Successful Use of Design of Experiment to Improve Treatment of Zn in a Pond System

Bernard Aubé[1] and Linda Byron-Fortin[2]

[1]EnvirAubé, 361 Aumais, Ste-Anne-de-Bellevue, Québec, Canada, H9X 4A9,
        aube@enviraube.com

[2]Blue Heron - Solutions for Environmental Management, 1300 Sandy Falls Road, Timmins,
        Ontario, P4N 7C3, lbyronfortin@blueheronenv.com

ABSTRACT

In spring 2003, the Kidd Mining Division of Falconbridge Limited experienced difficulties in reducing zinc concentrations to permissible discharge levels from their site runoff and mine dewatering systems. The neutral mine drainage from this site is treated with lime addition in an agitated chamber followed by an extensive pond system used for metal hydroxide precipitation and settling. Zinc is the primary metal of concern and is typically contained in concentrations of 10 to 50 mg/L. The problems experienced during the 2003 spring freshet were unexpected as the flowrates were low compared to previous years, when the treatment system performed satisfactorily. As soon as elevated Zn concentrations were measured throughout the treatment pond, emergency response procedures were initiated. Ferric sulphate was found to rectify the situation in the laboratory and was therefore added to the treatment system to improve Zn removal. The addition of ferric sulphate reduced the Zn concentrations to acceptable levels, but would be a costly means of ensuring proper treatment over the longer term. To investigate the cause of the elevated Zn concentrations, a review of historical data was conducted. The primary cause was determined to be due to low Zn concentrations in the waste water stream that, when pH was adjusted, caused the formation of very small individual hydroxide particles that do not settle quickly. This effect, coupled with the lower retention time of the ponds due to ice cover, hindered solid/liquid separation and resulted in higher Zn concentrations at the pond outlet. Various treatment alternatives were proposed to correct this situation, including ferric sulphate addition, treating at a very high pH, and sludge recirculation. A Design of Experiment (DOE) was used to evaluate the treatment alternatives for efficiency and cost. The DOE showed that all three options could work under certain conditions, but that treating with a high pH was prohibitively expensive, ferric sulphate was moderately expensive, and sludge recycling was the most promising option.

INTRODUCTION

Falconbridge Limited, Kidd Mining Division is a copper-zinc mine near Timmins in Northern Ontario, Canada. Mine production began in 1966 with an open pit and has since gone to underground development to exploit deeper parts of the ore body. Ore is transported by rail to the Kidd Metallurgical Division, 45 kilometres away. The site consists of a closed open pit, waste rock piles, mine shafts, roads, and surface buildings. The waste rock piles are gradually being removed and used as backfill in the mine.

A series of ditches and berms are used to collect all potentially affected water from the site and convey it by gravity to the treatment system. Unimpacted surface waters are diverted from the site to minimise the treatment volume. Underground mine water is combined with

the surface water drainage for treatment. There is very little control on the flowrate of the wastewater, as it is fed by gravity and is subject to precipitation and snowmelt. Flowrates can be as low as zero with freezing conditions in the winter (no runoff) and has reached a maximum of 272,400 m^3/day (189,167 L/min) during spring freshet of 2002.

The Pond Feed is identified as the "Inlet". The Inlet Zn concentrations are analytical results from samples taken just before the lime addition point. The Inlet water quality varies significantly due in part to the large variations in flowrate caused by snowmelt and precipitation. The average Inlet Zn concentration is approximately 26 mg/L and the average pH is 7.6. During spring, although the pH remains near neutral, the Inlet Zn concentrations are often below 10 mg/L. Copper and iron concentrations are normally below 5 mg/L and less than 1 mg/L in the spring. Other heavy metal contents are consistently lower than 1 mg/L.

An aerial photo of the treatment system is shown in Figure 1. The treatment system consists essentially of lime addition to a controlled pH followed by a series of ponds for settling of the newly formed metal hydroxide sludge. The lime silo and slaker are positioned near the edge of the waste rock piles. The lime slurry is then conveyed to the feed point of the treatment system where mechanical agitation is used to ensure proper dissolution of the lime. The pH is controlled using two pH probes to minimise the risk of upsets. A small primary settling pond (Primary Pond) collects some of the sludge immediately after neutralisation. Some polymer is added on a seasonal basis at the overflow of this pond, to aid in settling during periods of high flow.
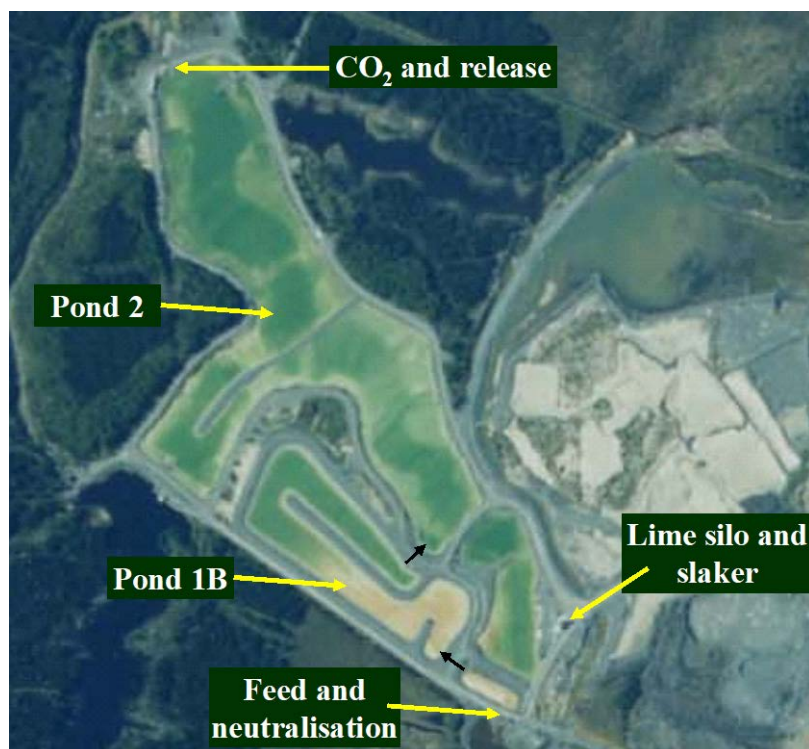

Figure 1: Aerial Photo of Kidd Mine Treatment System

Following the Primary Pond is Pond 1B. These two ponds are connected by a culvert through the berm (shown by a black arrow). In Figure 1, we can see that this pond is about half-full of sludge at the time the photo was taken. Another culvert connects Pond 1B to Pond 2, which

has an internal berm designed to prevent short-circuiting. At the overflow of Pond 2, carbon dioxide (CO_2) is added to bring the pH near neutral prior to final discharge. The pH and flowrate are monitored here and this is also where the regulated environmental samples are collected. Overall, the series of ponds has a retention time that can vary from less than one day at high spring flowrates to more than two months during dry summer or winter seasons.

Treatment Issue

For at least 3 years prior to spring 2003, the treatment system maintained compliance with regulatory limits. The primary challenge for treatment at Kidd Mine is a daily or grab sample limit of 1.0 mg/L Zn and a monthly average limit of 0.5 mg/L Zn. In spring 2003, although typical spring runoff flowrates were lower than historically experienced, traditional treatment methods utilized at the Kidd Mining Division were unsuccessful in reducing zinc concentrations to permissible levels. The final effluent exceeded the maximum zinc concentration limit of 1.0 mg/L. Immediate emergency response measures were initiated and Kidd Mine began an examination into the cause and possible solutions.

EnvirAubé was called on site to assess the situation, define the cause, and rectify the problems with treatment. Understanding that this was a settling problem and knowing that ferric sulphate was an excellent coagulant (Gregory and Duan, 2001), laboratory tests were initiated. These determined that ferric sulphate addition could help reduce the final Zn concentration. This was immediately applied in the treatment system and found to work very well. Within 24 hours, the outlet Zn concentrations were well within discharge guidelines.

Cause of Elevated Zinc Values

The first step in the project was to correct the situation, achieved by dosing approximately 25 mg/L of ferric iron (as ferric sulphate) in the ponds. Although the effectiveness of this action was immediate and excellent, to continue operating in this way would have been expensive. EnvirAubé was therefore asked to determine the cause of the high Zn concentrations and to develop a cost-effective means of treatment. Historical data was examined in detail to identify spikes in effluent Zn concentration and determine a common cause. Among the causes examined were organic complexation, pH control, flowrates, Inlet Zn concentrations, and ice conditions. Organic complexation was eliminated when the total organic carbon content was analysed and found to be too low to explain a concentration of up to 1 mg/L of Zn being untreated.

A number of particular points in the previous three years were examined closely. Although Kidd Mine had not previously exceeded their limits, there were other times where the Zn concentration exceeded 0.5 mg/L. These always occurred during the spring but not necessarily at the peak flowrate. One common thread was that the Inlet Zn concentration was unusually low during these events; usually less than 10 mg/L. The high discharge Zn values were also more likely to occur early in the spring, when there was still an ice cover over the pond.

Conversely, there were times when the Inlet Zn concentrations were less than 10 mg/L and the Zn was properly treated. After the detailed review of historical data, it was stipulated that the high Outlet Zn values are a result of the combined effects of low Inlet Zn concentrations, high flowrate, and ice cover conditions.

Previous operational experience has shown that low feed metal concentrations can cause the formation of colloidal hydroxide particles during lime neutralisation (Aubé and Arseneault, 2003). When low concentrations of dissolved Zn are brought to an alkaline pH, where the metal is insoluble, the result is the precipitation of small, isolated particles, which are too few to agglomerate and form larger grains. Flocculant addition, historically an effective additive to improve settling, is inefficient due to the small number of isolated particles. The colloidal particles uncollected by the flocculant are highly affected by water movement and do not settle easily. The particles of zinc (and other metals) can therefore travel through the treatment system thereby increasing discharge concentrations.

In the early stages of spring thaw, an ice cover remains over the pond. This cover can be as thick as 1 m during a typical Northern Ontario winter. Figure 2 illustrates this concept using a cross-section of the pond. This figure shows how the ice cover reduces the cross-sectional area of the pond. A smaller area will increase the velocity of the water for a given flowrate and decrease the retention time. A conceptual example of this effect is given in Table 1.
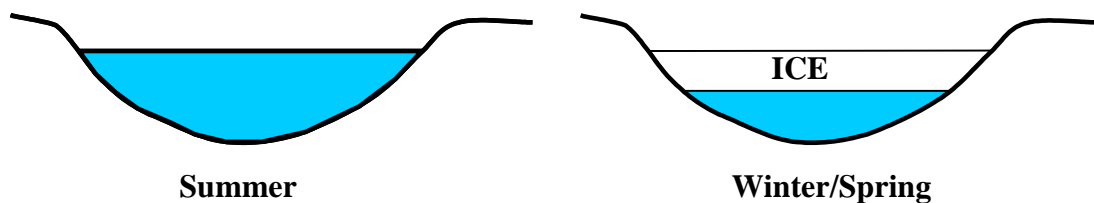

Summer   **Winter/Spring**
Figure 2: Conceptual Representation of an Ice Cover over a Settling Pond

Table 1: Conceptual Effect of an Ice Cover over a Settling Pond

Factor	Example Basis	Ice Cover Effect
Cross sectional area	1 m^2	0.5 m^2
Flowrate	1 m^3/s	1 m^3/s
Velocity	1 m/s	2 m/s
Retention time	1 day	0.5 day

<u>Combined Effects</u>
The combined effects of a low Inlet Zn concentration during spring thaw, the increased flowrate, and the ice cover result in small, difficult-to-settle solids which are subjected to a high velocity and low retention time. This was particularly true for 2003, as the treatment system had been shut down for two months (January and February) due to lack of waste water flow. This would have caused a thicker ice cover to form, therefore reducing the cross-sectional area of the pond more than previous years.

Treatment Options

It was already determined in the field that ferric sulphate addition could correct the situation and that flocculant addition (alone) was not effective. The problem was caused by the fact that the small particles produced could not settle in these difficult conditions. To avoid zinc exceedances and reduce long term zinc loadings to the receiver, the recommended strategy was to prevent formation of these minuscule particles. For this, more solids are required in the treatment system to help agglomerate and promote settling. Three options were put forth:

1)   Adding ferric sulphate (addition of iron hydroxide particles)
2)   Increasing the pH through traditional lime addition methods
3)   Recycling metal hydroxide sludge from the bottom of the treatment ponds

Each of these options adds solids/precipitates to agglomerate the dilute Zn hydroxides formed during neutralisation. Ferric sulphate creates ferric hydroxide precipitates which are known to help coagulate and settle other solids (Gregory and Duan, 2001). Increasing the pH over 12 with lime adds unreacted lime particles that will cause the same effect to occur. Recycling sludge to the front of the process may actually encourage the precipitation reactions to occur on the surface of existing solids. To determine which of these three options was most efficient for both cost and compliance, a design of experiment (DOE) was planned.

Test Methods

The DOE was to be completed using laboratory tests with 1 litre samples of simulated spring Inlet water. This "Raw Water" was formed by taking the actual Inlet water at the time of testing (summer 2003) and diluting it with clean fresh water taken from an adjacent stream. This Raw Water had a concentration of approximately 5 mg/L Zn, similar to the actual Inlet at the time the problems occurred. A large sample of this Raw Water was prepared in advance in order to ensure that the same conditions were used for all the DOE tests.

Sludge was collected from the bottom of Primary Pond to simulate sludge recycling in the field. A ferric sulphate solution was prepared with a slight dilution in order to ensure that precise dosages could be measured. The additives (ferric sulphate or sludge) were added in the amount required for the specific test. Sufficient lime was added to bring the 1-L volume to the desired pH. The resulting slurry was then mixed for 5 minutes and allowed to settle, covered. Samples were taken for analysis after 1 hour, 2 hours, and 24 hours. Sample collection was repeatedly done just below the surface of the 1-L of treated water, to ensure consistency.

DOE Design

The DOE was developed to optimise pH (through lime addition), ferric sulphate addition rate (ferric), and metal hydroxide sludge recycling (sludge). As the tests were relatively simple and rapid, a full-factorial design was chosen with the parameters and levels given in Table 2, resulting in a total of 48 tests. As per DOE standard procedure, the test sequence was randomised.

The pH values were chosen based on what is currently done at other treatment plants and what was known to work historically at Kidd Mine. A pH setpoint of 9.5 is typically sufficient for a high-density sludge plant to treat Zn (Aubé, 1999). The normal pH setpoint for Kidd was approximately 10.5. The pH value of 12.25 was added to comply with the theory above that additional solids are needed to help agglomerate and decant Zn hydroxides when the Inlet concentration is low.

Table 2: DOE Parameters

Variable	Number of Levels	Level 1	Level 2	Level 3	Level 4
pH	4	9.5	10.5	11.5	12.25
Ferric (mg/L)	4	0	5	15	25
Sludge (% vol)	3	0	5%	10%	

For ferric sulphate addition, the maximum value of 25 mg/L was based on what was done in the treatment system when the problem occurred. It was already known that this concentration was sufficient to treat the Zn efficiently. The intermediate concentrations were added to determine the minimum dosage required for proper treatment. For sludge, a volumetric ratio of 10% was used as this is near the maximum feasible flowrate that could be recycled. To accomplish this in the field, a permanent dredge would need to be installed in the Primary Pond. This would essentially simulate the Simple Recycle Process (Aubé, 2004) and produce a medium-density sludge.

DOE Results

With 48 tests and the use of a DOE software, many results were generated that cannot be presented here in full detail. The key results are the Zn-1hr and Zn-24hr samples. The 1-hr sample was used to determine if the Zn hydroxides were settling quickly, as this is critical to treatment in the spring. The 24-hr results simulate the final effluent as, although the pond system has a longer retention time (depending on the flowrate), the lab tests had totally quiescent conditions while the pond has a constant current. A successful test would have a total Zn content of less than 0.6 mg/L after 1 hour and less than 0.5 mg/L after 24 hours.

The DOE final Zn concentrations (Zn-24hr) as they relate to pH, sludge, and ferric are shown in. The overall average of all tests is shown as the dotted line at 0.46 mg/L.
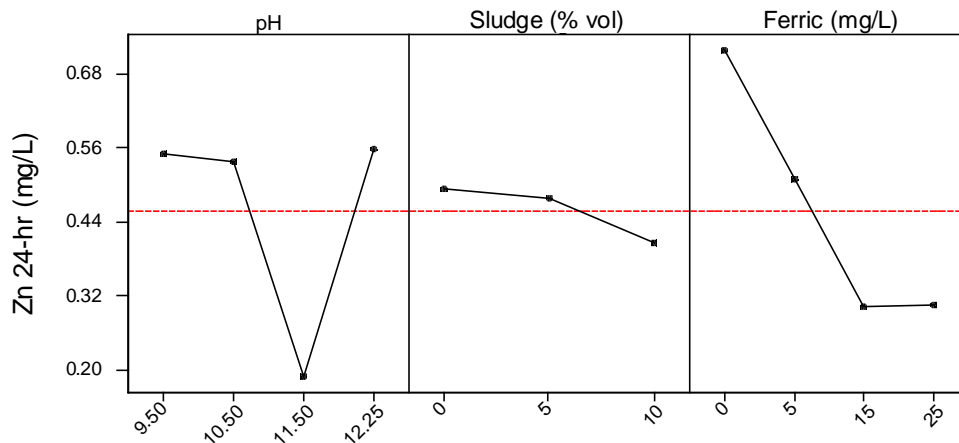

Figure 3: Main Effects for the Zn-24hr Sample

In the first section of Figure 3 (pH), each data point represents an average of all tests completed with that specific pH setpoint. As there were 48 tests and 4 pH setpoints, each data point is an average of 12 measured concentrations, representing the combination of 3 sludge addition setpoints and 4 ferric addition rates.

This plot shows clearly that the best results were obtained at pH 11.5. As will be shown by the interaction plots, this is due to the fact that tests completed at pH 11.5 were not greatly affected by sludge or ferric addition and resulted in good final results with and without additives. The other pH values had good results only in specific conditions. The center section suggests that the sludge addition had only a slight effect on the average result. The third section shows that ferric addition was clearly helpful up to 15 mg/L. Above that dosage, it appears that the added Fe does not significantly help.

The Main Effects Plots are simply the average of many data points and do not sufficiently explain what is happening when there are interactions between the variables. The most important interaction measured in this test is shown in Figure 4. This figure shows the Sludge-pH Interaction Plot for the Zn-24hr Sample. In this graph, each point represents the average of 4 tests; the four different ferric addition rates. The y-axis is the Zn concentration, the sludge addition rate is the x-axis and the lines represent the different pH setpoints, as per the legend. This Interaction Plot shows significant and opposite responses in sludge addition rate depending on pH.
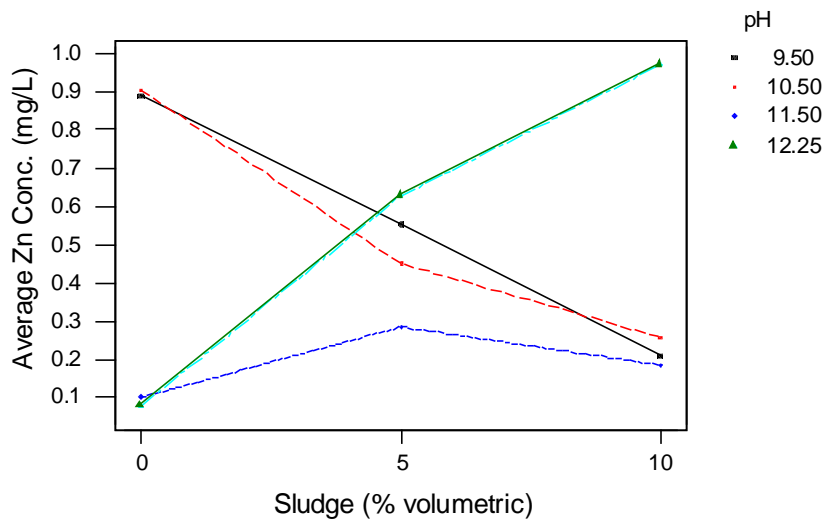
Figure 4: Sludge-pH Interaction for Zn-24hr

Figure 4 specifically shows that at pH's of 9.5 or 10.5, sludge addition improves the final Zn concentration significantly. In fact, sludge addition brings a non-compliant sample well into compliance (0.5 mg/L). The opposite is true for the pH setpoint of 12.25: adding sludge takes it from compliance to non-compliance. The 11.5 pH setpoint appears not to be affected by sludge addition. These opposing responses, depending on whether the pH is low or high, explain why the setpoint of 11.5 is the only one that (on average) meets the target of 0.5 mg/L at all sludge addition rates in the pH main effects plot (Figure 3).

Figure 5 shows a Sludge-Ferric Interaction plot created using all data but the tests run at pH 12.25. Those tests were removed from this plot due to the negative interaction described in the previous paragraph. Each data point in Figure 5 therefore represents the average of 3 tests instead of 4. The plot shows that the Zn average is highest when neither additive is used. It also shows that there is generally an improvement when using both together.
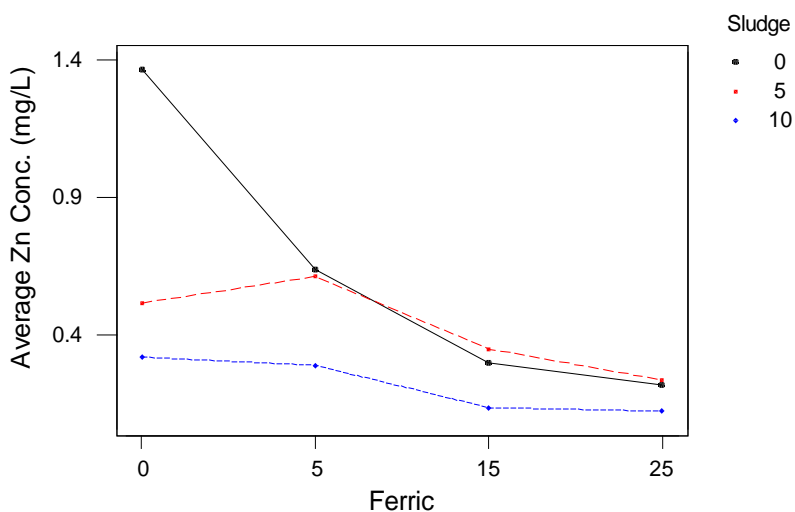
Figure 5: Sludge-Ferric Interaction Without pH 12.25 (Zn-24hr)

The primary criterion used to classify successful tests was a final Zn concentration of 0.5 mg/L or less. The secondary criterion was the Zn-1hr results, which indicate settling. It was

not expected that the 0.5 mg/L mark be attained after 1 hour, but a value of 0.6 mg/L would indicate that the hydroxides are settling at a sufficient rate. This is critical as the very high flowrates in spring, and in particular under ice cover, hinder settling due to strong currents. The successful tests are summarised here in order of pH.

<u>pH 9.5:</u>
For this pH setpoint, all of the tests with 10% sludge addition met the criteria for success while all tests without sludge or with only 5% addition did not. When 10% sludge was added, the actual resulting pH was of at least 10 even though the setpoint was 9.5. This is due to the high unreacted lime content of the sludge as no lime was added. To properly reproduce this treatment scenario in full scale, the pH setpoint should therefore be 10, as the sludge alone will not increase the pH sustainably. Since ferric addition appears to help, but is not necessary, the group including all pH setpoints of 9.5 can be represented by the simplest form: pH 10, 10% sludge, no ferric. As such, only this test scenario will be retained for further comparison.

<u>pH 10.5:</u>
For the pH 10.5 group, it is possible to either have 5% sludge and 25 mg/L ferric, or merely 10% sludge without ferric addition. Both these scenarios will be retained.

<u>pH 11.5:</u>
To meet the criteria at the 11.5 pH setpoint, a ferric addition rate of 15 mg/L without sludge, or a 10% sludge addition with 5 mg/L ferric are needed. Both these scenarios are retained.

<u>pH 12.25:</u>
The 12.25 pH setpoint easily meets all the criteria without addition of ferric or sludge. Ferric addition does not upset treatment, but is not necessary, while sludge addition was highly detrimental to treatment efficiency. For pH 12.25, the test without additives will be retained for cost comparison.

Statistical Significance

An analysis of variance was completed on the results for all of the variables as well as for the different samples. The results were excellent for ferric, which was always statistically significant with P-values of less than 0.05 (Whitley and Ball, 2002). The pH and Sludge were only statistically significant when the pH 12.25 tests were removed from the analysis. All three variables had a P-value of 0.032 or less without the pH 12.25 tests. This indicates that the test results are valid and that the laboratory experiments were successfully completed.

Treatment Costs

A comparison of expected treatment costs were made for each of the successful results. For each of the inputs to the plant, specific unit costs were assigned. These were then weighted, depending on the measured, set, or estimated consumption of the specific input. For example, lime addition was measured during the test. The lime costs can therefore be calculated using a specific dosage for each test. Sludge dredging costs were increased for added solids (such as

high pH and ferric addition) and decreased for recycling sludge as this will use some undissolved lime and increase sludge density. Carbon dioxide costs are affected only by the pH setpoint. Ferric sulphate costs are in direct proportion to the ferric dosage. Recycling sludge was estimated to represent the cost of renting an automated dredge and operating it in the Primary Pond. A relative cost of each of the retained options is displayed in Table 3.

Table 3: Relative Cost of Retained Options

pH	Sludge (%)	Ferric (mg/L)	Relative Cost ($/m^3)/($/m^3)
10.0	10	0	0.68
10.5	5	25	4.01
10.5	10	0	0.78
11.5	0	15	3.31
11.5	10	5	2.54
12.25	0	0	9.05
Average Actual Costs (01-02)			1.00

Table 3 shows the average treatment costs from 2001 and 2002 as 1.0 and all the estimated costs of retained tests relative to these. The results show that adding sludge would actually result in reduced costs compared to current practices. This is because unreacted lime is used, less sludge is created, and the pH setpoint can be relatively low. Each of these effects respectively saves costs on lime consumption, sludge dredging, and carbon dioxide consumption.

The table also shows that ferric sulphate would increase costs significantly and that treating to a pH of 12.25 would increase costs almost 10 times. Ferric addition costs are affected mostly by the consumption of this reagent. The cost of treating to a high pH is significant due not only to the enormous lime consumption but also the need to add much more carbon dioxide at the discharge. Adding excess lime also creates more sludge therefore increasing dredging costs as well.

Implications

The tests described here were developed to determine the best means of treating the Kidd Mine site runoff during spring freshet. The primary cause of the problems observed at this time was the low Inlet Zn concentration. This issue had been increasing in importance every year due in part to the progressive rehabilitation of the site. By removing the waste rock stored on surface, the Inlet Zn concentrations progressively decreased. It is likely that Kidd Mine will one day produce a runoff with consistently less than 10 mg/L of Zn which would be very difficult to treat without additives. This issue could therefore be a constant for all seasons during a transition period of many years.

This in part explains the critical importance of this project to Kidd Mine. In recent history, it was just the spring freshet that posed particular concerns for the treatment system. With constantly low Inlet Zn concentrations, a cost effective means of treatment is required. While adding ferric sulphate is a viable alternative to properly treat during short, sporadic campaigns, it would be cost prohibitive if required year round. This makes the option of recycling sludge from the Primary Pond worthy of further investigation.

Conclusion

The results from the design of experiment clearly show that recycling sludge from the Primary Pond would not only control the zinc concentration at the effluent, but would also

result in significant cost savings. Unfortunately, it was not possible to put these results into full-scale operation for spring 2004 due to resource constraints. A ferric sulphate addition system was therefore recommended and installed prior to the spring 2004 freshet and remains in use as required. It was also recommended that the sludge recycle be attempted in the field to validate the results issued from this project.

References

Aubé, B. 2004. "The Science of Treating Acid Mine Drainage and Smelter Effluents". Electronic PDF document available at: http://www.enviraube.com/english/tech-docs.html

Aubé, B., and Arseneault, B. 2003. "In-Pit Mine Drainage Treatment System in a Northern Climate" Presented at <u>Sudbury 2003 Mining and the Environment III</u>, May 25-28 2003.

Aubé, B. 1999. "Innovative Modification to High Density Sludge Process". <u>Proceedings for Sudbury '99, Mining and the Environment II</u>. September 13-17, Sudbury, Ontario, Canada, pp. 1103-1111.

Gregory, John, and Duan, Jinming, 2001. "Hydrolyzing metal salts as coagulants". <u>*Pure and Applied Chemistry*</u>, Vol. 73, No. 12, pp. 2017–2026, 2001

Whitley, E. and Ball, J.2002. "Statistics review 4: Sample size calculations" Published On-line at <u>Critical Care</u>, available at: http://ccforum.com/content/6/4/335