of about 5 mg/L (as $CaCO_3$).

Precipitate formed with kibble alum occurred at similar concentrations and exhibited similar properties to that formed by liquid alum.

***Figure 3-7 Kibbled alum alkalinity demand***



Note: Total aluminum results above the theoretical amount added is probably due to some floc being entrained with the laboratory sample.

### 3.3.3 Kibble alum buffers

$CaCO_3$ gave similar results to liquid alum tests and therefore is not repeated here. Refer section 3.1.3 for comments on buffers for liquid alum.

### 3.3.4 Kibble alum dissolution tests

Solid kibble alum used in these tests is 9 % aluminum and 17 % aluminum oxide as advised by Redox Pty Ltd. Independent tests showed these values to be conservative with aluminum content in the order of 10%.

To observe how quickly kibbled alum would dissolve, 10g was added to water pre-rotated in a 1 m deep settling cylinder and rested for 2 hours. This left a fine layer of larger kibble particles at the cylinder base.

After 2 hours, the surface liquor was decanted from the cylinder and lower water portion with remaining undissolved solids added to an imhoff cone. An equivalent sized water sample was added to a second imhoff cone and 10g of kibble added for comparison of initial crystal volume against the 2 hour sample. The Imhoff cone tests shown in Figure 3-8 clearly demonstrate that kibbled alum is substantially dissolved after 2 hours, with the left hand cone containing <0.5mL of residual solids, compared against a fresh sample containing 6.5mL and dissolving opaque layer to 10mL.

However, this test contains alum concentrations massively greater than would be added to any lake and is therefore only valid to demonstrate that dissolution of kibble alum will occur shortly after it is administered. This in conjunction with the rapid settling rate of Table 2 suggest it will have good penetration to depth while finer kibble particles will dissolve rapidly to also lock some DRP within the water column.

***Figure 3-8 Imhoff cone measure of kibble alum solids***

## 3.4 Alumina ($Al_2O_3$)

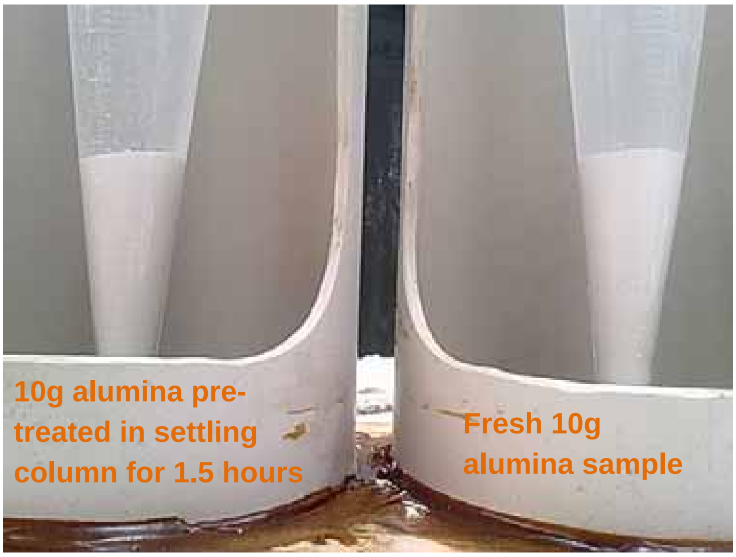
Aluminum oxide ($Al_2O_3$) is also known as activated alumina, a porous material ranging in size from a powder to approximately 1.5 mm diameter. Refer Appendix D section 7.5 for a particle size distribution. Based on aluminum content, only small amounts are theoretical required to lock phosphorus. However, the insoluble nature of this product requires that fine grades or highly porous granules are used for long exposure periods to lock phosphorus.

The low concentration of phosphorus in the first set of trials were inconclusive. The second set of trials spiked with phosphorus did not include alumina.

Figure 3-9 shows 10 g of activated alumina after 90 minutes in a settling column that has then been transferred to an imhoff cone for comparison against a fresh 10 g alumina sample. There is no discernable difference in settled volume with both tests recording 9.5mL.

As a non-soluble product, an advantage is alumina does not exert an alkalinity demand. This means significant quantities could be added to lakewater to form a layer over sediments without the complication of adding products to maintain alkalinity. A granule size that excludes powder would ensure it does not remobilise from sediments as it could be an irritant to organisms, but is very unlikely to exert any toxicity. Alumina contains traces (<1%) of sodium, calcium and iron oxides and quartz. No toxins are identified on the MSDS.

***Figure 3-9 Activated alumina residuals in water***



## 3.5 Buffer Products

### 3.5.1 Why buffer?

A discussion of lakewater chemistry is well beyond the scope of this report. It will suffice to note that the chemistry of lakewater is far more complex than noted below. However, for the purpose of simplicity, buffer acids and their salts act to control the pH of natural water systems. Two common buffers are noted here for Lake Rotorua; aqueous carbonate buffer and phosphate buffer. Both have buffers around pH 7, i.e. typical lakewater pH. In general terms pH is related to buffer concentration by the Henderson-Hasselbalch[7] Equation:-

$\mathrm{pH} = \mathrm{p}K_a + \log([\mathrm{base}]/[\mathrm{acid}])$ .............................Eqn 3-1

$\mathrm{p}K_a$ is the acid ionisation constant a t a given temperature.

Hence, as long as acid and conjugate base concentrations are equal, then pH is stable. A buffer resists change to pH by driving it's equilibrium equation to oppose an added base or acid.

The application of Equation 3-1 to carbonate and phosphate buffers is:-

$\mathrm{p}K = 6.4^* + \log([HCO_3^-]/[H_2CO_3])$ Eqn 3-2

$\mathrm{pH} = 7.21 + \log([HPO_4^{2-}]/[H_2PO_4^-]^\dagger)$ Eqn 3-3

* Value at $\mathrm{p}K_{a1}$

† By convention $[H_2CO_3]^\dagger$ is equal to the sum of actual carbonic acid concentration $[H_2CO_3]$ and dissolved carbon dioxide concentration $[CO_2(aq)]$ , i.e. $[CO_2(aq)] = [CO_2] + [H_2O]$

The buffering action of phosphate is practically removed by locking with aluminum. Calcite (or other soluble carbonate compounds) react with aqueous carbon dioxide as (or similar to) Equation 3-4 to produce bicarbonate, a key compound in buffering natural waters as noted in Equation 3-2.

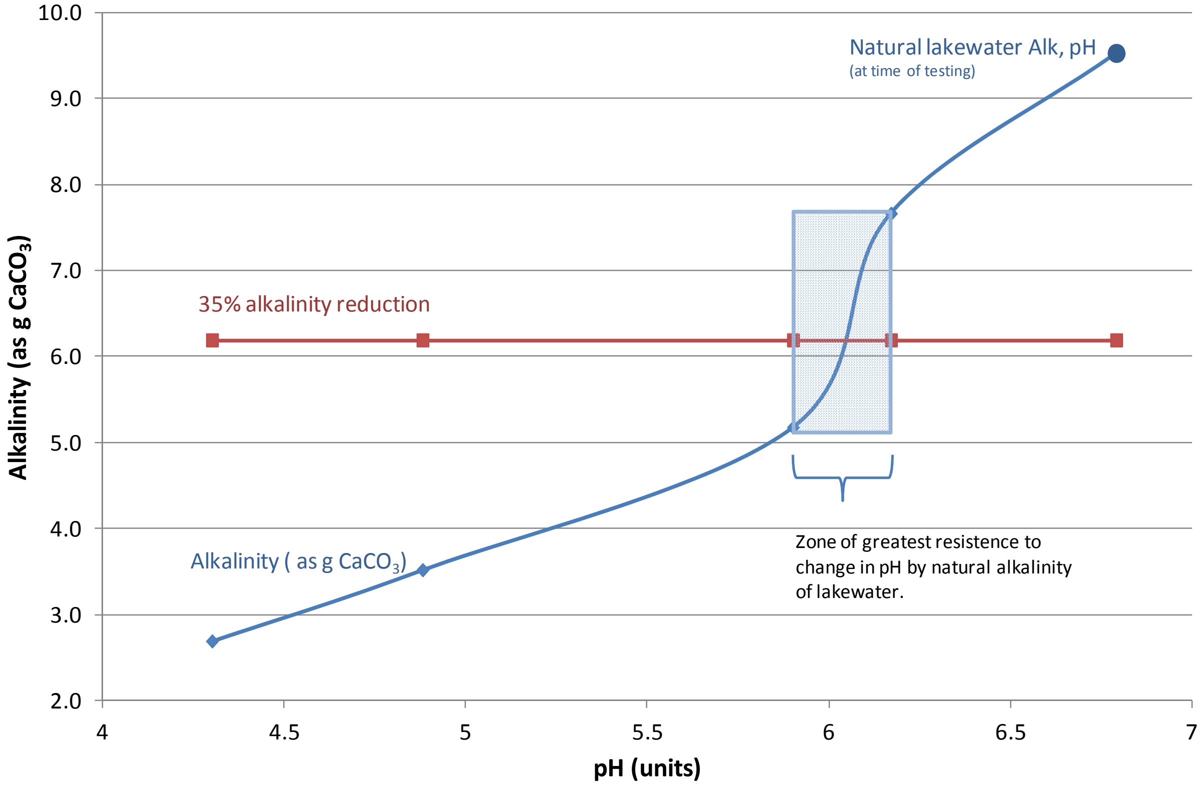
$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ Eqn 3-4

Hence carbonate equilibrium and to a lesser extent phosphate equilibrium buffer alkalinity and pH of lakewater. Adding an acid such as alum or carbon dioxide drives the equilibrium reaction of carbonate toward bicarbonate to compensate for the increase in acid. Once enough alum is added to change the pH by one unit, the buffer is deemed to be fully consumed. Therefore, adding a chemical that supports an existing buffer reaction is beneficial to maintaining water alkalinity and pH and the many other chemical and biological interactions that are not mentioned in this report.

Figure 3-10 shows a plot of alkalinity reduction with change in pH, determined from a single lakewater sample and therefore can only be considered indicative of lakewater alkalinity characteristics. As can be predicted from Eqn 3-2 carbonate buffering should occur just above pH 6. Figure 3-10 suggests mild buffering in this range. A horizontal line shows 35 percent reduction of alkalinity intersecting the alkalinity curve within the strongest zone of buffering at approximately pH 6.1. 45 precent and 53 percent reductions occur at respective pH values of 6.0 and 5.5.

A 35 percent reduction of alkalinity within the strongest buffer zone of lakewater is considered a conservative point to adopt for limiting alkalinity demand of phosphorus locking reagents. Phosphorus locking reagent dose regimes that would lower alkalinity beyond 35 percent, i.e. pH 6, should include buffers designed to maintain lakewater close to natural alkalinity levels.

***Figure 3-10 Alkalinity reduction with change in pH***



1. Three readily available products were selected to buffer alkalinity of aluminum coagulants. Calcium carbonate ($CaCO_3$ , calcite powder) was selected because of the beneficial bonding of phosphorus with calcium, local supply and pH stability characteristics (Ksp = $3.36 \times 10^{-9}$ for calcite, or saturated solubility of around 15 to 19 mg/L)[5&6].

2. Sodium carbonate was also tested because it dissolves readily in water at ambient temperature (~170g/l at 12°C)[5&6].

3. Sodium silicate liquid is alkaline and forms a floc when added to water. Tests have proved sodium silicate to be incompatible with alum for the purpose of locking phosphorus. The efficiency of alum to lock phosphorus reduced with increase of sodium silicate. Results are therefore not discussed in detail.

### 3.5.2 Calcium carbonate foam

Calcium carbonate ($CaCO_3$) is only partially soluble in water. The powder sample provided by McDonalds lime displayed a brownish hue that translated to any solutions it was added. This applied equally to the 1 percent solution used to adjust alkalinity of alum samples and to dissolution in alum test shown in Figure 3-11.

A dissolution test of $CaCO_3$ into 12mL of 62%w/v alum proved impractical as the mixture results in excessive foaming. Figure 3-11 shows foam formed immediately after introducing 1.2g $CaCO_3$ to alum compared to another 12mL test that had been left to rest. Neither sample increased the pH sufficiently for an aluminum hydroxide solution to form. Both tests were stopped at around pH 3.5.

***Figure 3-11 $CaCO_3$ in alum dissolution test***

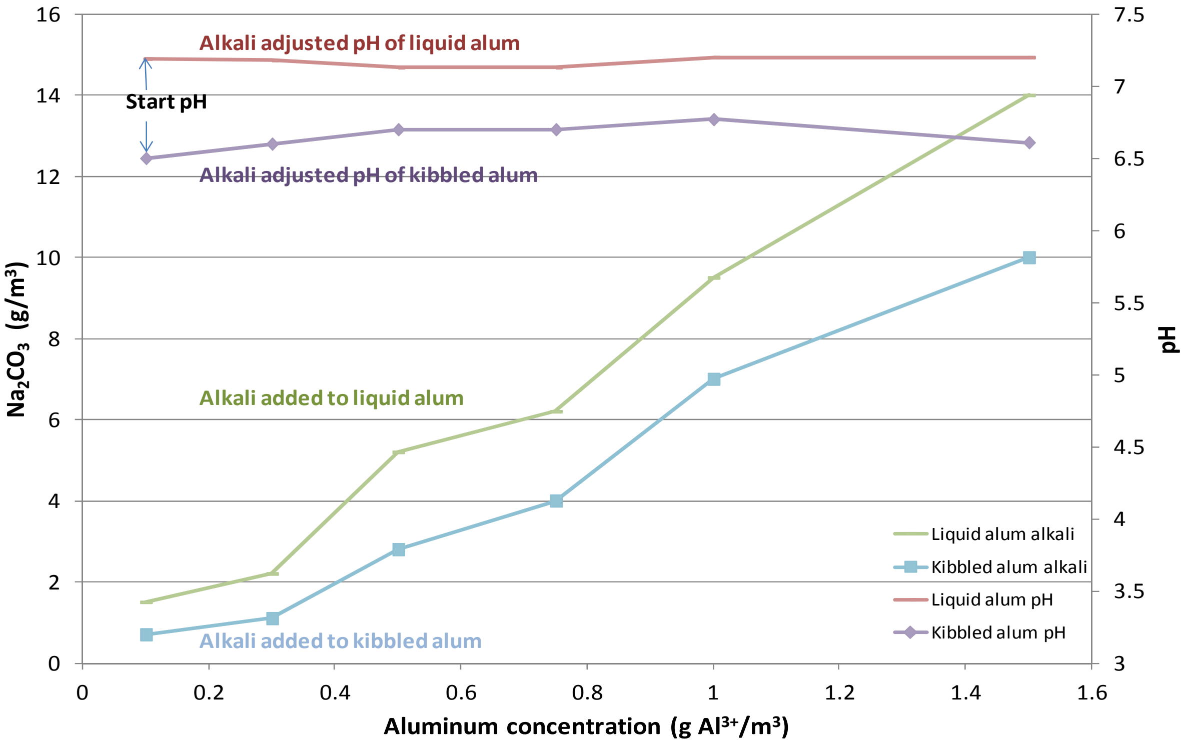
Like the calcium equivalent, sodium carbonate also produced foam when added to 62%w/v alum. It foamed less vigorously, but formed clumps of crystals. Despite $Na_2CO_3$ being highly soluble these clumps did not dissolve until painstakingly and forcibly broken apart. It is therefore not practical to add buffers to bulk liquid alum.

### 3.5.3 Sodium carbonate

Sodium carbonate ($Na_2CO_3$) is highly soluble forming a clear liquid in solution with water. A 1 percent solution is alkaline with pH~11.5. It can be used to adjust low pH doses of coagulants to correct alkalinity so that aluminum hydroxide to be fully formed.

Figure 3-11 examines alkalinity consumption in more detail by comparing the amount of buffer needed to maintain pH to the same value as it was before alum was added. It shows about 40 percent less buffer is required to maintain alkalinity of lakewater when dosed with kibbled alum.

*Figure 3-12 Comparison of kibbled alum and liquid alum on alkalinity*



A 1 percent solution was prepared to adjust the pH and alkalinity of tests, but would be used at much higher concentrations for liquid applications to lakewater, OR may be added in dry form sprinkled into water receiving liquid alum.

To examine dry applications further, a small sample of equal proportions of approximately 20mL each of kibbled alum and sodium carbonate were mixed and temperature compared with a 40mL sample of kibbled alum. A 0.8°C increase in temperature was noted for the mixed sample. The heat liberated by larger volumes of unequal proportions should be tolerable, but would require a test to confirm acceptability for the method of application. Good practice suggests dry chemicals be combined at the required proportions immediately prior to spreading.

Fusing of dry chemical forms was not observed.

### 3.5.4 Buffers mixed with liquid alum

Mixing buffer products with concentrated liquid alum serves no purpose other than to examine if they could be administered as a pre-batched solution to reduce the complexity and sophistication of the application process.

Figure 3-13 shows calcium carbonate powder and liquid alum mixture to the left, and sodium carbonate powder and liquid alum mixture to the right. The colour difference is clearly visible both in powder and solutions. Opaqueness of sodium carbonate solution is caused by bubbles and clumps of undissolved crystals, but it is predominantly a clear liquid. These clumps are probably due to alum forming a hydroxide coating that prevents direct contact of the active substances. A similar coating is thought to form on calcium carbonate since it would not all dissolve either even at the low pH of this test, pH~3.5.

***Figure 3-13 Carbonate buffer products in 62%w/v alum at low pH.***

As sodium carbonate is highly soluble, it is really only suited to a pH adjustment role. It may be added as, either; a solution applied via a separate sparge if applied by boat, or solid form mixed to preset ratios with coagulant solid, which is preferable for an aerial application.

By way of comparison, the right hand sample of Figure 7-3 ( in Appendix B) shows a 1 percent solution of calcium carbonate (0.5g in 50mL) that was thoroughly mixed and then settled for 12 hours. The layer of settled powder is clearly visible. The maximum solubility of $CaCO_3$ at 15°C is in the order of 10 mg/L, i.e. 0.0005g in 50mL, OR 0.001% soln. This saturated solution had a pH of 7.05.

## 4.1 Alum

Trials have confirmed similar phosphorus locking characteristics of kibble and liquid alum. Raw costs advised to Enviromex during report preparation for bulk liquid compared to bulk kibbled alum solid are \$337 /tonne and \$495/tonne respectively.

Equivalent costs for liquid and solid alum based on aluminum content per unit weight of product are:-

Bulk liquid alum: 43 kg $Al^{3+}$/T at \$337.55 alum/T gives \$ 7.87/kg $Al^{3+}$

Alum kibble: 90 kg $Al^{3+}$/T at \$495 alum/T gives \$5.50/kg $Al^{3+}$

Expressing these values as a cost to treat a hectare of lake at 20 metres depth at an active ingredient dose rate of 1 $gAl^{3+}/m^3$ gives:

Bulk liquid alum: \$ 1575 /ha/ 20m depth.

Alum kibble: \$ 1100 / ha/ 20m depth.

This comparison demonstrates the form of supply has considerable effect on alum product cost (as based on costs received for this study).

## 4.2 Buffers

A comparison of buffer addition costs based on 1 litre of liquid alum requires around 2.8 kg$CaCO_3$ OR 0.44 kg $Na_2CO_3$. Extrapolating these values and applying on the basis of treating 1 hectare of lake at 20 metres depth gives material costs of:-

$CaCO_3$ powder: \$0.36†/kg liquid alum OR \$493† / ha/ 20m depth at 1ppm$Al^{3+}$

$Na_2CO_3$ crystal: \$0.22/kg liquid alum OR \$302 / ha/ 20m depth at 1ppm$Al^{3+}$

† These values will increase accordingly if the dose required is closer to 4 kg$CACO_3$ that was indicated by some results of this work.

## 4.3 Application costs

Cost for application of liquid alum will be greater than for kibble alum since special storage will be needed to handle the volume of liquid. One tonne bags of kibbled alum can be stored in close proximity to the application staging location. Kibbled alum could also be batched with buffer material immediately prior to application.

Costs for application will be greater for $CaCO_3$ as the mass of product to be applied is considerably more than $Na_2CO_3$.

# Conclusions

There are multiple outcomes of the benchtop trail work advised in this report.

These are:

A. Lakewater samples collected for this study contained low concentrations of both total phosphorus and dissolved reactive phosphorus. This was corrected by spiking samples to achieve DRP in the normal range of lakewater 0.05 to 0.09mg/L. The spiking solution was supplied by regional councils laboratory. Laboratory analysis confirmed a total phosphorus value of 0.083mg/L and DRP of 0.043mg/L. Lakewater pH and alkalinity were 6.8 and 7.2 for the first set of samples, and 6.52 and 7.8 for the second set of samples ( alkalinity expressed as mg $CaCO_3$/L).

B. The control sample showed algae consumed about 50% of DRP while tests were performed. Despite this, strong DRP locking was demonstrated for both kibble and liquid alum forms.

C. Flocculation and settling of algae is demonstrated for liquid alum and solid kibble alum.

D. The interaction of algae and alum is unproven as a reliable means to lock phosphorus in lakewater. In the absence of further work to demonstrate aluminum locking of phosphorus released from decaying biomass, large scale application efforts need to target conditions that maximise locking of phosphorus onto aluminum. Application methods that apply reagents to the hypolimnion before or during benthic release of phosphorus are expected to have greatest benefit.

E. Liquid alum exerts a greater draw on lakewater alkalinity than does solid kibble alum. Tests suggest the difference could be as high as 40 percent. This value may vary for different suppliers because it relates to the acid residual remaining in kibbled alum.

F. Addition of alum 0.5 mg$Al^{3+}$/L causes greater than 35 percent reduction in alkalinity (9.5 g/$m^3$ as $CaCO_3$ lakewater reduces to 6). Therefore it is suggested any greater addition rate of alum also includes a buffer. Other simple alkalinity control measures are noted in the main text and summary.

G. Alkalinity correction using moderately alkaline calcium carbonate was hampered by the difficulty to achieve a uniform suspension. Other aspects are colour of solutions and light volumous solids that gradually settles to form a soft paste. Around 2.8 kg$CaCO_3$/litre 47%w/w liquid alum is expected to give acceptable alkalinity and pH. It's key advantage is that it is virtually impossible to cause high pH by overdosing.

H. Alkalinity correction using highly soluble alkaline sodium carbonate gave good results forming a clear liquid when mixed into solution, or, can be applied directly as powder or crystal solid forms that will not produce a settled solids layer. If selected, caution will be required to control pH to acceptable levels. Overdosing or uneven distribution will cause fluctuation of lakewater pH. It was established that 0.44 kg$Na_2CO_3$/litre 47%w/w alum liquid gave acceptable lakewater alkalinity. This value could be used at a larger scale trial.

I. Items G and H note that both buffer products were successful. Selection of a buffer depends on the objective. If it is intended to maintain the status-quo, then $Na_2CO_3$ is a better choice since there will be no residual effect. If it is intended to have a prolonged effect on alkalinity and/or benefit from calcium ion effects, then $CaCO_3$ is a better choice since a calcite deposit will form over lake sediment.

J. Kibbled alum is 40 percent more cost efficient than liquid alum in terms of active constituent ($Al^{3+}$) and also is likely more cost efficient for application to lakes.

K. Sodium carbonate is greater than 60 percent more cost efficient than calcium carbonate and will be more cost efficient to apply to lakes, regardless of boat or aerial application method. However, should this product be made into solution for application (not recommended), then greater care will be required due to the highly alkaline nature of this product.

L. Liquid alum produced floating solids when dosed at, or above 0.3 mg/L $Al^{3+}$ (5.3 litres of 47% alum/ 1000$m^3$ lakewater). A liquid alum dose of 0.5 mg/L $Al^{3+}$ (8.8 litres of 47% alum/1000$m^3$ lakewater) produced the strongest floating algae rich floc in benchtop trials after overnight low energy mixing. It is premised that some algae may be floating to compensate for the presence of alum. It is therefore recommended that alum is not administered when significant algae is present.

M. Dissolved oxygen of lakewater was not affected during the trials. There is no need to aerate while applying reagents.

N. Sodium silicate produced floc when mixed at equivalent concentrations to other coagulants, but proved ineffective to lock phosphorus. It also adversely affected locking of phosphorus when used as an alkali enhancing agent with alum.

O. Activated alumina is effectively insoluble in lakewater, settles reasonably rapidly although some opaqueness may be visible for a few hours after depending on the method of application. Though not fully tested, it is unlikely that alumina will enhance alum characteristics.

P. Bulk 62%w/v liquid alum should not be mixed directly with buffer solutions to administer to lakewater. Separate sparges are required for boat application, or separate craft for aerial application.

# References

1. National Lime Association Bulletin 213, Seventh Edition 1995, Fig 1-b Neutralisation Graph, comparing lime with other alkaline materials.
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3. Boltac Series Stirrer manual, 2011.
4. Delta Chemical Corporation, MSDS 132 for Sodium Aluminate.
5. Sawyer, McCarty, Parkin, Fourth Edition, Chemistry for Environmental Engineers.
6. Wikipeda on-line encyclopedia, [http://en.wikipedia.org](http://en.wikipedia.org). ‘calcite solubility’
7. General Chemistry, 2nd Edition, P.W. Atkins and J.A. Beran, Scientific American Library, 1992.

# Limitations

Enviromex NZ Limited has prepared this report for the use of Bay of Plenty Regional Council in accordance with the usual care and thoroughness of the consulting profession. It is based on generally accepted practices and standards at the time it was prepared. No other warranty, expressed or implied, is made as to the professional advice included in this report. It is prepared in accordance with the brief and for the purpose outlined in Section 1 of this report.

The methodology adopted and sources of information used by Enviromex NZ are outlined in this report. Enviromex has made no independent verification of this information beyond the agreed scope of works and Enviromex assumes no responsibility for any inaccuracies or omissions. No indications were found during our investigations that information contained in this report as provided to Enviromex was false.

This report was prepared during September to December using water samples from Lake Rotorua collected on 21st September and 11th November. These samples reflect conditions prevailing at that time. Enviromex disclaims responsibility for lakewater quality that differs from the samples.

This report should be read in full. No responsibility is accepted for use of any part of this report in any other context or for any other purpose or by third parties. This report does not purport to give legal advice. Legal advice can only be given by qualified legal practitioners.

## Purpose

The following aims were highlighted in the proposal for work covered in this study:-

- confirm the range of alum application rate to achieve phosphorus locking is expected to be in the range of 0.3 to 1.0 ppm $Al^{3+}$,
- confirm if the desired application rate will result in some, little or no sediment cap potential,
- check availability and solubility of solid alum forms and mixing requirements to achieve same as liquid alum,
- check behaviour of alum in relation to various alkalinity stabilising substances,
- check availability and cost of non-alkalinity adjusting $Al^{3+}$ coagulants,
- gain an understanding of logistics of ‘at point of use’ solid alum mixing requirements compared with liquid alum application by assessing preliminary costs for likely contracted options.

## Equipment

1. PB: gang stirrer (6 jar unit)
2. PB: Computer (to drive gang stirrer)
3. PB: Sample collection pump
4. PB: Battery (12v)
5. PB: Sampling pump (column extraction)
6. PB: Various syringes (1, 2.5, 5, 10, 20 and 50mL)
7. PB: Settling columns
8. PB: Imhoff cones
9. PB: Scales: 3 kg x 1g and 500g x 0.1g
10. PB: Thermometer
11. PB: Filtered water (for chemical makeup)
12. PB: pH meter
13. PB: Calculator
14. PB: Extension lead and multiplug box
15. PB: Stirring and cleaning implements and other small items
16. PB: Chemicals:-
    - Alumina, $Al_2O_3$
    - Kibbled alum, or
    - Flake alum
    - Calcite powder ($CaCO_3$)
    - Hydrated lime as $Ca(OH)_2$
    - liquid alum ( fresh sample from bulk tank)
    - Prepare 1% alum liquid and 10% calcite at site.

17. JM: boat
18. JM: 20 litre sample containers (say 2 or 3 of)
19. JM; Alkalinity measurement equipment
20. JM: Table
21. JM: Chilli, bottles and filters from Hills

## Setup and timing

Location: Utuhina facility

Setup: Wednesday 21 September ( PB will travel to Rotorua in the morning and setup early afternoon. Equipment test early afternoon and get alum from Puarenga plant.

H&S Plan: JM

Water sample collection: Wednesday afternoon, after John's tour we go out on the lake to collect 20 litre samples.

Thursday: Laboratory trails

Friday: Finish remaining trials, despatch samples and pack up.

## Proposed Trials Regime

Step One: Collect lakewater samples

Use sampling pump to draw samples from preferred depths of lake

Measure and record temperature and pH

Keep samples cool.

Step Two: Liquid alum buffer addition rate

Prepare a buffered slurry of liquid alum with:-

- $CaCO_3$
- $Ca(OH)_2$

Determine buffer which is best and easiest to use.

Would adding water make application easier?

Step Three: Phosphorus addition test for alum

To check treatment effectiveness of locking of phosphorus onto **alum** at various concentrations. This has been done on streamwater, but as far as I can tell has not been done for lakewater.

Use stock alum supplied at 47%w/w with SG of 1.32 and $Al^{3+}$ of 4.3%.

- 47W/w is same as 62%w/v
- 1% alum soln requires 16.13mL of 62%w/v made up to 1 litre.

- 1% alum soln contains 915.5 mg $Al^{3+}$/litre
- 1 mg $Al^{3+}$ is contained in 1.09 mL of 1% alum soln.

The following table uses this relationship to determine dose rates for 1 L samples in the gang stirrer programmed for 60 seconds rapid mix at 180rpm, then 60 seconds at 80rpm, then 600 seconds at 20 rpm, then stop and rest.

Complete yellow highlighted samples first over short timeframe. Save lower concentration samples for longer mixing timeframe. Note later step.

| ppm $Al^{3+}$ | $0_{control}$ | 0.05 | 0.1 | 0.3 | 0.5 | 0.75 | 1.0 | 1.25 | 1.5 | 1.75 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1% alum (mL) | 0 | 0.05 | 0.11 | 0.33 | 0.55 | 0.82 | 1.1 | 1.37 | 1.64 | 1.91 |
| P:Al ratio$_{calc'd}$ | | | | | | | | | | |
| pH | | | | | | | | | | |
| Alkalinity | | | | | | | | | | |
| Al | | | | | | | | | | |
| TP | | | | | | | | | | |
| $Al_{filtered}$ | | | | | | | | | | |
| $P_{filtered}$ and/or DRP | | | | | | | | | | |
| 47% litres of alum/1000 m$^3$ | 0 | 0.88 | 1.76 | 5.29 | 8.81 | 13.2 | 17.6 | 22.0 | 26.4 | 30.8 |

Sample temperature: °C

If the pH is less than 6.5, or alkalinity less than 5mg/L as $CaCO_3$, then repeat with alkaline adjusted solution of alum to attain >10mg/L $CaCO_3$.

Check the effect an economic merit of $CaCO_3$ and $Ca(OH)_2$ powder.

Repeat to get duplicate samples.

### Step Four: Phosphorus locking test for aluminate ($Al_2O_3$)

Repeat the above using alumina, available from RioTinto (Tiwai smelter), or possibly from Orica (source of aluminum they use to manufacture alum soln).

| ppm $Al^{3+}$ | $0_{control}$ | 0.1 | 0.3 | 0.5 | 1.0 | 1.5 |
|---|---|---|---|---|---|---|
| 0.1% alumina (mL) | 0 | 0.11 | 0.33 | 0.55 | 1.1 | 1.64 |
| P:Al ratio$_{calc'd}$ | | | | | | |
| pH | | | | | | |
| Alkalinity | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Al | | | | | | |
| TP | | | | | | |
| $Al_{filtered}$ | | | | | | |
| $P_{filtered}$ and/or DRP | | | | | | |
| $Al_2O_3$/1000 $m^3$ | 0 | | | | | |

Sample temperature: °C

Step Five: Solids behaviour

Fill three settling columns with lake water, then

i. Create a small amount of rotation of water in the cylinder to mimic lake movement and then gingerly apply alum at 1ppm $Al^{3+}$to the settling column surface, leave for half a day and then sample TP and DRP.

ii. Use a slurry of alum liquid and alkali buffer. Compare with gang stirrer results.

iii. Similar for alumina and compare with gang stirrer results.

iv. Gingerly apply solid alum flake or kibble with buffer to mimic aerial application. Determine the settling rate. Leave in column to see if the alum dissolves and disperses by diffusion. Sample toward the end of the trial to see what has happened to the phosphorus.

These tests provide a useful understanding of the effect of mixing energy on creating bound phosphorus when compared against the gang stirrer results

Step Six: Solid alum behaviour in water column

Use results from settling tests in step five iv to determine the settling time to reach depths of 12 metres to 20 metres. Set gang stirrer to create a similar water movement velocity to the settling rate and run for time to reach various depths. Pour off water and place residual into imhoff cone to get a measure of the residual volume.

May look at some method of weighing pre-dosed volume against post-test residual volume to determine percentage dissolved.

Step Seven:

Check the effect of post-mixing of alkali buffer after alum has been contacted with water. This can be done either in the settling columns or as a gang-stirrer method. Check performance of different buffers as below:

| | | | | | | |
|---|---|---|---|---|---|---|
| ppm $Al^{3+}$ | 0.1 | 0.5 | 1.0 | 0.1 | 0.5 | 1.0 |
| 1% alum (mL) | 0.11 | 0.5 | 1.1 | 0.11 | 0.5 | 1.1 |
| Buffer type | A | A | A | B | B | B |
| P:Al ratio$_{calc'd}$ | | | | | | |
| pH | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Alkalinity | | | | | | |
| Al | | | | | | |
| TP | | | | | | |
| $\mathrm{Al}_{\mathrm{filtered}}$ | | | | | | |
| $\mathrm{P}_{\mathrm{filtered}}$ and/or DRP | | | | | | |

Step Eight: Extended mild mixing of low concentration alum.

Same as Step One, except gang stirrer run at low rpm for an extended period.

| ppm $\mathrm{AL}^{3+}$ | $0_{\mathrm{control}}$ | 0.05 | 0.1 | 0.3 | 0.5 |
|---|---|---|---|---|---|
| 1% alum (mL) | 0 | 0.05 | 0.11 | 0.33 | 0.55 |
| P:Al ratio | | | | | |
| pH | | | | | |
| Alkalinity | | | | | |
| TP | | | | | |
| $\mathrm{Al}_{\mathrm{filtered}}$ | | | | | |
| $\mathrm{P}_{\mathrm{filtered}}$ and/or DRP | | | | | |
| 47% Litres of alum/1000 $m^3$ | 0 | 0.88 | 1.76 | 5.29 | 8.81 |

# Method Detail

APPENDIX B

## 7.1 Principal Equipment

### 7.1.1 Gangstirrer

A computer controlled gangstirrer of up to six test samples allowed chemicals to be contacted with water.

Settings used to mix 1 litre samples of liquid alum were:-

| | |
|---|---|
| 180 rpm for 1 minute | rapid mix to represent initial impact of chemicals entering the water |
| 120 rpm for 1 minute | medium transitional mixing |
| 20 rpm for 5 minutes | low intensity mixing to represent submerged conditions |
| 0 rpm for 60 minutes | Settling of coagulated matter |
| Bottled for ≥3 days | Chemical contact time. |

Kibbled and liquid alum were made up to 1 percent solutions for gangstirrer tests.

Alumina was made up to a 0.1 percent suspension for gangstirrer tests.

These solutions allowed delivery of target concentrations of $Al^{3+}$ to 1 litre test samples.

### 7.1.2 Settling column

Three 100mm diameter by 1 metre high, static neutralised acrylic settling columns were used to examine the characteristics of products added to a water column. Settling velocity was gauged by visual observation of kibble or powder products falling through the water column as timed by stopwatch. These columns were also used to study low energy absorption of phosphorus for comparison with gangstirrer results.

### 7.1.3 Imhoff cone

The Imhoff cone is a calibrated scale cone used to indicate the amount of material taken up by the water column after a specified period of contact.

## 7.2 Analyses

Practically all tests were analysed for:

- Total phosphorus
- Dissolved reactive phosphorus
- Total aluminum, and
- Filtered aluminum.
- Some samples were analysed for alkalinity to check any time related change.

## 7.3 Liquid alum

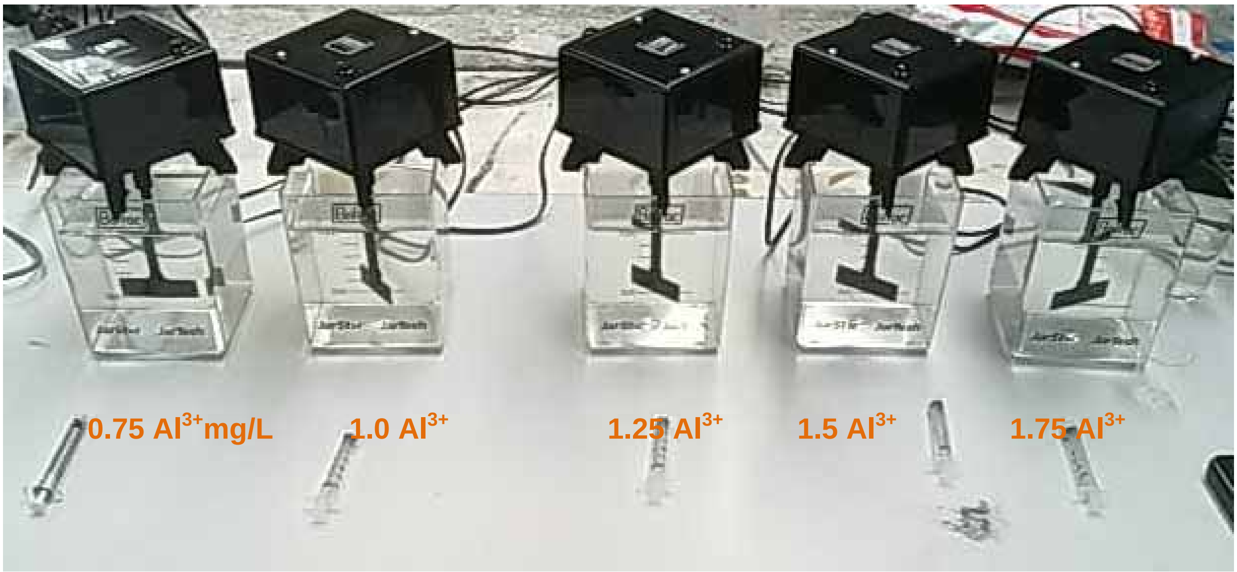
Liquid alum at 47%w/w used in this trial came from the bulk tank at Utuhina. A drain valve on the pump suction line was used to collect 500mL. This product contains 8.1% $Al_2O_3$.

### 7.3.1 Contact/concentration tests

Gangstirrer tests examine phosphorus reduction for various amounts of added aluminum. These tests give an indication of the mass of aluminum needed to achieve a desired effect in the lake.

A 1 percent solution of liquid alum (16.13mL made up to 1 litre) was used to dose 1 litre lake water samples to achieve aluminium ion concentrations of 0, 0.05, 0.1, 0.3, 0.75, 1.0, 1.25, 1.5 and 1.75 mg/L. Figure 7-1 shows the gangstirrer processing samples during settling (Refer also to Gangstirrer heading of Appendix A). A control sample is also included, although not shown in Figure 7-1. All samples in this test produced a floc of green-tinged solids representing coagulation and settlement of algae. To examine the remaining fraction of phosphorus and aluminum likely to remain in the water column and exclude algae solids from the samples, 250mL samples for analysis were extracted using a pump suction hose inlet at mid-depth of each jar. Samples were extracted starting with 0.75$Al^{3+}$mg/L and systematically progressed toward the most concentrated sample. The pump system was flushed prior to each sample.

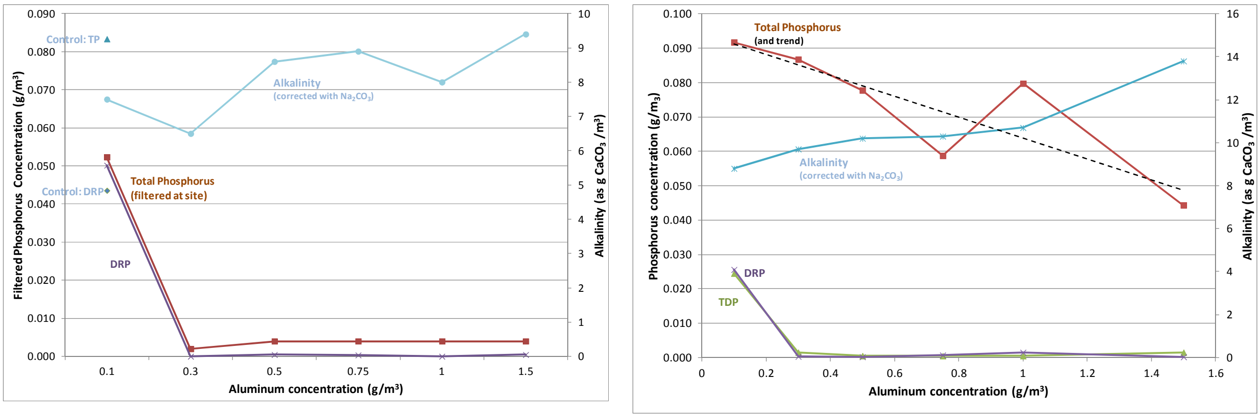
***Figure 7-1 Liquid alum tests 0.75ppm to 1.75ppm $Al^{3+}$(L to R)***



### 7.3.2 Algal uptake of DRP

To investigate uptake of spiked DRP by algae, two sets of identical tests were completed with the exception that one set was filtered at site shortly after coagulation tests were complete to remove algae. Figure 7-2 shows filtered results to the left and unfiltered to the right. All filtered sample phosphorus in the control analyte should have been DRP. However results for the control analyte gave a total phosphorus value of 0.083mg /L and DRP of 0.05 mg/L. Unfiltered results were total phosphorus of 0.09mg/L and DRP 0.025mg/L. These results show rapid uptake of DRP by algae during testing and continued uptake when samples were chilled on ice until analysed at the laboratory. Despite this, both results in Figure 7-2 show complete adsorption of DRP and filtered P by an aluminum dose of 0.3 mgAl$^{3+}$/L. They also show there is no appreciable difference between the analysis of filtered P and DRP.

***Figure 7-2 Examining algal uptake of DRP***



## 7.3.3 Direct buffer of conc alum

A 12mL sample of 62%w/v alum was treated with concentrated alkali solution to demonstrate formation of aluminum hydroxide solids when made to neutral pH. The left hand sample in Figure 7-3 shows aluminum hydroxide solids of sufficient density to easily support a plastic spoon. It is obvious that intimate contact of aluminum with phosphorus will be severely restricted if added to lakes in this form. It is therefore not recommended liquid alum be directly mixed with buffer solutions for addition to lakes. Liquid alum can only be added with separate application of buffer through a separate sparge or by adding the buffer in solid form.

***Figure 7-3 Alkali adjusted 62%w/v alum solution***

### 7.3.4 Settling column

Two settling column tests were completed for liquid alum. Lakewater filled columns were pre-agitated by rotating the column surface at 120rpm. This was done to mimic high energy introduction into the water such as from an aerial drop or boat sparge. Alkali adjustments were made using sodium carbonate solution to predetermined values; then1 percent alum solution was added to achieve required aluminum concentrations within each water column.

Aluminum concentrations:

- 1.0 ppm $Al^{3+}$, (7.5mL 1% alum soln. in 7 litres) and
- 0.3 ppm $Al^{3+}$, (2.3mL 1% alum soln. in 7 litres).

Each column water surface was agitated at 120rpm for 2 minutes at approximately 1.5h intervals to mimic surface activity. The columns were left to settle overnight.

Samples were extracted from below surface into 250mL bottles.

## 7.4 Kibbled Alum

Poolmaster supplied a 2 kg container of kibbled alum from Redox Pty Ltd. This product contains 17 percent $Al_2O_3$ and has an average granule size of 1.3mm.
Figure 7-4 shows a sample in relation to a 1mL syringe and 2 kg container.

*Figure 7-4 Redox kibbled alum*

### 7.4.1 Contact/concentration tests

Similar to 7.3.1, except;

1. The amounts of kibble to be added to samples were too small to accurately weigh. This was overcome by making a 1 percent solution of kibble alum by adding 7 g kibble to 700mL of filtered water.
2. The 1 percent kibble alum solution was added to water samples in the same way and same concentrations as liquid alum for0.75mg $Al^{3+}$/L, 1.0, 1.25, 1.5 and 1.75.

### 7.4.2 Settling column

Same as 7.3.4 with 1 percent kibbled alum solution added to lake water to achieve 1.0 mg/L $Al^{3+}$. Each cylinder holds close to 8 litres capacity.

***Figure 7-5 Settling columns***

The settling columns were also used to determine the settling velocity of kibble and alumina products by timing the rate if decent of product solids. A visual estimate of the amount of product settled gave average and 90 percentile rates.

### 7.4.3 Imhoff Cones

These calibrated scale cones allow volumes of settled solids to be quantified. In these trials they were used to compare 10 g kibbled alum with one hour of retention time in the settling columns against a fresh 10 g sample of kibble. Figure 7-6 shows 10 grams of kibbled alum settled into 6.5mL volume and an opaque layer with relatively sharp interface with the water at 10mL volume.

***Figure 7-6 10g of kibbled alum immediately after adding to water***

## 7.5 Alumina

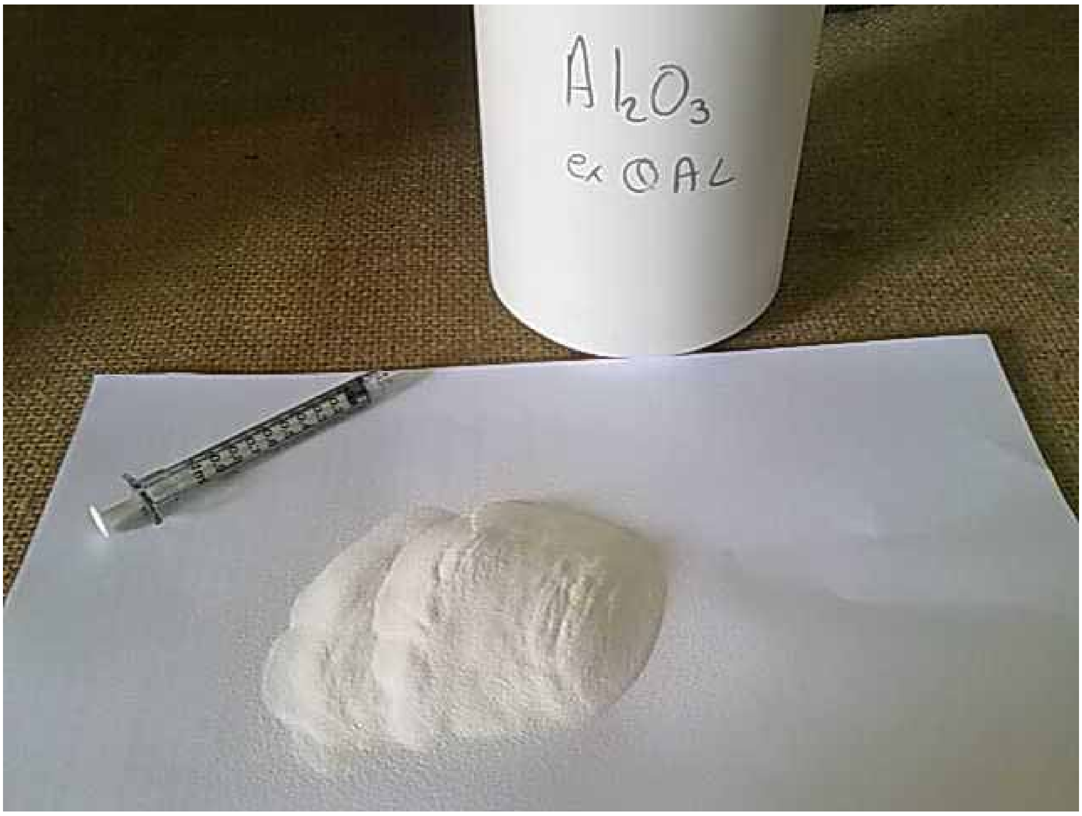
RioTinto supplied a sample of powdered alumina ($Al_2O_3$). This product is nearly completely insoluble with greater than 90% of particles sized between 45 and 200µm, as per Table 3.

*Table 3 Particle size distribution for activated alumina*

| Date | < 5µm | < 10µm | < 20µm | < 45µm | < 200µm |
|---|---|---|---|---|---|
| 12/09/2011 | 0.45 | 1.77 | 3.28 | 7.25 | 100.00 |

Figure 7-7 shows a sample of the powder in relation to a 1mL syringe and 2L plastic container.

*Figure 7-7 Alumina powder used by RioTinto at Tiwai Smelter*



### 7.5.1 Contact/concentration

Same as 7.4.1, except 0.1% solution used to achieve 0.1 mg $Al^{3+}$/L, 0.3, 0.5, 1.0 and 1.5.

It was necessary to keep the 0.1% suspension fully mixed to extract a representative dose for each sample. This required the gangstirrer be set to 300rpm.

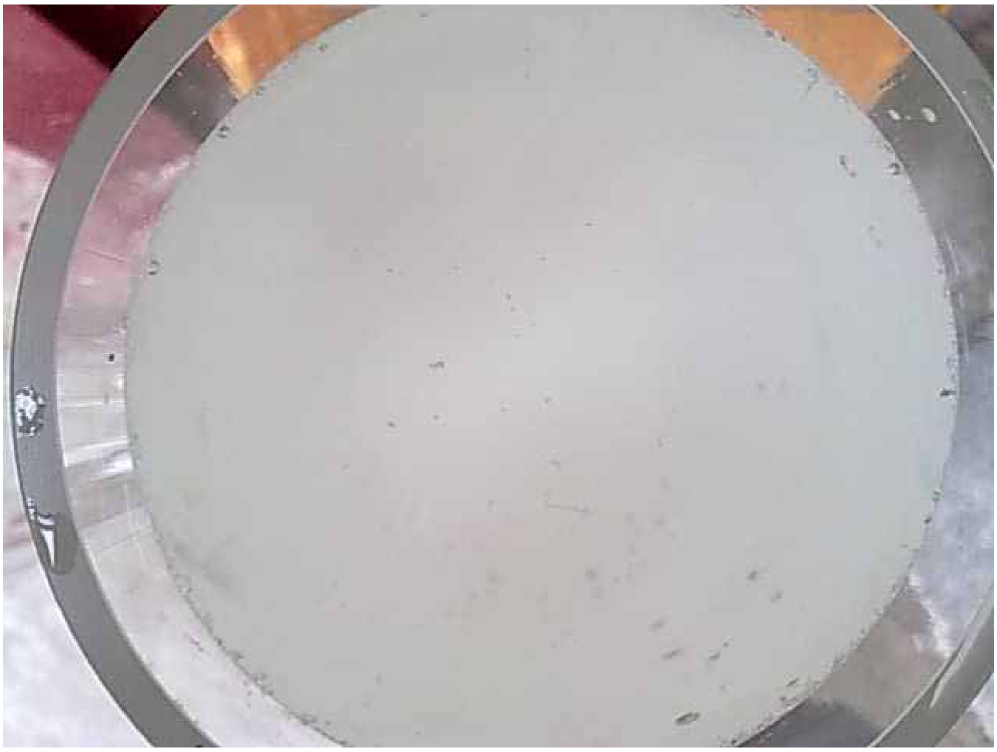
All gangstirrer samples were extracted with alumina in suspension and the laboratory instructed to leave the samples for 1 week before completing the analyses. This gave an overall contact time of 11 to 12 days.

### 7.5.2 Settling column

Same as 7.4.2. A 1ppm $Al^{3+}$ suspension of alumina was added to pre-rotated lakewater in a settling column. The alumina quickly collected at the cylinder base. The sample was left for only 1 hour because of time constraints and then sampled from just below the surface.

Figure 7-8 shows the opaque fluid formed when excess (10g) alumina is added to a 1 metre deep settling column for a settling rate test. The column base is just visible after a few minutes. However, 10g of alumina works is approximately 1300 $mgAl^{3+}/L$. There is no observed visible change to lakewater opaqueness when alumina is dosed at low concentrations equivalent to liquid alum and kibble alum trials.

***Figure 7-8 Settling column with 10g of alumina 15 minutes after addition.***



| **Lake Sample 1 (not P adjusted)** | | | Laboratory Analysis results | | | | |
|---|---|---|---|---|---|---|---|
| CoC ref | Sample | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ $CaCO_3$ | TP g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
| 937509 | Liquid Alum tests | | | | | | |
| 32 | LA1 Control | 0 | 9.5 | 0.012 | 0.00075 | 0.172 | 0.026 |
| 26 | LA3 0.05 | 0.05 | 8.9 | 0.008 | 0.00085 | 0.055 | 0.017 |
| 27 | LA3 0.1 | 0.1 | 8.8 | 0.011 | 0.00055 | 0.097 | 0.034 |
| 28 | LA3 0.3 | 0.3 | 7.5 | 0.004 | 0.00025 | 0.207 | 0.020 |
| 29 | LA3 0.5 | 0.5 | 6 | 0.003 | 0.00085 | 0.115 | 0.017 |
| 33 | LA1 0.82 | 0.75 | 5.0 | 0.014 | 0.00065 | 0.727 | 0.123 |
| 34 | LA1 1.10 | 1 | 4.0 | 0.016 | 0.0005 | 1.113 | 0.396 |
| 35 | LA1 1.37 | 1.25 | 2.6 | 0.012 | 0.00085 | 1.349 | 0.224 |
| 36 | LA1 1.64 | 1.5 | 2.3 | 0.04 | 0.00035 | 0.861 | 0.407 |
| 37 | LA1 1.91 | 1.75 | 1.8 | 0.014 | 0.00035 | 3.395 | 1.301 |

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ $CaCO_3$ | TP Ca g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 11 | LA1 Ca C | 0 | 19.4 | 0.019 | 0.01315 | | |
| 12 | LA1 Ca 0.82 | 0.75 | 22.1 | 0.02 | 5.00E-05 | | |
| 13 | LA1 Ca 1.10 | 1 | 22.6 | 0.018 | 5.00E-05 | | |
| 14 | LA1 Ca 1.37 | 1.25 | 24.1 | 0.018 | 0.00025 | | |
| 15 | LA1 Ca 1.64 | 1.5 | 29.7 | 0.05 | 0.00035 | | |
| 16 | LA1 Ca 1.91 | 1.75 | 28.6 | 0.03 | 5.00E-05 | | |

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ $CaCO_3$ | TP Na g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 17 | LA1 Na C | 0 | 9.5 | 1.768 | 1.65465 | | |
| 18 | LA1 Na 0.82 | 0.75 | 6.2 | 0.021 | 0.00185 | | |
| 19 | LA1 Na 1.10 | 1 | 7.9 | 0.016 | 0.00125 | | |
| 20 | LA1 Na 1.37 | 1.25 | 6.5 | 0.01 | 0.00065 | | |
| 21 | LA1 Na 1.64 | 1.5 | 7.4 | 0.026 | 0.00055 | | |
| 22 | LA1 Na 1.91 | 1.75 | 10.3 | 0.011 | 0.00055 | | |

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ $CaCO_3$ | TP g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 25 | CLA Na 0.3ppm | 0.30 | 5.3 | 0.005 | 0.00035 | 0.235495 | 0.022539 |
| 23 | CLA Na 1.0ppm | 1.00 | 2.3 | 0.002 | 0.00145 | 0.380943 | 0.127827 |

Kibbled Alum tests

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ CaCO$_3$ | TP g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| | | 0 | 9.6 | | | | |
| 1 | KA2 0.82 | 0.75 | 4.5 | 0.014 | 0.00045 | 1.191 | 0.071 |
| 2 | KA2 1.10 | 1 | 3.4 | 0.012 | 5.00E-05 | 1.063 | 0.096 |
| 3 | KA2 1.37 | 1.25 | 2.7 | 0.01 | 0.00025 | 1.751 | 1.126 |
| 4 | KA2 1.64 | 1.5 | 2.2 | 0.011 | 0.00015 | 0.953 | 0.383 |
| 5 | KA2 1.91 | 1.75 | 2.1 | 0.013 | 0.00015 | 2.783 | 0.570 |

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ CaCO$_3$ | TP Ca g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 6 | KA2 Ca 0.82 | 0.75 | 16 | | 0.03235 | 0.879 | 0.345 |
| 7 | KA2 Ca 1.10 | 1 | 22 | 0.039 | 5.00E-05 | 0.972 | 0.654 |
| 8 | KA2 Ca 1.37 | 1.25 | 27 | 0.03 | 0.00025 | 1.275 | 0.820 |
| 9 | KA2 Ca 1.64 | 1.5 | 16.2 | 0.027 | 0.00065 | 0.741 | 0.215 |
| 10 | KA2 Ca 1.91 | 1.75 | 27 | 0.023 | 0.00015 | 1.744 | 0.605 |

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ CaCO$_3$ | TP g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 24 | CKA Na 1ppm | 1 | 6.1 | 0.004 | 0.00045 | 0.389543 | 0.017326 |

937477 Alumina tests

| | | Al$^{3+}$ dose g/m$^3$ | Alk g/m$^3$ CaCO$_3$ | TP g/m$^3$ | DRP g/m$^3$ | Al $_{total}$ g/m$^3$ | Al $_{filtered}$ g/m$^3$ |
|---|---|---|---|---|---|---|---|
| 1 | SA4 0.2 | | | 0.013 | 0.00055 | 0.033 | 0.003 |
| 2 | SA4 0.6 | | | 0.015 | 0.00005 | 0.033 | 0.0024 |
| 3 | SA4 1.0 | | | 0.011 | 0.00005 | 0.06 | 0.01 |
| 4 | SA4 2.1 | | | 0.014 | 0.00035 | 0.041 | 0.003 |
| 5 | SA4 3.1 | | | 0.014 | 0.00005 | 0.123 | 0.0027 |
| 6 | CSA1 | | | 0.01 | 0.00075 | 0.028 | 0.004 |

**Lake Sample 2 (P adjusted to 0.083mg/L)**

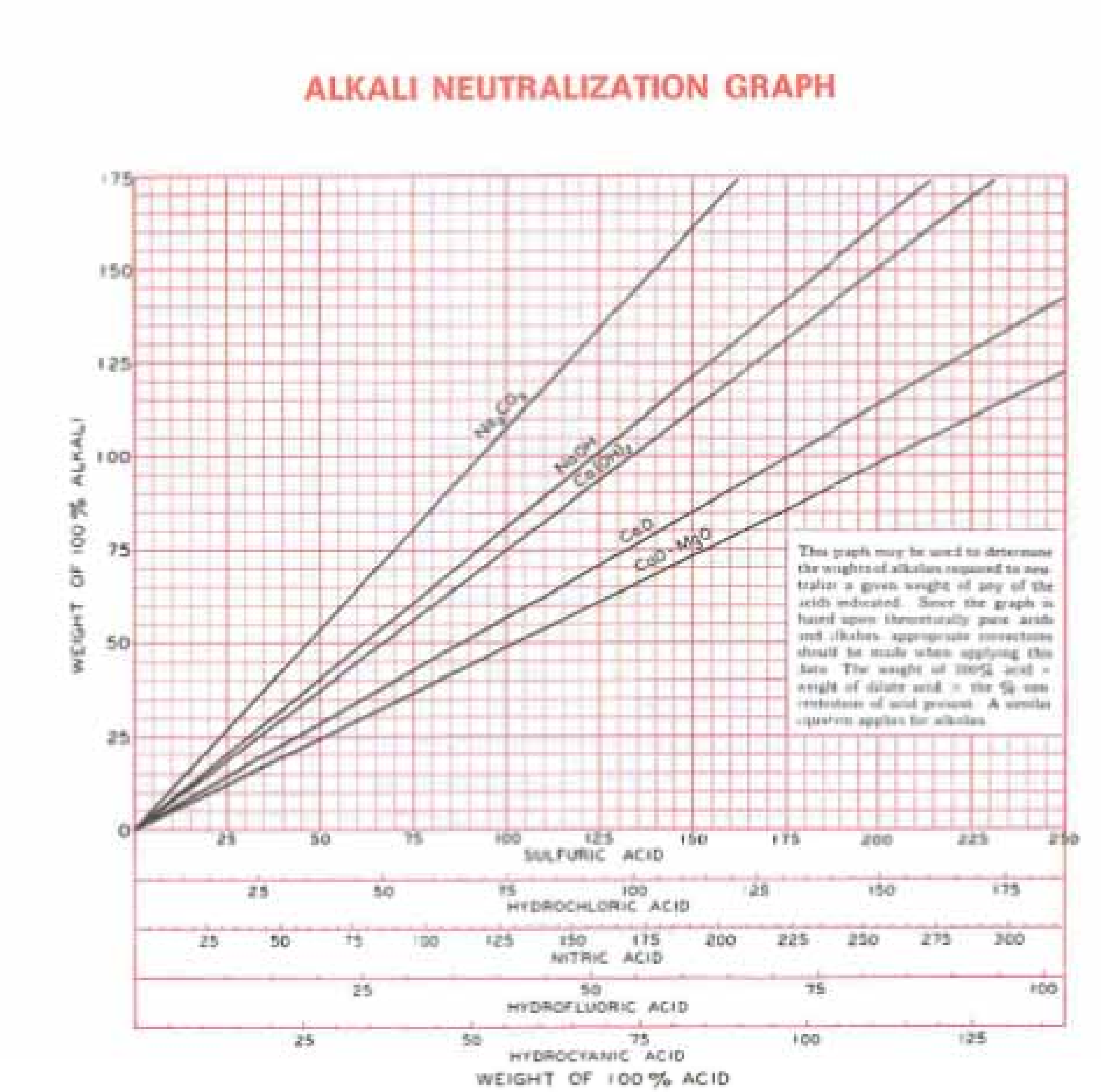
| CoC ref | Sample | DO mg O$_2$/L | Al$^{3+}$ dose g/m$^3$ | Alkalinity g/m$^3$ CaCO$_3$ | TP g/m$^3$ | TDP g/m$^3$ | DRP g/m$^3$ | pH $_{start}$ units |
|---|---|---|---|---|---|---|---|---|
| 1 | Control | 11.04 | 0.0 | 7.8 | 0.083 | | 0.04355 | 6.52 |
| 2 | LA 0.1F | | 0.1 | 7.5 | 0.052 | | 0.05015 | 6.32 |
| 3 | LA 0.3F | | 0.3 | 6.5 | 0.002 | | 0 | 6.43 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4 | LA 0.5F | 0.5 | 8.6 | 0.004 | | 0.00045 | 6.3 |
| 5 | LA 0.75F | 0.75 | 8.9 | 0.004 | | 0.00035 | 5.86 |
| 6 | LA 1.0F | 1 | 8 | 0.004 | | 0 | 5.58 |
| 7 | LA 1.5F | 1.5 | 9.4 | 0.004 | | 0.00045 | 5.3 |
| 1 | LA 0.1 | 0.1 | 8.8 | 0.092 | 0.0245 | 0.0256 | 7.09 |
| 2 | LA 0.3 | 0.3 | 9.7 | 0.087 | 0.0015 | 0.0003 | 6.8 |
| 3 | LA 0.5 | 0.5 | 10.2 | 0.078 | 0.0005 | 0.0002 | 6.54 |
| 4 | LA 0.75 | 0.75 | 10.3 | 0.059 | 0.0005 | 0.0007 | 6.35 |
| 5 | LA 1.0 | 1 | 10.7 | 0.080 | 0.0005 | 0.0015 | 6.15 |
| 6 | LA 1.5 | 1.5 | 13.8 | 0.044 | 0.0015 | 0.0002 | 5.26 |
| | | | | | | | |
| 1 | K 0.1 NaC | 0.1 | 8.7 | | 0.0025 | 0.0023 | 6.41 |
| 2 | K 0.3 NaC | 0.3 | 7.7 | | 0.0005 | 0.0005 | 6.4 |
| 3 | K0.5 NaC | 0.5 | 8.3 | | 0.0015 | 0.0007 | 6.04 |
| 4 | K0.75 NaC | 0.75 | 8.7 | | 0.0015 | 0.0002 | 5.82 |
| 5 | K1.0 NaC | 1 | 10.2 | | 0.0065 | 0 | 5.52 |
| 6 | K1.5 NaC | 1.5 | 10.7 | | 0.0005 | 0.0001 | 5.19 |
| 1 | K 0.1 SiO | 0.1 | 8.9 | | 0.0345 | 0.03475 | 6.41 |
| 2 | K 0.3 SiO | 0.3 | 7.7 | | 0.0125 | 0.01115 | 6.4 |
| 3 | K 0.5 SiO | 0.5 | 7.9 | | 0.0055 | 0.00305 | 6.04 |
| 4 | K 0.75 SiO | 0.75 | 7.9 | | 0.0045 | 0.00245 | 5.82 |
| 5 | K 1.0 SiO | 1 | 7.9 | | 0.0045 | 0.00485 | 5.52 |
| 6 | K 1.5 SiO | 1.5 | 8.2 | | 0.0045 | 0.00745 | 5.19 |
| 1 | SiO2 0.33 | 0 | 8.5 | | 0.0425 | 0.03915 | 6.7 |
| 2 | SiO2 0.55 | 0 | 10.8 | | 0.0565 | 0.05245 | 6.67 |
| 3 | SiO2 0.82 | 0 | 16.7 | | 0.0605 | 0.05855 | 6.82 |
| 4 | Si02 1.1 | 0 | 16.2 | | 0.0705 | 0.05945 | 6.6 |
| 5 | SiO2 1.64 | 0 | 19 | | 0.0675 | 0.06295 | 6.65 |

Results are below the detection limit of 0.004

Assumed the same as other kibbled alum results

This table was used to determine the equivalent dose of soda ash to hydrated lime.



This graph may be used to determine the weights of alkalies required to neutralize a given weight of any of the acids indicated. Since the graph is based upon theoretically pure acids and alkalies, appropriate corrections should be made when applying this data. The weight of 100% acid = weight of dilute acid × the % concentration of acid present. A similar equation applies for alkalies.

Source: National Lime Association Bulletin 213, Seventh Edition 1995, Fig 1-b Neutralisation Graph, comparing lime with other alkaline materials.