# APPENDIX 5

# PHOSPHATE ROCK REQUIREMENT FOR BOOMERANG LAKE - LABORATORY EXPERIMENTS

# BOOMERANG LAKE PHYTOPLANKTON, 1995

# 1995 NATURE PAPER CONTROLLED REVERSAL OF LAKE ACIDIFICATION BY TREATMENT WITH PHOSPHATE FERTILIZER

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# PHOSPHATE ROCK REQUIREMENT
# FOR
# BOOMERANG LAKE

## Laboratory Experiments
## to Determine
## Best Rock Type and Application Rates

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## 1.0 Introduction

Phosphate rock has been tested over the past three years as an experimental treatment for removal of dissolved metals and acidity from Boomerang Lake. Natural phosphate rock contains calcium phosphates which, upon addition to acid mine drainage, form iron phosphate precipitates at relatively low pH.

To scale up and optimize the addition in terms of economics and efficacy, laboratory experiments are required.

In 1992, 1993 and 1994, tests have been performed in the lab and field. In the laboratory, it has been clearly shown that addition of natural phosphate rock to acid mine drainage induces the precipitation of iron, aluminum, zinc and copper, raises the pH and overall neutralizes acidity.

Unfortunately, applications of natural phosphate rock in Boomerang Lake (1,000,000 $m^3$) have not resulted in appreciable water quality changes. Presently, it appears that an insufficient quantity of phosphate rock was added, and/or dissolution of the type of natural phosphate rock was too slow as it settled to the sediments.

The results of four laboratory experiments, petformed in series, are described below. For these experiments, Boomerang Lake water (B-8) was collected on February 28, 1995.

## 2.0 Experiment 1 pH and Chemistry of Phosphate Rock-Treated Boomerang Lake Water

Objective: To examine the effect of phosphate rock additions (Code 31) on pH, the time course of pH changes and the chemistry of the water at different pHs. This will help decide the dosage of phosphate rock and provide a target pH.

## 2.1 Method

A glass jar containing 2 L of Boomerang Lake water was set up in the laboratory, and stirred using a magnetic stirrer. A dose of 0.4 g of Code 31 phosphate rock was added to the surface **of** the vigorously stirring water. The phosphate rock was rapidly mixed into the sample. The water pH was monitored continuously. When the pH value reached a plateau, another 0.4 g code 31 was added. This processes was continued until 2.4 g had been added. During this monitoring period, water samples were extracted from the 2 L system when the pH reached 4.0, **4.5,** 5.0, **5.5,** 6.0 and 6.5. After the final Code 31 phosphate rock addition, pH was monitored periodically over a 9 day period to determine long term pH changes. The jar was kept covered between measurements to minimize evaporatory water **loss.**

## 2.2 Results and Discussion

### Code 31 Addition and pH

The stirring **of** water provided optimum conditions for interaction between the code31 phosphate rock and the Boomerang Lake water sample. The time course of pH in relation to additions of code 1 are shown in Fig l a (0-146 min) and Fig I b (0-2236 min). Following the first addition of code 31 ($0.2 g.L^{-1}$), pH rose from 3.37 to 3.81 in 75 seconds, and nearly 4.5 within 20 minutes after which pH remained relatively stable (Fig la).

Following addition of another $0.2 g.L^{-1}$ of code 31 (cumulative concentration, $0.4 g.L^{-1}$), there was a rapid rise in pH within 2 minutes (Fig la). Thereafter, pH rose gradually and stabilized at approximately pH 5, at which point a further $0.2 g.L^{-1}$ dose of code 31 was added. This elevated the pH to 5.3. Another dose **of** code 31 was added bringing the total to $0.8 g.L^{-1}$ and left overnight. The pH rose to 5.91. Further additions of phosphate rock were made. With each addition, the change in pH was smaller (Fig 1b). After the final addition (total $1.2 g.L^{-1}$), the jar was stirred for several days and the pH periodically monitored. There was a very slow rise in pH to 6.5 (Fig Ib) and, eventually, to 7.1 after 8 days (data not shown). Clearly, dissolution of phosphate rock is continued over the final days, albeit at a slower rate than in the first hours of the experiment in conditions of lower pH.

## Water Chemistry and pH

Each addition of code 31 increased pH. Overall, this experiment provided a pH ranging from 3.37 (no code 31) to higher than 6.5 (1.2 $g.L^{-1}$ code 31). Analysis of water through this pH range can provide an insight into what processes are occurring. Water samples 100 mL in volume were collected prior to addition of each dosage of code 31. These samples were filtered and acidified and submitted for elemental analysis by ICAP. Acidity of samples was determined by titration with NaOH in a Metrohm, Titrino Autotitrator.

The ICAP data for the most abundant elements is summarised together with acidity data in relation to pH **of** the sample in Table 1 and Figures 2a and 2b.

Following addition of the first 0.2 $g.L^{-1}$ code 31 and an increase of pH to **4,** there was an increase in dissolved Ca and P. This is due to dissolution of these most abundant elements present in phosphate rock.

With further code 31 additions and increase in pH, Ca concentrations continued to rise to 115 $mg.L.^{-1}$. In contrast, at pHs greater than **4.5,** P concentrations declined. Presumably, removal of dissolved phosphate by precipitation consumed some of the dissolved phosphate liberated from the phosphate rock.

The dissolution of phosphate rock and increase in pH was associated with a decline in acidity from the original 96 $mg.L^{-1}$ equiv. $CaCO_3$ (no code 31 addition) to 17.2 $mg.L^{-1}$ following addition of a total of 1.2 $g.L^{-1}$ and an increase in pH to 6.5.

There was a steady decline in Al concentration with increase in pH. Initially, the

Boomerang Lake water sample contained 3.5 $mg.L^{-1}$ Al at pH 3.37 (no phosphate rock addition). At pH 6.5, the Al concentration was below the detection limit (0.025 $mg.L^{-1}$). Copper showed a similar pattern of decline.

Following the addition of the first 0.2 $g.L^{-1}$ of code **31,** most of the Fe had dropped out of solution by the time pH had reached **4** (declining from 3.6 $mg.L^{-1}$ to 0.234 $mg.L^{-1}$). The Fe concentration declined further as the pH rose. The Fe is precipitating as either phosphate or hydroxide.

Zinc concentration showed little change **as** pH was increasing to pH 5 (around 17-18 $mg.L^{-1}$). **As** the pH rose higher than pH 5, Zn dropped out of solution. At pH 6.5, only 6.2 $mg.L^{-1}$ remained.

**Mn,** Mg, K and Na exhibited no clear change in concentration over the course of the experiment.

## 3.0 Experiment 2 - Phosphate Rock Type and Change in pH

Objective: To determine the reactivity of different types *of* phosphate rock with Boomerang Lake water.

### 3.1 Methods

Stirred System: One litre of Boomerang Lake was stirred vigorously with 0.2 g of one of three types of phosphate rock and pH change with time was monitored. The 3 types of phosphate rock used were code 31, a very fine formulation; code 132, a small particle size, calcined phosphate rock; and phosphate Byproduct, a very coarse material. The latter was ground fine (<1 mm particle size using mortar and pestle) for this experiment. Grinding was performed since it is not possible to add representative samples of less than 2 or 3 g of the phosphate Byproduct, due to the coarseness and heterogeneity of this material. The time course of the pH change with this material may be expected to be faster than with unground material (not tested) due to exposure of a greater surface area to the water. Final pH will probably be similar.

Stirred then Static System: A second set of jars was set up and stirred for 30 minutes to emulate the conditions which would be experienced in Boomerang Lake as the material falls through the water column. Thereafter, the jars were left to stand and pH monitored at the surface, middle and bottom of the jar. This will mimic conditions once the phosphate rock has reached the bottom of the lake.

### 3.2 Results and Discussion

The results are shown in Fig 3a for the early observations (0-97 min) and in Fig 3b for the long term (0-8000 min) for the stirred systems.

With code 31, pH rose rapidly to pH 4 within 11 minutes, to pH 4.13 in 21 minutes and to pH 4.23 in 47 minutes. Thereafter, pH increased further to 4.85 within 136 hours of stirring.

In the system with phosphate Byproduct, there was an initial small decline in pH, followed by a slow but steady increase. By the end of the observations, pH had reached 5.13, a value higher than the system with code 31 added. However, the initial rate of increase was much slower than in the system with code 31.

Upon addition of code 132, the pH declined over the first 10 minutes. The subsequent rise in pH was extremely slow. By the end of the observation period, a reading of only 4.11 had been achieved.

In the unstirred systems, changes in pH were very much less with all three types of phosphate rock (Fig. 3c). Data for the middle of the jar (8 cm above bottom and below surface) is presented. Data for the top and bottom samples were generally similar. The stirring process clearly increases reaction rates by increasing the exposure of the rock surface to the Boomerang Lake water. These results indicate that once the phosphate rock has reached thee bottom of Boomerang Lake, reaction with the water and consequent changes in pH, acidity and ion concentrations will be very slow. Much of the 'action' occurs within the period of passage through the water column.

## 4.0 Experiment 3 - Boomerang Lake Water Column

Obiective: To determine time for code 31 phosphate rock to fall through the water column and the changes in pH occurring during that time period.

### 4.1 Methods

A vertical plexiglass column of length 2.45 m and internal diameter 6 cm was constructed. The set up is shown in Schematic 1. The column was filled with 7 L of Boomerang Lake water. A dose of 1.4 g of code 31 phosphate rock was added as a slurry to the top of the column. Water was periodically drawn off at the bottom of the column. Phosphate rock and precipitate particles which had settled to the column bottom since the previous sample was taken were also collected in the drawn-off sample by gentle agitation of the settled solids with a magnet. A preliminary test-run was carried out with distilled water with pH adjusted to that of Boomerang Lake (pH 3.4) with $H_2SO_4$ (pH will affect CO, gas production, the ascent of bubbles of which will affect the settling rate of fine particles). This run was performed to test the system and determine how and when to sample. The experiment itself was run with Boomerang Lake B8 water in the column. Code 31 phosphate rock was chosen, as previous experiments determined that it reacts more rapidly than other materials tested and since it is finer, will likely remain longer in the water column (before settling) and, therefore, have more effect per unit weight on water chemistry.

The pH was determined for each sample collected immediately on collection (the phosphate rock will continue to react with the water). The sample was filtered as soon as possible through 0.45 $\mu m$ pore cellulose acetate filters. The filters were dried in a drying oven and weighed to determine the total phosphate rock (plus any precipitated material) in each sample. Some filtered samples were titrated against NaOH to determine acidity.

## 4.2 Results

Figure 4 shows the pH of samples against time in the column. After an initial fluctuation, there was a rapid rise in pH from 3.44 (collected 9 minutes following code 31 addition) to pH 4.3 at 20 minutes. This pH value is similar to that observed following 20 minutes of stirring (Fig l a and 3a).

The titration data (Table **2)** shows that from an initial 109 $mg.L^{-1}$, acidity declined to 60 $mg.L^{-1}$ for a sample collected 18 minutes after addition of code 31 to the column. After this time, the acidity remained constant, i.e. there was no further net acidity consumption.

Figure **5** shows the time course of code 31 settling time through the column. Fig 5a shows the accumulated weight of code 31 taken from the bottom of the column and Fig 5b shows the amount of code 31 collected per unit time. Although settling occurs over a period in excess of 3 h, most material (> 60 % of collected material) settles out between 18 and 48 minutes. The pH of samples collected for most of this period (22-48 minutes) was in the 4.3 to 4.5 range.

In the field, some turbulence undoubtedly occurs which will add to the settling time. Therefore, it can be anticipated that a pH of 4.3 can be achieved well before the material settles to the bottom of the lake.

## 5.0 Experiment 4 - Boomerang Lake Water Column with Sediment

Objective: To determine the effect code 31 phosphate rock addition on Boomerang Lake water in the presence of a sediment layer

Previous experiments established the time course of Code 31 settling and its relationship to pH and other aspects of water chemistry. This experiment sought to determine the consequences of phosphate rock (type and rate as to be applied in the field) on Boomerang Lake water set up over Boomerang Lake sediment and with circulation to provide conditions closer to those encountered in the field than employed previously in the laboratory column tests. Interactions at the interface between the sediment layer and the water layer will influence the effects of phosphate rock addition both in the short and long term.

### 5.1 Methods

The column set up previously as described above. The column was drained and rinsed out prior to set up of the fourth experiment. Boomerang sediment (depth of **0.4** m) was place in the column. A slow circulation of the water column was achieved by means of a peristaltic pump with a flow through of 5 $mL.min^{-1}$. At this rate, the entire column will circulate in approximately **24** h. The cycling water entered the water column 10 cm above the sediment and was withdrawn just below the water surface. This exchange of water mimics the mixing which occurs in the field. The column was left to establish equilibrium for a period of 26 days prior to addition of phosphate rock. Within a day of addition of water to the sediment, an orange precipitate layer, presumably Fe(III) hydroxide had formed on the sediment surface. Within 7 days, a darker band began to appear below the orange layer suggesting reduction of the Fe(III) hydroxide. Over the next few days, dark zones, apparently randomly distributed, developed throughout the sediment profile at the plexiglass-sediment interface. These black zones were in turn surrounded by a grey-brown zone, which was surrounded by a pale-orange zone. The general colour of the interface was orange-brown, suggesting the occurrence of some iron oxidation here

1.6 g of Code 31 phosphate rock was added as a slurry as described previously. Prior to and following addition of phosphate rock, samples were withdrawn from the top and bottom (between cycling port and sediment surface) of the column for determination of pH. Acidity was determined on selected, filtered samples. These have been submitted for ICAP analysis to determine the effect of the phosphate rock (in the presence of a sediment layer) on Boomerang Lake (B8) water chemistry.

## 5.2 Results

The time course pH at the top and bottom of the column following phosphate rock addition are shown in Figure 6. The experiment was run one month after the column was set up. There was little change in pH during this period. The pH of water at the top of the column was consistently higher than that at the bottom. Following set up of the column, acidity was higher at the bottom of the column than at the top. Following addition of code 31 phosphate rock, the rate of pH change and final pH were similar to those found previously without water circulation and without a sediment. Changes in pH at the top of the column were observed within 6 minutes at the top of the column and 12 minutes at the bottom of the column. The pH change occurred in two distinct phases. The first phase, lasting about 30 minutes and shown in Figure 6a, saw the pH at the top of the column rise from 3.6 to 4.3 and at the bottom of the column from 3.3 to 4. The second phase, shown in Figure 6b saw a slow and gradual increase in pH to 5.3 at the top and 4.8 at the bottom of the column. This suggests that the phosphate rock was continuing to change the water chemistry after particulates had settled. Rate of phosphate rock settling was similar to that noted in previous experiments. The water column became clear within approximately **5** h suggesting that most of the solid code 31 particles had settled by this time.

Acidity titrations for the bottom of the column from the time of addition of code 31 to 90 h following addition are shown in Figure 7. After column set up, the acidity of the water column (bottom) declined from about 110 mg.L$^{-1}$ to 70 mg.L$^{-1}$ over a 30 day period prior to addition of phosphate rock (data not shown). Following phosphate rock addition, there was a decline in acidity from 70-80 mg.L$^{-1}$ to 40-50 mg.L$^{-1}$.

## 6.0 Summary and General Discussion

- A 0.2 g.L$^{-1}$ dose of code 31 phosphate rock with stirring in a jar or settling through a 2.5 m deep water column increases the water pH from 3.4 to pH 4.2 - 4.3 in about 20-25 minutes.
- Code 31 can raise pH of Boomerang Lake water to > 7 with continuous optimised reaction (vigorous stirring) over a week-long period.
- Raising the pH of Boomerang Lake water to 4.5 with code 31 phosphate rock (0.2 g.L$^{-1}$) results in removal of > 95 % of the Fe and 30 % of the Al.
- Raising pH of Boomerang Lake water to 6.5 with code 31 phosphate rock (1.2 g.L$^{-1}$) results in removal of 99.8 % Fe, 99.3 % Al and 66 % of the Zn.
- Code 31 is the best material, as it is finer (longer settling time) and is more reactive than either Phosphate Byproduct or code 132.
- Code 31 has a median settling rate of approximately 10 cm.min$^{-1}$ in unstirred conditions.
- Stirring, or settling time through a water column, is required for effective interaction between code 31 and Boomerang Lake water.
- In the presence of a sediment layer, pH of Boomerang Lake water rises in two phases following addition of 0.2 g.L$^{-1}$ code 31 phosphate rock, an initial rapid phase to 4.2 and a slow subsequent rise to 4.8-5.3 by 90 h following the addition.

Of the materials tested, code 31 is clearly the phosphate rock of choice for addition to Boomerang Lake. At a rate of 0.2 g.L$^{-1}$, pH can be raised to pH 4.2-4.5 within half an hour or within the time it takes the material to settle to the bottom of the lake, sufficient to remove most of the Fe and some of the Al from the water. Perhaps more important, this pH is much more favourable for algal growth and biopolishing of Zn than the pH of 3.4 currently found in the lake. Following the settling period, there is continued slow reaction of the phosphate rock at the sediment surface as indicated by a continued slow rise in pH. Phosphate rock could be used to remove Zn by raising pH to 6.5 or 7 but the quantities required (at least 1.2 $g.L^{-1}$ or 1200 tonnes for the whole lake) may be prohibitively expensive and such a pH could not be achieved while the code 31 **is** reactive, i.e. before the material settles to the bottom of the lake.

## 7.0 Recommendation

From the results of these experiments, it is recommended to add 200 metric tonnes of code 31 to Boomerang Lake using a technique whereby the code 312 material is pre-slurried.

While the effect of temperature upon reaction rates was not tested, it is likely that the phosphate rock would best react at higher lake water temperatures in summer, e.g. 20°C.

'able 1: Experiment 1 - Chemistry of samples collected at different pH values

| Parameter | | 'hospha Rock - ode 31 | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Original B8 | | 'hospha Rock added | | | | |
| | | 0 g/L | 0.2 g/L | 0.2g/L | 0.4g/L | 0.8 g/L | 1.2 g/L | 1.2g/L |
| pH | units | 3.37 | 4.00 | 4.50 | 5.00 | 5.50 | 5.90 | 6.50 |
| Acidity | mg/L | 96.0 | 73.9 | 66.0 | 51.1 | 39.5 | 29.1 | 17.2 |
| Al | mg/L | 3.51 | 2.99 | 2.47 | 1.43 | 0.61 | 0.10 | <0.025 |
| Ca | mg/L | 79.5 | 91.3 | 95.3 | 98.0 | 98.5 | 103.0 | 115.0 |
| Cu | mg/L | 0.21 | 0.24 | 0.21 | 0.14 | 0.05 | 0.02 | 0.01 |
| Fe | mg/L | 3.61 | 0.23 | 0.16 | 0.13 | 0.04 | 0.04 | 0.01 |
| Mn | mg/L | 7.01 | 6.64 | 6.77 | 6.68 | 6.44 | 6.36 | 5.98 |
| P | mg/L | <0.06 | 2.53 | 2.72 | 2.33 | 1.69 | 1.17 | 0.68 |
| K | mg/L | 3.30 | 2.40 | 2.50 | 3.00 | 1.90 | 2.70 | 3.40 |
| Na | mg/L | 2.98 | 3.46 | 3.43 | 3.51 | 3.51 | 4.07 | 4.62 |
| Zn | mg/L | 18.30 | 17.50 | 17.70 | 16.90 | 15.20 | 12.30 | 6.19 |

Table 2: Experiment 3 - Column Experiment
Acidity of samples

| Sample # | Time in column (min) | *pH | Acidity (mg/L) |
|---|---|---|---|
| Original | 0 | 3.28 | 109 |
| 1 | 3 | 3.76 | 75 |
| 3 | 9 | 3.74 | 82 |
| 6 | 18 | 4.38 | 60 |
| 9 | 33 | 4.5 | 56 |
| 12 | 60 | 4.71 | 57 |
| 15 | 99 | 4.52 | 58 |

Table 3: Experiment 3 -Column Experiment

Chemistry of Water vs Time

| Element | 0 minutes | 35 minutes | 21 hours |
|---|---|---|---|
| Zn | 13.9 | 13.0 | 11.6 |
| Fe | 0.38 | 0.07 | <0.05 |
| P | 0.37 | 5.36 | 4.20 |
| Al | 2.92 | 2.64 | 1.64 |
| Mn | 4.72 | 4.56 | 4.24 |
| c u | 0.12 | 0.08 | 0.05 |

All values are in mg/L.

Fig 1a
code-31 and pH

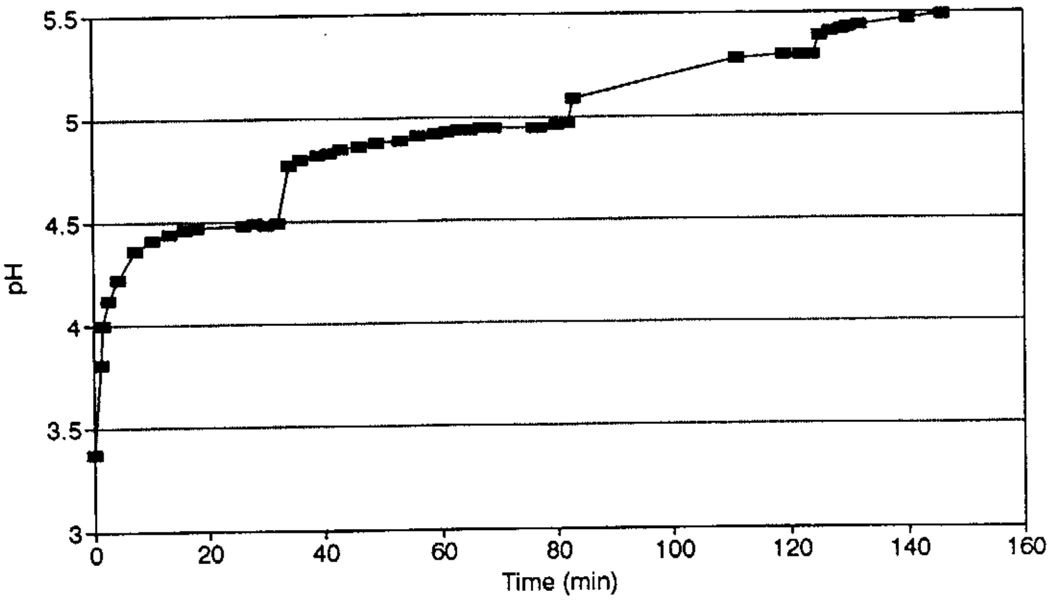



Fig 1b:
code-31 and pH

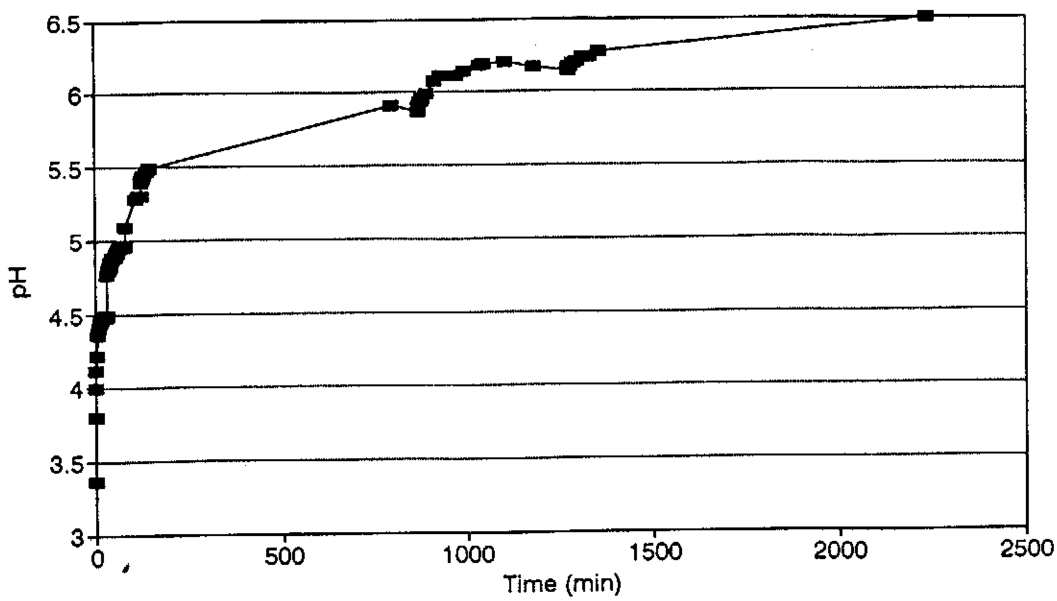


Fig 2a: Experiment 1
code 31-effect of pH on chemistry

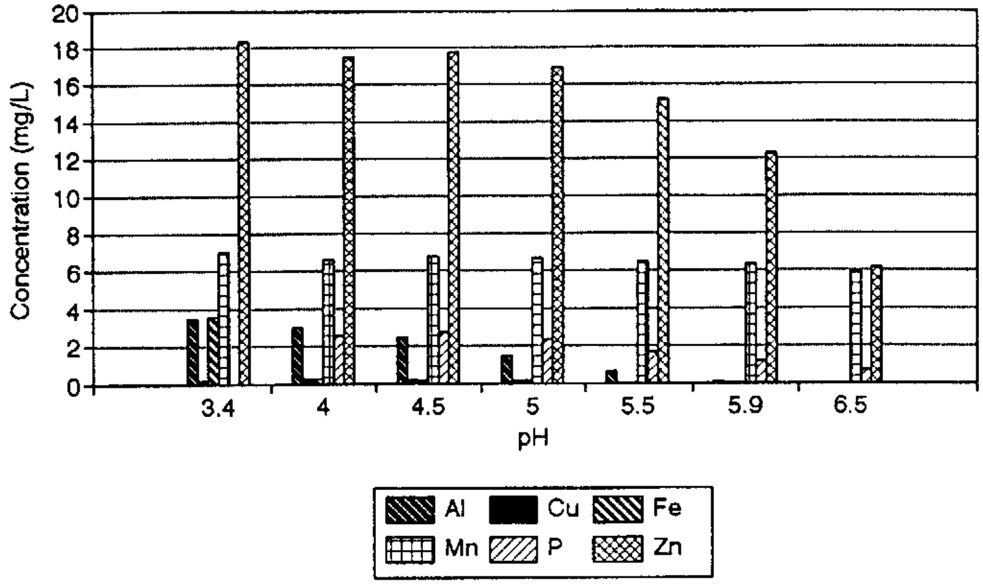



Fig. 2b: Experiment 1
code 31-effect of pH on chemistry

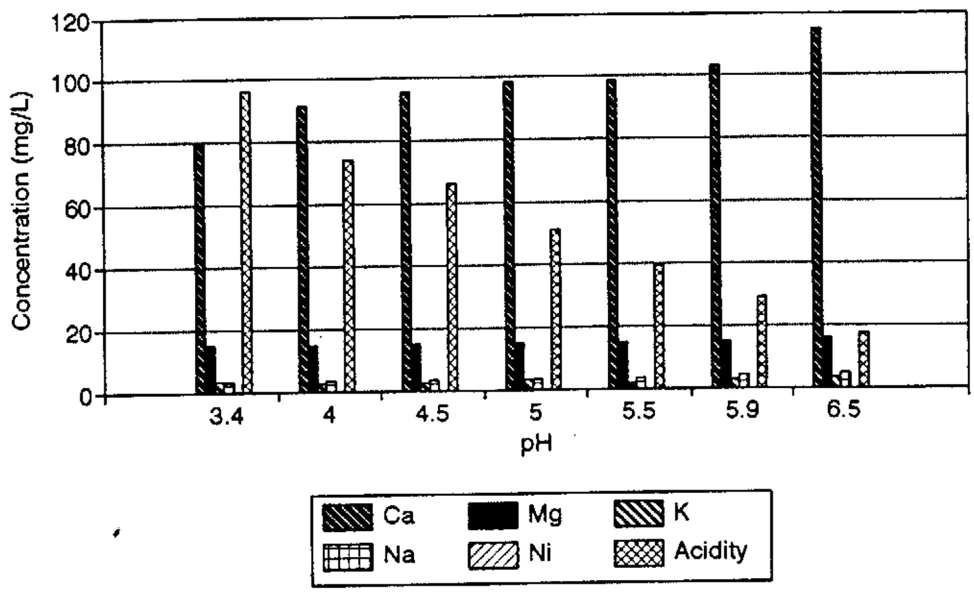


Fig 3a: Experiment 2
Reaction Rates-Stirred Jars

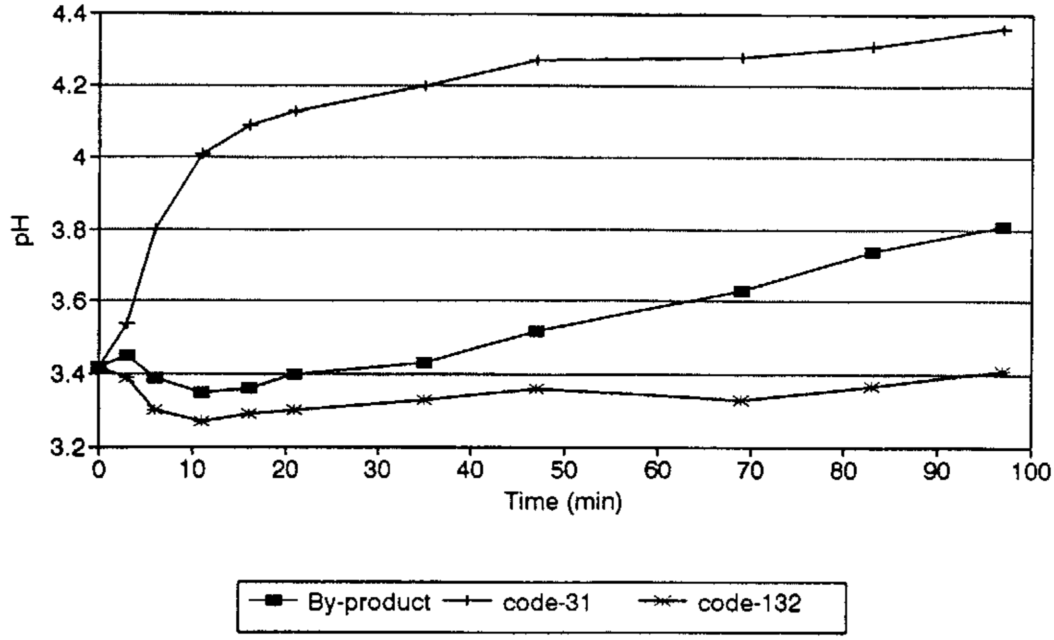



Fig 3b: Experiment 2
Reaction Rates-Stirred Jars

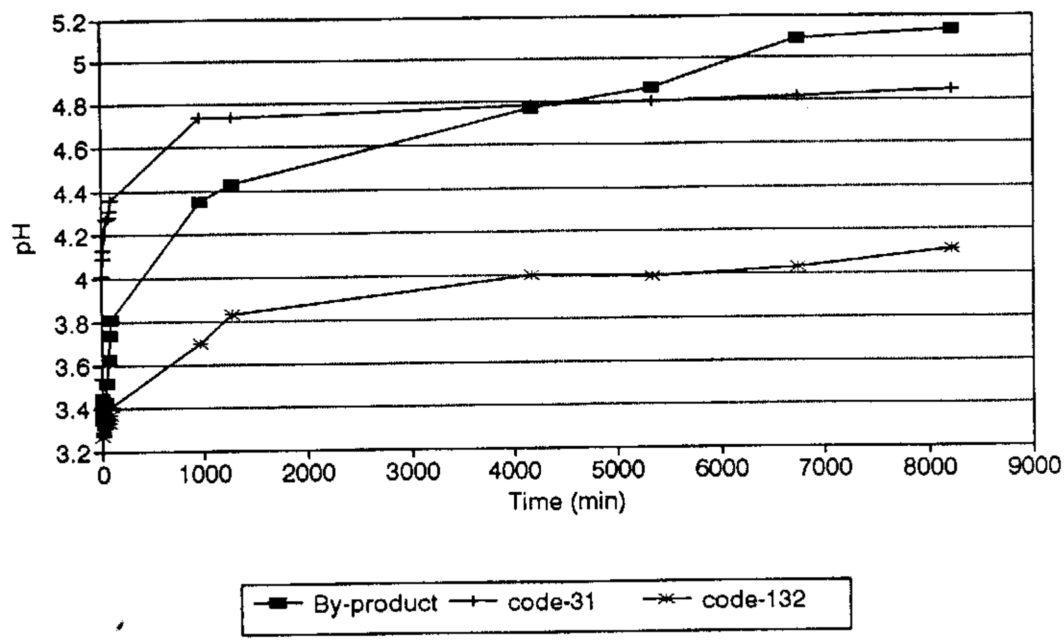


Fig 3c: Experiment 2
Static jars-Middle(8cm above phosphate)

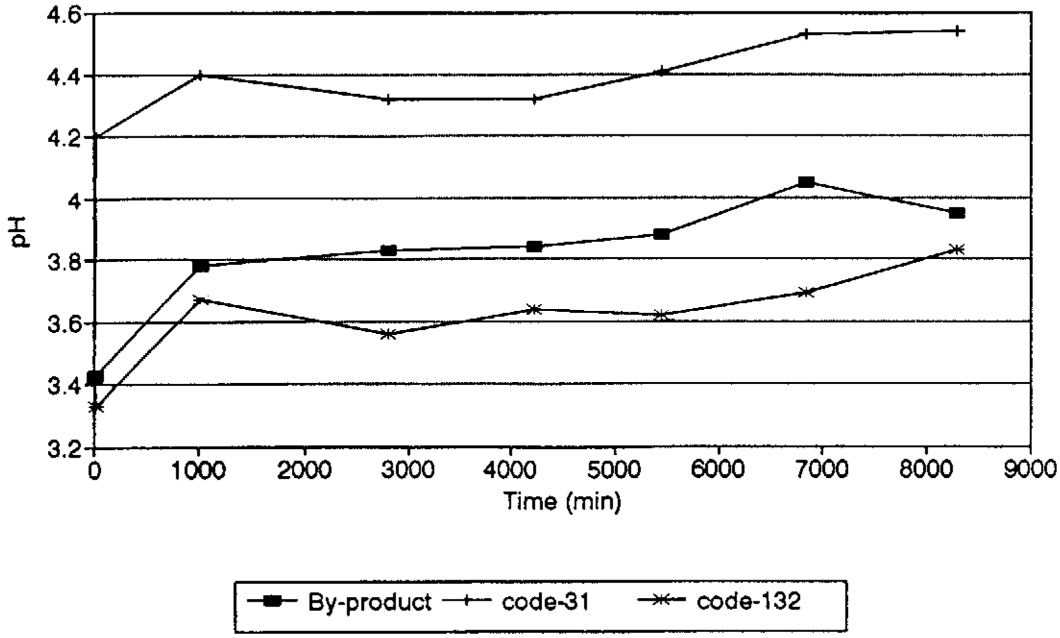



Fig 4:Boomerang Lake Column Expt
Time in column and pH of samples

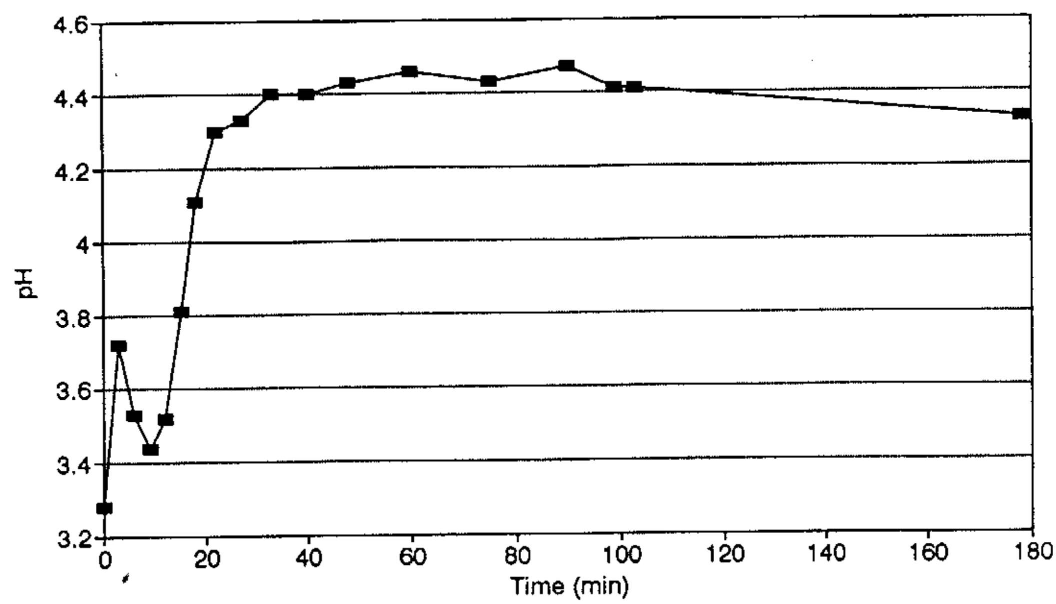


Fig 5a:Boomerang Lake Column Expt.
Time in column and code 31 settling

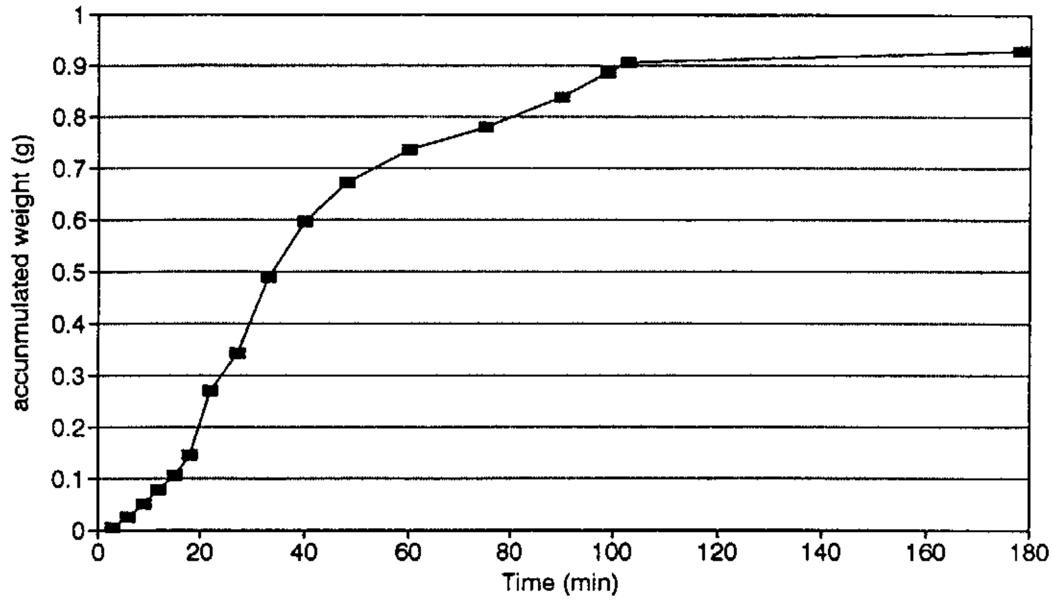



Fig 5b:Boomerang Lake Column Expt.
code 31 settling with time

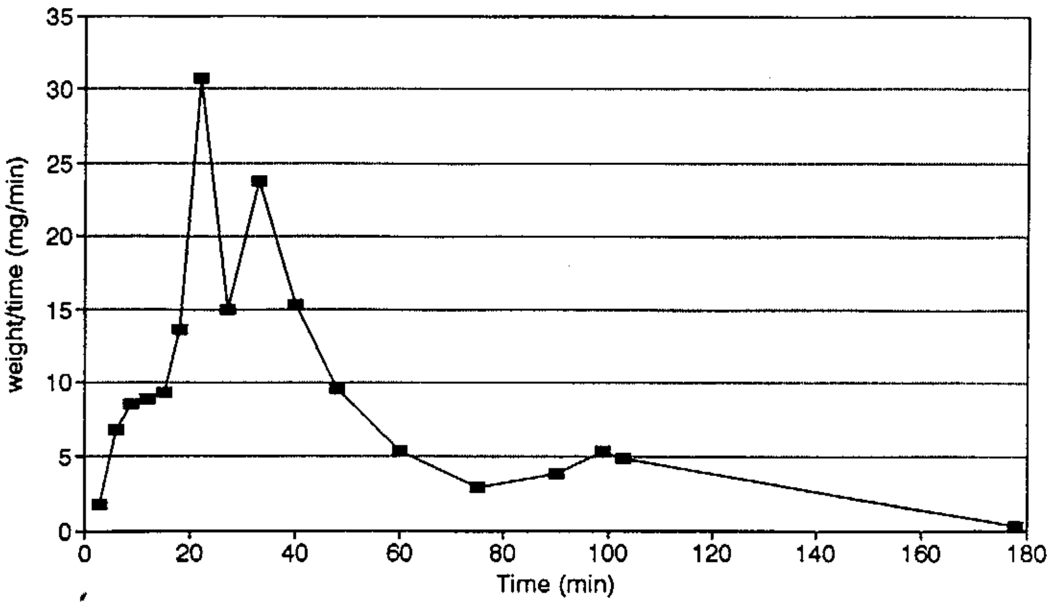


Fig. 6a: B8 water/sediment/code 31
Top and Bottom samples, early changes

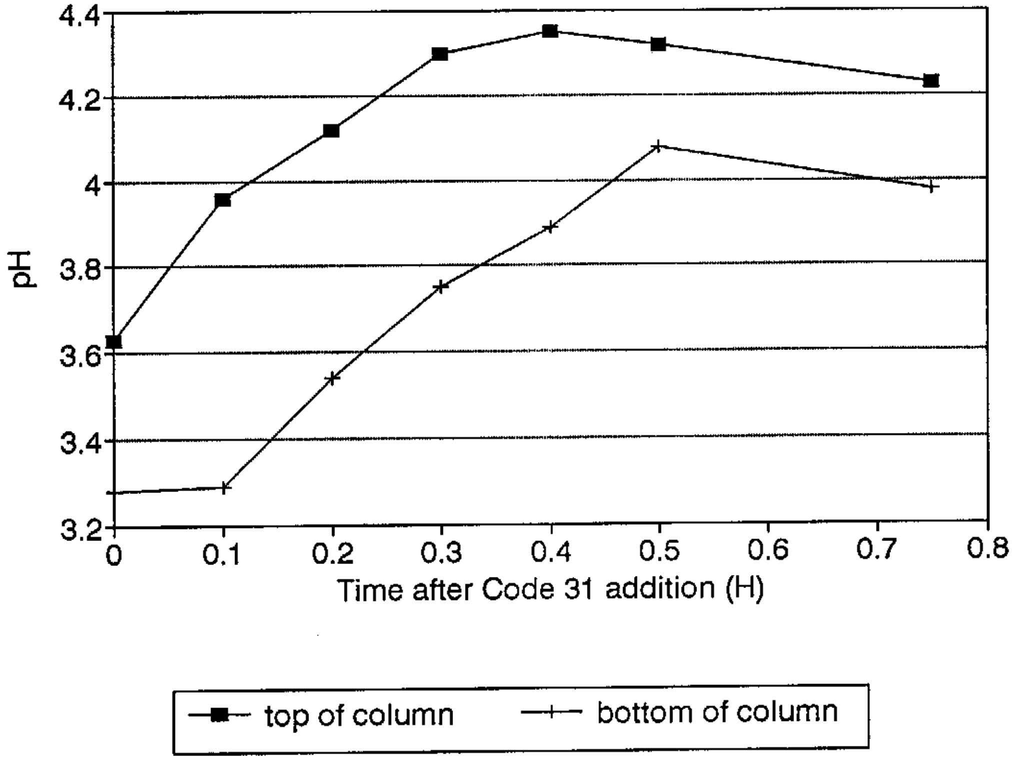



Fig. 6b:B8 water/sediment/code 31
Top and Bottom samples, 0-94 h

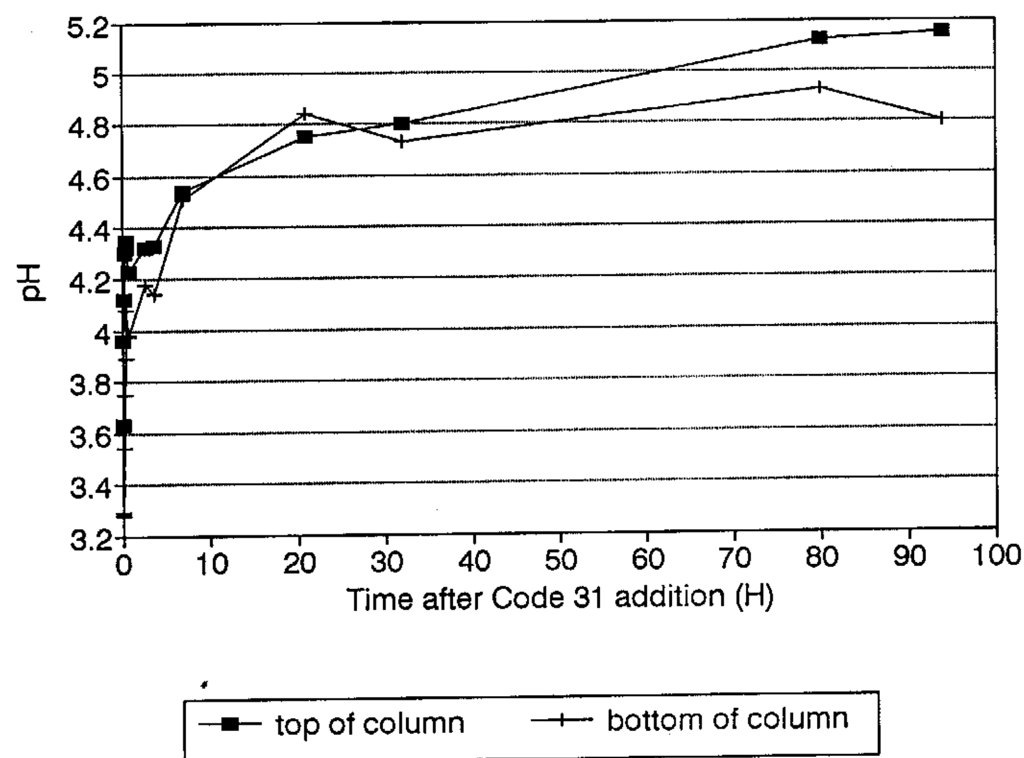
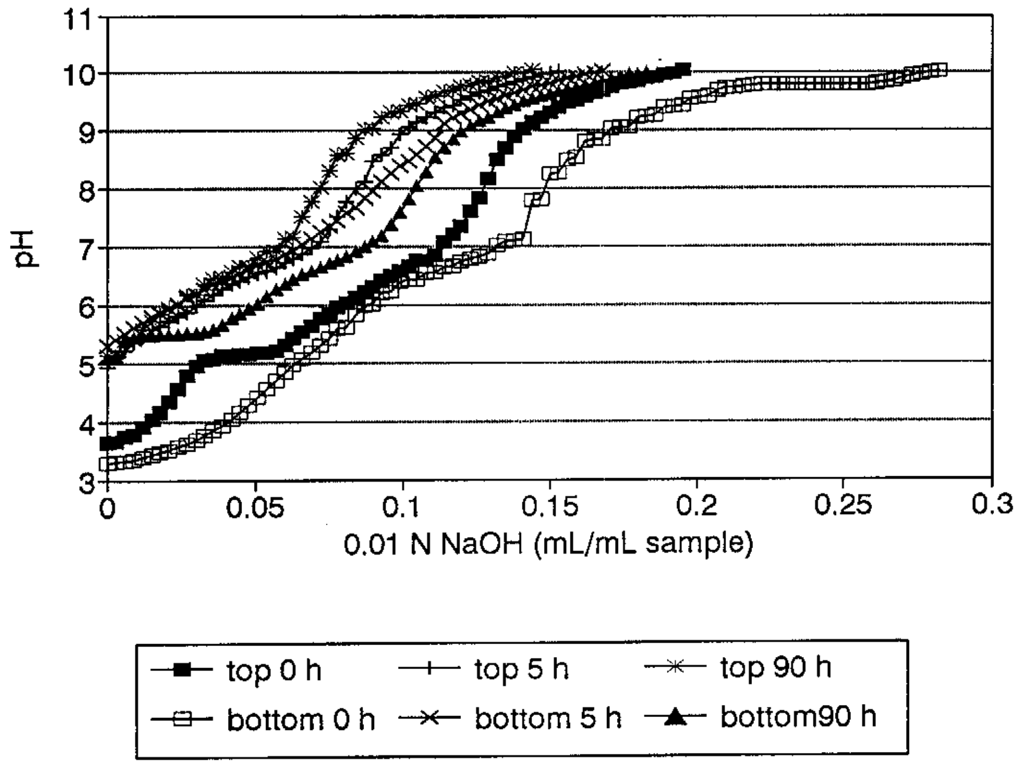


Fig. 7: Sediment column titrations
Top and Bottom samples



## Schematic 1: Column Experiment Set-up