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THE GECO PROCESS: A NEW HIGH DENSITY SLUDGE TREATMENT FOR ACID MINE DRAINAGE

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Abstract: A new acid mine drainage (AMD) treatment process is currently operating at Noranda Mining and Exploration, Geco Division. This is a two-step neutralisation process, in which recycled sludge is contacted directly with AMD in the first reactor, and a lime slurry is added in the second reactor, where aeration is also provided. This is different from the conventional High Density Sludge (HDS) Process in that there is no lime/sludge mix. The pH in the first reactor increases from 3.3 to about 8, thus precipitating the Zn and Fe in solution prior to contact with lime and elevation of the pH to 9.2. Analytical results have shown that CaCO₃ is created by dissolution of CO₂ from aeration and Ca from lime addition in the second reactor. The calcite formed in the process and recycled to the first reactor is responsible for the AMD neutralisation in this first step. Some Mn and Mg are also precipitated in the second reactor and re-dissolved in the first reactor after recycling. Results have shown that a higher density (>35% solids), low viscosity sludge can be produced. Microscopic analysis has shown that the solids formed in this process are individual, apparently spherical particles, as opposed to the amorphous agglomeration resulting from other treatment processes.

Key Words: Acid mine drainage, treatment, lime neutralisation, precipitation, high density sludge

INTRODUCTION

Acid mine drainage (AMD) is typically characterised by a pH of 2.5 to 5, with high concentrations of heavy metals such as Fe (10-2000 mg/L), Zn (2-1000 mg/L), Cu (0-100 mg/L), Pb (0-50 mg/L) and Al (0-200 mg/L), usually associated to $SO_4^{2^-}$. Treatment of this water (Figure 1) is traditionally done by raising the pH of the water to a value ranging from 8.5 to 9.5 to precipitate the metals and then separating the precipitates from the treated water prior to release. A variety of alkaline materials



Figure 1. Block Diagram of Typical AMD Treatment.

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can be used for increasing pH, but the most common are hydrated lime $(Ca(OH)_2)$ and quicklime (CaO), due to their relatively low cost. Limestone $(CaCO_3)$ can sometimes be used for pre-treatment, but the kinetics of calcium carbonate dissolution at the desired final pH are too slow for efficient use in a treatment plant. Sodium hydroxide (NaOH) can be used when hardness of the plant effluent is a concern.

In AMD containing iron in ferrous form (Fe²⁺), aeration of the slurry is usually done in the final neutralisation reactor in order to oxidize the ferrous iron to ferric iron (Fe³⁺). Iron oxidation is important because ferric oxy-hydroxides are considerably more stable than ferrous hydroxides in the resulting sludges (MacDonald et al, 1989).

In most treatment facilities, a clarifier is used for solid-liquid separation. The clarifier produces an effluent ready for discharge into the environment and a sludge which is to be disposed of or stored. Polymers are used for flocculation as the fine metal hydroxides settle slowly unless the particles are agglomerated. Use of a clarifier also offers the option of recycling some of the sludge and promoting precipitation of the fresh metals onto the surface of the recycled solids. This recirculation of solids in a specific way and with a defined recycle to feed ratio is known to help promote densification of the sludge (Kostenbader and Haines, 1970 and Kuit, 1980).

An AMD treatment plant without recycle will produce a sludge of <1 to 5% solids (MacDonald et al, 1989) which, over years of operation, can result in high sludge disposal costs, particularly for mines which are no longer operating. In operating mines where treatment is necessary, co-deposition of sludge with tailings is often practiced and sludge density is not considered to be a concern.

NTC Pilot Plant

A pilot plant was designed to treat 1 L/min of AMD while reproducing any of a large variety of treatment processes. This plant has been used to simulate processes at many Noranda sites, and was brought to Geco Division on two separate occasions: the first was a preliminary comparison of high density processes (Kuyucak et al, 1993), and the second pilot plant campaign was initiated in order to optimize the existing process (Payant and Aubé, 1996). Although reference is made to the first set of tests, the focus of this paper is set primarily on results of the second pilot plant campaign and operation in the full scale.

For the pilot plant, all tanks and flows of specific treatment processes were simulated with representative retention times in interchangeable reactors. Air was sparged at 1 SCFM in the neutralisation reactor, lime was added to control pH at the same setpoint as that of the treatment plant, and a flocculant was added for clarification of the final effluent. A two-meter high clarifier, with a low rise velocity of 0.62 m/h, was used for solid/liquid separation. A rake mechanism similar to those of full-scale clarifiers pushed the settled sludge towards the centre cone. Sludge recycling was done according to process design.

The pH and flowrates throughout the treatment system were measured continuously and recorded at two hour intervals. Samples of feed, reactor slurries, sludge and effluent were taken twice daily for analysis. Whenever the clarifier sludge was bled, a sample was weighed and dried for determination of solid content and viscosity tests were performed regularly. The solids production of the influent was tested once to three times daily. This was done by neutralising and aerating 500 mL of feed, then filtering the slurry and determining the total solids produced by drying. The solids production was then used to determine the recycle ratio (defined as the amount of solids recycled over the amount of solids produced by the incoming feed).

High Density Sludge Process

The High Density Sludge Process (HDS) is presented for comparison, as it is currently considered the state of the art in AMD treatment (Kuit, 1980). Typically, sludges from 10 to 25% solids are formed with this process (Figure 2). The AMD is generally fed into a Rapid Mix Tank (RMT), where it is contacted with a lime/sludge slurry to bring the pH of the combined slurry to 9 or 9.5. The RMT (shown in dashed lines) was not included in the original design, but was often used to offer better pH control in the process. Retention time of this tank varies normally from 2 to 10 minutes.

The Lime Reactor (LR) has a retention time typically ranging from 30 to 90 minutes. Air is sparged in the LR for ferrous oxidation.

The Floc Tank is used to contact the polymer to the precipitates for floc formation. Trials at Noranda treatment plants have shown no difference of effluent or sludge quality when polymer was added after the Floc Tank only. This suggests that the Flot Tank is unnecessary and that is baffled launder (trough) with flocculant additions at a minimum of two points could adequately replace it.



A portion of the sludge from the clarifier underflow is recycled to the lime/sludge mix tank. The sludge recycle rate is controlled by the feed rate and a pre-determined ratio of solids recycled to solids formed. This ratio is typically between 10:1 to 30:1, or 10 to 30 kg of solids recycled for each kg of solids formed in the process. This means that at least 90% of the solids in the LR are from recycled sludge. The lime addition is controlled to keep pH at the desired setpoint.

Geco Process

The Geco Process is comprised of two main reactors and a clarifier (Figure 3). In this process, the AMD is fed to the first reactor (R#1), where it is contacted to recycled sludge, only. The pH in R#1 is not controlled as the recycle rate is set either to produce a specific recycle to feed solids ratio (similar to that of the HDS Process) or to control the suspended solids content in the process



Figure 3. The Geco Process.

reactors. In the preliminary tests presented here, the recycle rate was controlled to a volumetric recycle to feed ratio. Lime addition is done in the RMT. The RMT is again used for improved pH control, and is not an essential part of the treatment system. The final neutralisation step is effected in Reactor #2 (R#2) where aeration is supplied for ferrous oxidation. The Floc Tank is also a non-essential part of the system as polymer addition in the launder feeding the clarifier is sufficient.

GECO PILOT PLANT CAMPAIGN

Introduction

Noranda Mining and Exploration, Geco Division ended operations in November, 1995. The mine had operated for nearly 40 years recovering Cu and Zn minerals from a sulphide ore body. The Geco Waste Water Treatment Plant (WWTP) was commissioned in April 1995, seven months prior to mine closure. It replaced a conventional low-density treatment plant which had been operating for about 20 years. The present WWTP design was based on a feed flowrate of 2000 USGPM (7570 L/min). After treatment, the clarifier overflow is released to the environment and the sludge is to be stored underground, in the abandoned mine workings.

At the Geco WWTP, both the RMT and Floc Tank (Figure 3) are included. Table I shows the summary of the Geco WWTP design. The large pH range in R#1 is due to two different operating modes: at low recycle, the pH was maintained near 4.5 to 5, and at high recycle, the pH was between 7.5 and 8.5.

| Vessel | Approximate Retention Time (min) | Flows into the Tank | pH | |
|----------------|-------------------------------------|------------------------------|-----------|--|
| Reactor #1 30 | | AMD, Recycled Sludge | 4.5 - 8.5 | |
| Rapid Mix Tank | 3 | Lime Slurry, Overflow of R#1 | 9.2 - 9.7 | |
| Reactor #2 | 40 | Air, Overflow of RMT | 9.2 | |
| Floc Tank | 3 | Flocculant, Overflow of R#2 | 9.2 | |

Table I. Geco Waste Water Treatment Plant Design.

In the early start-up of the treatment plant, attempts were made to bring the sludge density up to the design 20% solids by incrementally increasing the recycle rate. The resulting sludge became very viscous at solid contents as low as 10%. Samples of sludge with 7.5 to 9% solids registered viscosities of 26000 to 34000 cP. The centrifugal pumps designed to convey the sludge to R#1 or to the sludge storage tank could not drive such a viscous fluid. The sludge had to be watered down in order to be pumped, therefore defeating the purpose of producing a high density sludge.

A pilot program was undertaken to help optimize the treatment process, while attempting to minimize the necessary changes to the WWTP. A series of tests were planned, aimed at efficiently treating AMD while producing a high density, low viscosity sludge. The low viscosity of the sludge is important as the abandoned mine shaft which will be used for discharging sludge is over 2 km away and at a higher elevation.

Pilot Testing

The pilot plant was initially set up to reproduce the current operations of the WWTP. The same series of four tanks were installed and an AMD feed of 1 L/min was pumped from the feed-line to the actual WWTP. The typical raw water chemistry is shown in Table II.

| | pН | Fe | Zn | Al | Mn | Cu | SO₄ | Solid Production | |
|-----------|-----|--------|--------|--------|--------|--------|--------|---------------------|--|
| | - | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (g/L) | |
| Raw Water | 3.3 | 300 | 40 | 15 | 5 | 2 | 2500 | 0.5 | |
| Effluent | 9.2 | 0.5 | 0.05 | 0.5 | 0.1 | 0.05 | 2500 | | |

Table II. Typical Water Chemistry at the Geco WWTP.

Three key processes are presented in Table III, where the test conditions are compared to those of the WWTP. For the WWTP, the recycle rate shown in the table represents the operating conditions prior to the pilot program. As previously mentioned, in these early stages sludge recycling was controlled as a volumetric ratio of the feed rate, with a 12% recycle representing 120 mL/min at the pilot plant feed rate of 1000 mL/min.

| | Sludge recycle (volumetric ratio, %) | pH in R#1 | Flocculant used |
|--------|---|-----------|-----------------|
| WWTP | 2 | 4.5-5.5 | Percol E10 |
| Test 1 | 3 | 5.7-6.3 | Percol E10 |
| Test 2 | 12 | 7.8-8.5 | Percol E10 |
| Test 3 | 12 | 7.9-8.3 | Percol 727 |

Table III. Pilot Plant Tests.

The recycle in the WWTP was also controlled to a specified volumetric ratio of the feed, equal to about 2%. At this ratio, a clean effluent was produced and the sludge was maintained at a density of about 5 to 7% solids. It was at ratios of 3 to 4% that the sludge formed in the WWTP became too viscous to pump. For Test 1, the pilot plant recycle was set at 30 mL/min for a volumetric ratio of 3%. Figure 4 shows the change in solid content of the sludge with time.

As shown in this figure, the sludge density increased steadily for the first four days, but then decreased suddenly. This was caused by high viscosity sludge turning with the rakes in the clarifier. As the sludge was not raked toward the cone, recycling caused a hole to form in the centre and low density sludge was therefore collected and recycled. This is know as a "donut" formation and can occur on the full scale as well as the pilot scale. When this happens in a full-size clarifier, the viscous sludge must be pumped out entirely. In the pilot scale, it was possible to break up the donut by accelerating and reversing the rakes. After breaking up the donut and continuing the recycle, the process continued to form a viscous sludge. The test was terminated when the peristaltic pumps could no longer convey the sludge to the first reactor due to the high viscosity. The maximum density

achieved with this process was 14.8% solids. These results agreed well with those of the full scale WWTP.

Test 2 was run with a volumetric recycle ratio of 12% and no other change from the base case (Test 1). As there seemed to be a risk of forming a sludge of very high viscosity, which could be difficult to remove from a full size clarifier, this had not been attempted in the WWTP. The change in density with time (Test 2, Figure 4) shows that the solid content of the sludge increased until it surpassed 35%. At this density, the sludge was still easily pumpable and fluid; viscosities of 400 to 700 cP were measured at solid contents of 34 to 38%. By increasing the recycle ratio from the start, the sludge formed had a completely





different consistency. This test was continued past the time displayed in Figure 4 to stabilize at a solid content of 37 to 39%, with a maximum measured at 39.2% solids. The maximum sludge density previously achieved with this pilot plant with any process was below 25%.

Test 3 was a repetition of Test 2 with a different flocculant. Percol E10 had been used for the initial tests as it was the polymer used in the WWTP. In an attempt to improve the effluent quality, bench tests were carried out to try different flocculants. These tests showed that a better effluent clarity could be obtained with Percol 727, thus this product was piloted. The viscosity of the sludge was the same with Percol 727, but the steady state density, although excellent (>25%), was lower than that achieved with Percol E10.

Other Tests

Two other processes not shown in Figure 4 were tested, both at a 12% sludge recycle. The first test was essentially the same as the Geco Process, only R#1 was replaced by the RMT. The AMD/sludge contact time was therefore 5 minutes as opposed to 30 minutes. Lime was added directly to R#2. The results from this test were similar to those of Test 1 in that the sludge was very viscous and donuts were formed. These results suggest that a long residence time in R#1 is necessary for the Geco Process to create a pumpable sludge.

The other process consisted in recycling only enough sludge to R#1 to bring the pH in this reactor to 5.0, mixing the remaining recycled sludge with lime and adding the lime/sludge mix to R#2. This process also resulted in a viscous sludge too thick to pump at a sludge density below 15% solids.

The HDS Process had also been piloted at Geco, but this was done in 1993 (Kuyucak, 1993) with a considerably more acidic raw water quality. The ratios of ferrous to ferric and Zn to iron were essentially the same, but the concentrations were higher by a factor of about three. In this case, the maximum density achieved with the HDS Process was about 16%. Viscosities were not measured but, as the test was aborted when the sludge could no longer be pumped, the viscosity must have been well above 1000 cP. The Geco Process was not developed at that time and was therefore not tested with the same water quality.

Sludge Chemistry

To explain the differences in the sludges created with a high or low recycle ratio, chemical analyses were done on the sludges. The major components of the sludges are presented in Table IV. The carbonate determination was done at a separate laboratory and not on Test 1. For heavy metals, no significant differences between the analytical results are evident. The higher Fe content and lower Zn for the WWTP is probably due to variations in the feed Zn/Fe ratios during formation of the sludge. The SO₄ content is significantly higher for the WWTP sludge. This may be explained by the longer residence time (over twice as long) of the effluent water in the clarifier since gypsum precipitation is relatively slow as Ca and SO_4 approach their equilibrium concentrations. The effluent from both the WWTP and the pilot tests showed a saturation index averaging near +4 for gypsum, when activities are included in the thermodynamic equilibrium calculations (Drever, 1988). A longer residence time in the clarifier will allow more gypsum to be formed and increase both the Ca and SO, concentrations in the sludge. But, although the gypsum content is higher in the WWTP, the Ca content is higher in Test 2. This may be related to carbonate formation and calcite $(CaCO_3)$ precipitation as explained in the Process Chemistry section (at a lower pH in R#1 carbon dioxide may evolve, whereas at high pH it will remain in solution). It should also be mentioned that some sulphate in the sludge may be the result of adsorption with oxy-hydroxides; this is difficult to establish with a mostly amorphous sludge. X-Ray Diffraction was done on all these samples and found only traces of calcite and no other crystalline formation at concentrations above detection limit.

| | Solids | Al | Ca | Cu | Fe | Mg | Mn | SO4 | Zn | CO ₃ |
|--------|--------|------|------|------|------|------|------|------|------|-----------------|
| | % | % | % | % | % | % | % | % | % | % |
| WWTP | 8.8 | 1.39 | 3.11 | 0.19 | 31.1 | 2.95 | 0.69 | 7.09 | 4.39 | 2.15 |
| Test 1 | 16.0 | 1.47 | 2.39 | 0.22 | 29.8 | 1.88 | 0.69 | 4.98 | 4.97 | |
| Test 2 | 38.6 | 1.82 | 3.78 | 0.27 | 27.2 | 1.95 | 0.61 | 3.65 | 5.20 | 4.95 |

Table IV. Chemical Analysis of the Sludges.

Sludge Microscopic Analysis

As the analytical results offered very little explanation for the differences in the sludge viscosities, air-dried samples of sludge were submitted to a scanning electron microscope (SEM). Photo 1 shows the sludge from Test 1 at a magnification of 3000. At this magnification, no individual particles could be isolated and the solids seem to be a simple agglomeration of amorphous precipitates. Photo 2 shows a sample of sludge from Test 2 taken at the same scale. Here, a number of apparently spherical nodules of 1 to 3 μ m are shown. This difference in the physical aspects of the precipitates may explain the difference in viscosity of the two sludges.

The formation of nodules in Test 2 must be caused by precipitates from R#1 forming onto the surface of the recycled solids. The dissolving carbonates and/or hydroxides bring the pH high enough for most heavy metals to precipitate and the pH-increasing reactions (dissolution) may be occurring simultaneously with the precipitation reactions. The recycled sludge therefore acts as seeding points for the formation of metal hydroxides. The possibility of the metals precipitating and co-precipitating in the first reactor has been confirmed by the analysis of the filtered slurry from R#1, as 99% of the Fe, Zn, and Al were no longer in solution. In Test 1, the pH in R#1 was too low for the removal of



Photo 1. SEM Photo of Sludge from Test 1 at 3000X Magnification.



Photo 2. SEM Photo of Sludge from Test 2 at 3000X Magnification.

any ferrous or Zn from solution and their precipitation was therefore occurring entirely in R#2 where extremely fine amorphous precipitates were formed.

Process Chemistry

From chemical analysis of the raw water, filtered slurries, and the sludge and slurry solids, a set of reactions are suggested as the controlling mechanisms for the Geco Process. The average concentrations used to perform the mass balance and define these equations were taken from 150 hours (~6 days) into Test 2 until the end of the test at 475 hours (~20 days). This time frame was chosen to obtain results that were representative of the steady state conditions, while assuring that enough data was available for statistically meaningful averages. At 150 hours, the sludge density was about 25% solids and it increased to 35% solids after 100 more hours (Figure 4). The sludge density was then maintained between 35 and 39.2% for the remainder of the test (9.5 more days).

The following series of equations were surmised from the analytical results, known reactions, and thermodynamic data. As the solids formed in the process are essentially amorphous, actual proof of the chemical composition of the precipitates is difficult to obtain. Thermodynamic data and Eh-pH diagrams were helpful in determining the possible combinations of reactions but do not take kinetics into account. These reactions are therefore the best idea to date of the mechanisms involved in the formation of high density sludge within the Geco Process. Reactions expected in the two different reactors are separated and explained individually.

In R#1:

$$CaCO_3 \Rightarrow Ca^{2+} + CO_3^{-2} \qquad (1)$$

Reaction (1) is supported by an increase in dissolved Ca concentration in R#1 of 236 mg Ca per L of feed. Calcite dissolution is considered to be the major reaction responsible for the increase in alkalinity in the first reactor. If any unreacted lime remained in the sludge, it would also have dissolved in R#1.

$$CO_3^{2-} + H^+ \Rightarrow HCO_3^{--} (2)$$

At a pH between 8 and 8.5, nearly 98% of the dissolved inorganic carbon will be in HCO_3^{-1} form (2). The carbonate from calcite therefore reacted with hydrogen ions to form bicarbonate, unless it precipitated with another cation. This reaction was partly responsible for the increase in pH from 3.3 in the raw water to 8 or 8.5 in R#1.

The inorganic carbon equilibrium at different pH values can help explain why the sludge from Test 2 contained higher concentrations of calcite. When the process was running at a low recycle ratio, as was the case in the WWTP prior to pilot testing and during Test 1, the pH in the first reactor was often below 5. At a pH of 5 in R#1, over 95% of the carbonate was in the $CO_{2(aq)}$ form and could evolve from the slurry as carbon dioxide gas. During Test 2, when the pH in R#1 was above 8, the inorganic carbon, being mostly in the bicarbonate form, remained in solution and did not evolve. There was therefore a higher concentration of inorganic carbon fed into R#2 during Test 2 than there was from Test 1 or the WWTP. As the pH was increased to 9.2 in R#2, the higher concentration of carbon in Test 2 would favour calcite formation with the Ca from lime (see equations (11), (12) and (13)). This explains why the sludge from Test 2, at high recycle and high pH in R#1, contained considerably more calcite than the WWTP sludge.

$$Mg(OH)_2 \Rightarrow Mg^{2+} + 2OH^{-}$$
 (3)

Approximately 40 mg/L of Mg were dissolved in R#1. Reaction (3) is considered to contribute up to a third of the total alkalinity imparted to the raw water in R#1. Although it is possible that some Mg in the sludge had precipitated as carbonates, Eh-pH diagrams (Brookins, 1988) suggest that the hydroxide would be dominant at the process water conditions.

There is also a small amount of Mn (<2 mg/L) dissolving in R#1 but it is not known if the Mn in the sludge is in the form of a carbonate, an oxide or hydroxide. Eh-pH diagrams for Mn suggest that all these species could exist, depending primarily on the redox potential of the water and redox in the reactors was not measured during the pilot campaign. It is also important to consider that these diagrams represent the expected species found at equilibrium and the retention times of the process do not allow for complete equilibrium to occur.

$$Fe^{2+} + CO_3^{2-} \Rightarrow FeCO_3$$
 (4)
 $Fe^{2+} + 2OH^- \Rightarrow Fe(OH)_2$ (5)

Ferrous iron may be precipitating with the CO_3^- from calcite. Reactions (1) and (4) may be combined to result in direct transformation of calcite to ferrous carbonate. The Fe in the raw water at Geco was essentially all in the ferrous form. During Test 2, the raw water Fe content averaged 312 mg/L and 10% of this iron was oxidized to ferric in R#1. In R#2, at least 80% was in the ferric form. Equilibrium Eh-pH diagrams suggest that, in the presence of carbonate, FeCO₃ is the dominant precipitate at low redox in the pH range of 6.8 to 9.4 (Brookins, 1988). The total dissolved Fe in R#1 at steady state was typically between 0.4 and 2.5 mg/L.

$$Fe^{3+} + 3OH^{-} \Rightarrow Fe(OH)_{3}$$
 (6)

The ferric iron in R#1 likely precipitated as an oxy-hydroxide, shown in reaction (6) as a hydroxide for simplicity. As the precipitates were amorphous, mineralogical analysis was inconclusive. It is possible that some of the ferric precipitates formed FeOOH, but this could not be confirmed. As previously mentioned, the ferric fraction of the total iron in R#1 represented approximately 10% of the Fe supplied from the raw water.

$$Zn^{2+} + 2OH^{-} \Rightarrow Zn(OH)_2$$
 (7)

Some Zn in R#1 could have been co-precipitating with Fe or precipitating as carbonates, but at pH 8 to 8.5, the Zn hydroxide is dominant. Approximately 15 mg/L of Al and 2 to 3 mg/L of Cu also precipitated to <1 mg/L in R#1.

In R#2:

The lime consumption of the Geco Process is equivalent to that of the conventional process or the HDS Process. This is expected, as the alkalinity needed to raise the pH and precipitate the metals for a specific raw water quality is constant. Given that the final products are treated water and hydroxide sludge for all processes, the alkalinity (or quantity of lime) needed for treatment remains the same for all processes. For the Geco Process, this means that the amount of lime used to bring the R#1

overflow (with a pH of 8.5 and low concentrations of dissolved metals) to pH 9.2 in R#2 is equivalent to the lime needed to bring an equivalent volume of raw water from pH 3.3 and 300 mg/L Fe to pH 9.2. The following equations may help elucidate this concept a little further.

$$FeCO_{3} + 5/2H_{2}O + 1/4O_{2} \Rightarrow Fe(OH)_{3} + CO_{3}^{-2} + 2H^{+}$$
(8)

$$Fe(OH)_{2} + 1/2H_{2}O + 1/4O_{2} \Rightarrow Fe(OH)_{3}$$
(9)

$$Fe(OH)_{2} + H_{2}O \Rightarrow Fe(OH)_{3} + H^{+} + e^{-}$$
(9A)

$$1/4O_{2} + H^{+} + e^{-} \Rightarrow 1/2H_{2}O$$
(9B)

In R#2, reactions (8) and/or (9) are certain to occur as aeration increases redox and oxidizes the ferrous iron to ferric. The transformation of ferrous carbonates to ferric hydroxides is an acidic reaction, whereas oxidation of ferrous hydroxides to ferric hydroxides via (9) is not. The hydrolysis reaction in (9) may be considered acidic, but the reduction of oxygen is basic, as shown in reactions (9A) and (9B). This is indication of ferrous precipitation in R#1 being as carbonates as this reaction would consume much of the added lime in R#2. Adsorbed or co-precipitated ferrous which could oxidize and react to completion in R#2 would also consume some lime.

$$CO_{2}(g) + H_{2}O \Rightarrow HCO_{3}- + H^{+}$$
(10)
$$HCO_{3}^{-} \Rightarrow CO_{3}^{2} + H^{+}$$
(11)

Aeration also adds CO_2 to the system. The dissolution of carbon dioxide at high pH is an acidic reaction. At pH 9.2, the dissolved carbon balance results in approximately 93% as HCO_3^- , 7% as CO_3^{2-} and <1% as $CO_2(aq)$ or H_2CO_3 . Note that reaction (11) can proceed both ways as CO_3^{2-} dissolved from reaction (8) could be partially converted to HCO_3^- . But due to carbon dioxide dissolution and calcite precipitation (equation (13)), the reaction is believed to move towards the right.

 $Ca(OH)_2 \Rightarrow Ca^{2+} + 2OH^-$ (12)

3.

The dissociation of lime not only increases pH, but also adds a considerable amount of Ca to the system. The average lime consumption for Test 2 was 0.67 g/L of raw water. This corresponds to an increase of 362 mg Ca/L of feed.

$$Ca^{2+} + CO_3^{-2} \rightarrow CaCO_3$$
 (13)

The balance of Ca added to R#2 from lime dissolution, minus the actual increase in concentration and the estimated amount precipitated with SO_4 , results in a deficiency of over 200 mg/L which seems to have precipitated as calcite. If reactions (11) and (13) are combined, the formation of calcite from bicarbonate can be considered as an acidic reaction. Reactions (8) and (12) can be combined to complete the cycle of ferrous carbonate to calcium carbonate, via the formation of ferric hydroxide.

$$Mg^{2+} + 2OH^{-} \Rightarrow Mg(OH)_2$$
 (14)

The Mg concentration in R#2 was 40 mg/L lower than that in R#1. Other reactions include the precipitation of 6 to 12 mg/L of Mn, conversion of any Zn carbonates to Zn hydroxides, and some

 $CaSO_4$ •2H₂O precipitation. The Ca, Mg, and Mn which are precipitating in R#2 and re-dissolving in R#1 eventually reach a steady-state where the input to the system is equivalent to the loss in the sludge bled from the plant. In the case of carbonate, the input is equivalent to the $CO_{2(aq)}$ fed to the system from the water and from aeration.

Scale-up Results

Following the successful trial in the pilot scale, a high recycle rate was attempted in the full-scale WWTP to simulate Test 2. Sludge density quickly increased beyond the desired 20%, but the clarifier overflow did not consistently meet the required 1 mg/L Fe limit. The suspended solids (SS) in the overflow were analyzed and found to contain approximately 30% Fe. Although the required limit in SS for the Geco effluent is 15 mg/L, it cannot contain more than 3 mg/L in order to meet the 1 mg/L limit for total Fe concentration. The Geco clarifier was originally designed for the low density treatment plant which was built over 20 years ago. Although modifications were made to the clarifier in order to handle the heavier sludge, it may not be large enough to handle slurries with up to 3% solids when the overflow must consistently contain less than 3 mg/L SS.

Further tests with the pilot plant showed that, although a polishing pond would do little to improve effluent quality, sand filtration could assure that the required limits are consistently met. Sand filtration will also eliminate effects of small process upsets which could increase the suspended solids content of the clarifier overflow. A sand filtration system has been installed at Geco and was commissioned in the spring of 1997. At the time this paper was written, the sludge was consistently controlled above 20% solids with samples up to 29% solids after less than two weeks of operation in high density mode. Measured viscosities were in the 100 cP range at solid contents near 20%. Total iron concentrations in the clarifier overflow were sometimes above the 1 mg/L limit, but the sand filtration effluent met discharge limits consistently. The recycle control strategy and operating guidelines now need to be optimised for steady and reliable treatment of the Geco AMD.

CONCLUSIONS

The Geco Process, a new acid mine drainage treatment method, can produce low viscosity sludges with densities higher than 35% solids. Pilot testing defined the need for high recycling rates for the sludge/AMD contact in the first reactor. At Noranda Mining and Exploration, Geco Division, this process outperformed every other process tested and is implemented in the full scale. Full scale treatment has thus far consistently produced a low-viscosity sludge above 20% solids with samples of up to 29% solids.

Further tests at Geco and other sites will help to better understand the process chemistry and determine the dependence of the process performance on raw water quality.

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