Mine Wastewater Treatment Using Novel Processes

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ABSTRACT

Water used in industrial processes acquires contaminants derived from the materials and processes the water comes in contact with. In the case of mining applications, these contaminants often make the water undesirable for reuse within the mine circuit or for discharge from the site. Treatment of mine process water to make it acceptable for reuse or discharge requires methods that are resistant to a wide variety of potentially corrosive or scaling species, capable of handling a range of contaminants and function for long periods under relatively harsh conditions with minimal maintenance. This paper will discuss evaluations of mine water treatment systems that utilize several robust methods to treat mine wastewater. Concentration of wastewater contaminants using reverse osmosis followed by contaminant removal by precipitation will be discussed. The paper will focus on maximizing cost performance, lowering energy use, limiting the use of chemicals and minimizing the impact of the system on the environment.

INTRODUCTION

Growing demands on finite and variable water supplies across the world have resulted in greater government scrutiny and pressure on industry to more efficiently manage water resources. The mining industry has long been perceived as a problem area for water management due to the relatively high volumes of water used in mining applications and the wide range of contaminants that appear in wastewater derived from mining operations (Bowell 2000; Amezaga et al. 2011). As a result, managing wastewater from mining operations is often very challenging. Treatment is typically necessary to make the water suitable for reuse within the operation and is normally a requirement to meet increasingly strict discharge limits if the water is to be released back to the environment. Mine wastewater often has many contaminants exceeding use or discharge limits so treatment is accomplished by creating a purification circuit made up of multiple systems targeted to a site-specific contaminants. Identification of treatment methods that complement one another is the key to successful mine water treatment.

One of the most common mine water contaminants is sulfate ion. This ion is often the dominant contaminant in a mine operations wastewater (Bowell 2000). High sulfate water is associated with several industrial mining and mineral processing operations. One of the most common of these is Acid Mine Drainage (AMD), also known as Acid Rock Drainage (ARD), where decomposition by oxidation of pyritic solid material waste associated with mine operations yields surface water with sulfate concentrations in the 1500 to 8000 ppm sulfate range. It is worthwhile to note that AMD water also typically contains numerous other contaminants such as iron, manganese and other heavy metals. Neutral wastewaters typically contain sulfate concentrations of around 4000 ppm (Miller 2005). Since sulfate discharge limits are in the range of 250 to 2000 ppm this water must be treated before release into the environment. Much research has been directed towards sulfate removal in AMD applications due to the associated large water volumes and widespread occurrence.

Over the last 20 years several treatment schemes have emerged that are aimed at reducing the concentration of sulfate in mine wastewater to levels approaching discharge requirements. In a chemical precipitation example described by Geldenhuys an inexpensive source of metal ion is used to precipitate metal sulfate salt (Geldenhuys et al. 2003). In this method, acidic high sulfate (AMD) water is treated with limestone and then subsequently with lime. Inexpensive limestone reacts with the low pH feedstock in the first step to remove a portion of the calcium sulfate as $CaSO_4 * 2H_2O$ precipitate (Reaction 1). Subsequent treatment with lime to pH 12.26 removes additional calcium sulfate as $CaSO_4 * 2H_2O$ (Reaction 2).

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 {*}2H_2O + CO_2 \qquad (1)$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 {*}2H_2O \qquad (2)$$

This method is capable, with sufficient residence time, of producing an 1100 ppm sulfate water stream from a 3000 ppm sulfate feedstock. Though relatively inexpensive, this method requires a low pH feedstock for the limestone treatment portion to be effective and does not produce an effluent that will meet typical sulfate discharge requirements.

Other precipitation methods utilize barium sulfide as a barium source for barium sulfate precipitation (Maree et al. 2004) or include a source of aluminum with slaked lime to allow precipitation of ettringite or jarosite (Tait et al. 2009; Smit and Sibliski 2003). These methods, however, are dependent on regeneration of the barium ion source from the collected precipitate or require a heat source to achieve the desired precipitation efficiency.

Another example of a treatment utilized for high sulfate mine water is reverse osmosis. In this process feedstock is pretreated with scale inhibitors and filtered through a multimedia filter or an ultrafilter to limit membrane scaling as the liquid is passed across a reverse osmosis membrane under high pressure. Water migrates across the membrane, excluding most dissolved ions, producing a low sulfate permeate than can be discharged, reused or blended with other wastewater streams to meet discharge requirements (Sobana and Panda 2011). Recoveries of 60 to 70% of a 100 ppm sulfate permeate from a 5000 ppm sulfate solution may be regarded as typical. The reject stream from such an operation would contain roughly 12,300 to 16,400 ppm sulfate in 30 to 40% of the feedstock stream volume. Although this technique produces an effluent that meets typical discharge limits, reverse osmosis is more costly than chemical precipitation techniques and produces a substantial volume of highly concentrated sulfate reject water that cannot be discharged without additional treatment.

In this paper we present laboratory and pilot test results for a treatment that utilizes reverse osmosis and chemical precipitation to provide an effective means of treating high sulfate mine water for reuse or discharge. It will be demonstrated that by applying reverse osmosis to a sulfate containing mine wastewater a high sulfate reject stream is generated that is well suited for treatment with slaked lime to precipitate $CaSO_4 * 2H_2O$. Neutralization of the product water from a one hour residence time precipitation stage with carbon dioxide followed by blending with low sulfate RO permeate yielded a solution with a sulfate concentration below 1000 ppm. Results of field testing at a mine site desiring a cost-effective, robust and rapid means of meeting sulfate discharge requirements demonstrated the effectiveness of the process for meeting the locations discharge limits.

Calcium Sulfate Di-hydrate Precipitation

Calcium sulfate occurs in three forms but for most water treatment applications $CaSO_4 * 2H_2O$ (gypsum) is the predominant phase. Gypsum is a naturally occurring ionic crystalline solid that forms in many industrial processes where calcium and sulfate are present in concentrations exceeding saturation limits. Industrially, gypsum is a byproduct of the dihydrate process of phosphoric acid production, deposits on heat exchangers in cooling systems due to gypsums inverse solubility relationship with temperature and fouls reverse osmosis systems when the solubility of gypsum is exceeded near the membrane surface. As a result of its widespread occurrence, the precipitation of gypsum has been extensively studied both academically and industrially.

Gypsum precipitation occurs by a series of processes whose relative importance is dependent on the presence of inhibitors, relative supersaturation and on seed crystal surface area (Packter 1974; Gunn 1976). One process associated with gypsum precipitation is the formation of crystal nuclei from supersaturated calcium sulfate solution. In this process, prenucleation aggregates of calcium ions and sulfate ions form within the supersaturated solution. While many disassociate, some of these aggregates achieve the necessary size and structure to make dissolution energetically unfavorable and become crystal nuclei. The rate of nuclei formation is a function of the supersaturation, with several authors reporting the initial precipitation rate is proportional to the square of the relative supersaturation (low supersaturation or seeded) (Klepetsanis and Koutsoukos 1989) or to the relative supersaturation raised to the fifth power (high supersaturation unseeded) (Hamdona and Hadad 2008). In practice a period of time, known as the induction period, occurs in unseeded supersaturated calcium sulfate solutions before detectable precipitation is observed. During this induction period the concentration of nuclei grows over time until a detectable level of precipitation is reached. At high supersaturations, where homogeneous nucleation dominates (Alimi et al. 2003), the induction time is proportional to the inverse of the square of the supersaturation (Fan et al. 2010). A second process associated with the precipitation of gypsum is the growth of the existing gypsum crystals. In this process ordered growth of existing gypsum particles takes place by incorporation of calcium and sulfate ions into growth sites on the crystal surface. The rate of ordered growth is dependent on the gypsum surface area and on the supersaturation. It is worthwhile to note that when sufficient crystal surface is present no gypsum precipitation induction period is observed. Gypsum crystal growth rates are consistent with a surface controlled crystal growth mechanism (Klepetsanis et al. 1999).

Although both nucleation and crystal growth take place simultaneously within a supersaturated solution one process is often the dominant means of gypsum formation. For example, in unseeded solutions nucleation is dominant initially but becomes less important as the number of nuclei reaches a level where the gypsum surface is sufficient to allow ordered crystal growth to dominate. In seeded systems, such as continuous crystallizers, relatively few nuclei may be formed and most precipitation occurs through crystal growth. To achieve relatively rapid and predictable precipitation of crystals of a size readily removed in a continuous precipitation system it is beneficial to recirculate a portion of the precipitate back to the reaction chamber to act as seed. Use of crystallization product as seed for gypsum precipitation, rather than using synthetic gypsum seed, has no adverse impact on the rate of precipitate formation (Tait et al. 2009).

Gypsum Precipitation Using Slaked Lime

When slaked lime is used as a calcium source for gypsum precipitation the concentration of calcium present at any given time is dependent on the concentration of hydroxide ion (solution pH). As gypsum precipitation progresses the dissolved calcium that is consumed is partially replenished by dissolution of slaked lime to yield calcium ions and hydroxide ions. Calcium is removed from solution as a result of gypsum precipitation while hydroxide ion is not. As a result the concentration of hydroxide builds as dissolved sulfate is removed. Eventually the pH of the solution reaches a level that prevents sufficient calcium from dissolving and exceeding the gypsum Ksp. In practice as this limit is approached the rate of gypsum precipitation experiences a sharp decrease. The use of slaked lime to precipitate gypsum is further complicated by the tendency for gypsum to precipitate on slaked lime particles and block further dissolution of calcium derived from the slaked lime. This necessitates the use of excess slaked lime to ensure sufficient soluble calcium to exceed gypsum solubility. In addition, the solubility of gypsum increases above a pH of about 11.5, reaches a maximum at a pH of about 12.7 and then decreases at higher pH values. For example, at 35°C and pH 12.7 the solubility of gypsum is about 50% greater than at pH 7.0 (Yuan et al. 2010). This increase solubility may be due to the formation of $CaOH^+$. Thus, the overall rate of gypsum precipitation using slaked lime is a function of pH and the quantity of slaked lime present.

EXPERIMENTAL METHODS

Reagent grade chemicals were used in all laboratory testing unless otherwise noted. Concentrated reagent hydrochloric acid used in laboratory tests and concentrated industrial hydrochloric acid used in field tests were each analyzed by titration prior to use to determine acid concentration. The laboratory concentrated hydrochloric acid was 37.1% by weight and the concentrated hydrochloric acid used at the mine site was 27% by weight. Laboratory test solutions were prepared using deionized water. The 10% slurry of slaked lime used in laboratory testing was prepared using deionized water and was maintained as a uniform suspension with constant stirring using a magnetic stirrer. Solution pH was measured using an Orion Model SA720 pH meter calibrated at 25°C using pH 7.0 and 10.0 calibration standards supplied by VWR International. Immediate sulfate analyses of laboratory samples and of field samples were performed using a barium sulfate turbidity based test with aid of a Hach Model DR2400 spectrophotometer. Reverse osmosis 85% recovery concentrate was obtained using a pilot RO system operated at a mine site. Calcium analyses were performed using a Perkin Elmer Analyst 200 atomic absorbance spectrometer. Chloride concentrations were determined using a Dionex Model DX600 Ion Chromatograph.

Laboratory Gypsum Precipitation Tests

Laboratory batch studies were performed to characterize the amount of gypsum precipitate formed at varying lime and hydrochloric acid dose levels in 1 liter beakers at ambient temperature. Solutions were filtered using a 0.45 micron filter after a 1 hour residence time and the sulfate level immediately analyzed. In a typical experiment, 500 mL of RO concentrate was placed in a 1 liter beaker and stirred with a PTFE-coated magnetic stirrer. Concentrated hydrochloric acid was then injected below the surface of the solution using a syringe and then 10% slaked lime slurry was added. After 1 hour the pH of the solution was measured and the solution filtered under vacuum using a 0.45 micron filter. The sulfate content of the solution was then immediately measured and recorded. A portion of the filtered solution was then diluted and analyzed to determine the concentrations of chloride and calcium.

Analogous experiments were performed to characterize the kinetics of gypsum precipitation. These experiments were performed in a manner similar to the precipitation experiments described above with the exception that portions of the stirred test slurry were removed at desired time intervals using a 60 mL syringe. These slurry samples were then filtered using 0.45 micron syringe filters and immediately analyzed for sulfate.

Carbon Dioxide Neutralization Test

A laboratory batch carbon dioxide neutralization experiment was performed to characterize the neutralization of the slaked lime treated RO concentrate. In a 5 liter beaker a 3 liter sample of RO concentrate containing 16,500 ppm sulfate was treated with concentrated hydrochloric acid at a dose of 46.4 pounds per 1000 gallons followed by addition of 10% slaked lime slurry at a dose level of 105.3 pounds slaked lime per 1000 gallons and then stirred with a PTFE coated magnetic stirrer for 1 hour. The suspension was then filtered using a 0.45 micron filter and the filtrate placed in a 5 liter beaker. A portion of the filtrate was analyzed to determine sulfate concentration. Carbon dioxide was added to the solution at a rate of 357 milliliters per minute using a gas dispersion tube and the solution pH monitored using a pH electrode. Samples were collected at intervals of approximately 0.5 pH units using 60 mL syringes and the samples were filtered using 0.45 micron syringe filters. The filtered samples were analyzed to determine the concentrations calcium and sulfate.

Onsite Pilot Studies

A pilot study was performed over the course of 2 months at a mine site in Latin America. A skid mounted RO system with cross-wound membranes was used to treat the mine wastewater. A sand filter and 10 micron cartridge filters were operated before the membranes to protect them from soil and suspended particulate material. Sulfuric acid was added to the feed water before the membranes to adjust the pH to 7. A calcium sulfate specific RO scale inhibitor, Nalco PC504T, was fed into the feed water at 2.5 ppm in order to protect against gypsum scale formation on the membranes. Flow rate of feed water to the membranes was maintained at about 340 gallons per hour throughout the study and recovery averaged a consistent 80% with a peak of 85%. Membrane cleaning was performed approximately every 70 hours.

Concentrated hydrochloric acid containing 27% hydrochloric acid by weight was fed to the concentrate from the RO unit at a level of 60.6 pounds per 1000 gallons concentrate and the resulting solution was delivered to a precipitation vessel. This dose is roughly equivalent to a dose rate of 43.6 pounds laboratory concentrated hydrochloric acid per 1000 gallons concentrate. Slaked lime was fed to the precipitation vessel at a level of 227 pounds slaked lime per 1000 gallons concentrate. Residence time of the liquid in the precipitation vessel was one hour. The supernatant from the precipitation vessel was then treated with carbon dioxide to pH 8.1.

RESULTS AND DISCUSSION

Water Quality

The RO concentrate used for laboratory studies was obtained from a mine site in Latin America. The composition of the RO concentrate and diluted RO concentrate samples, as well as the range of composition of the RO feed water, are shown in Table 1.

High sulfate mine waste water falls within a range of concentration from 1500 to 8500 ppm sulfate. As seen in the table, the mine water RO feedstock used in this study was consistently within the typical range of high sulfate mine water. The RO concentrate collected for laboratory gypsum precipitation studies was representative the upper limit of expected sulfate concentration. Similarly, diluted RO concentrate samples prepared were representative of the middle and lower expected sulfate concentrations of the RO concentrate.

Table 1. Water composition samples used for laboratory testing

Measurement	RO Feed Water Range	RO Concentrate	Diluted Concentrate 1	Diluted Concentrate 2
pH	8.5 to 9.3	8.3	8.3	8.3
Sulfate	2320 to 3300	16500	13750	12500
Chloride	20 to 25	96	81	70

Laboratory Gypsum Precipitation Kinetics Tests

An investigation of the kinetics of gypsum precipitation in an RO concentrate sample containing 13750 ppm sulfate in the presence of slaked lime and hydrochloric acid indicates that sulfate precipitation is rapid over the first 40 to 60 minutes and proceeds very slowly thereafter as shown in Figure 1. As seen in the figure, a total of about 9750 ppm sulfate precipitates as calcium sulfate under the conditions of the test. This calcium sulfate precipitation is greater than 95% complete within 30 minutes and is 97% complete within about an hour. After about two hours the precipitation is 100% complete. No further change in sulfate level occurred after 12 hours. Under the conditions tested, a gypsum precipitation treatment system based on slaked lime addition can operate with 97% gypsum removal efficiency at a residence time of one hour.

Laboratory Gypsum Precipitation Tests

A series of gypsum precipitation tests were performed using RO concentrate generated at the Latin American mine site and diluted concentrate prepared to simulate the range of concentrate composition expected at the site described above. At this site the sulfate ion discharge limit is 1000 ppm and the chloride ion discharge limit is 500 ppm. The pH of the effluent must be no less than 6.0 and no greater than 9.0. For an average 80% recovery, this means that for the effluent to meet discharge limits the treated concentrate must contain no more than about 5000 ppm sulfate and no more than about 2500 ppm chloride prior to blending with RO permeate. Slaked lime alone fed at 82.8 pounds per 1000 gallons can only bring the sulfate concentration down to about 7500 ppm from a high of about 16,500 ppm. This does not meet the discharge limits of the mine site and is considerably higher than the 1100 ppm reported by Geldenhuys. In this case the solution pH reached a level of 12.59, preventing dissolution of sufficient slaked lime derived calcium to exceed the gypsum solubility.

Hydrochloric Acid Addition

One means of improving sulfate removal using slaked lime is to add an acid to partially neutralize the excess hydroxide formed during gypsum precipitation. A series of 1 hour residence time laboratory experiments were performed wherein hydrochloric acid was added to the RO concentrate prior to slaked lime slurry feed. The addition of acid was expected to increase the concentration of dissolved calcium derived from slaked lime and thus increase the quantity of gypsum precipitate formed. The results of experiments performed with three potential RO concentrate compositions at a constant concentrated hydrochloric acid feed rate of 46.4 pounds per 1000 gallons are summarized in Figure 2. As seen in the figure, at an initial sulfate concentration of 12,500 ppm the treated sulfate level is less than 4500 ppm over the range of slaked lime feed levels tested. At 13,750 ppm sulfate, the expected average sulfate concentration in

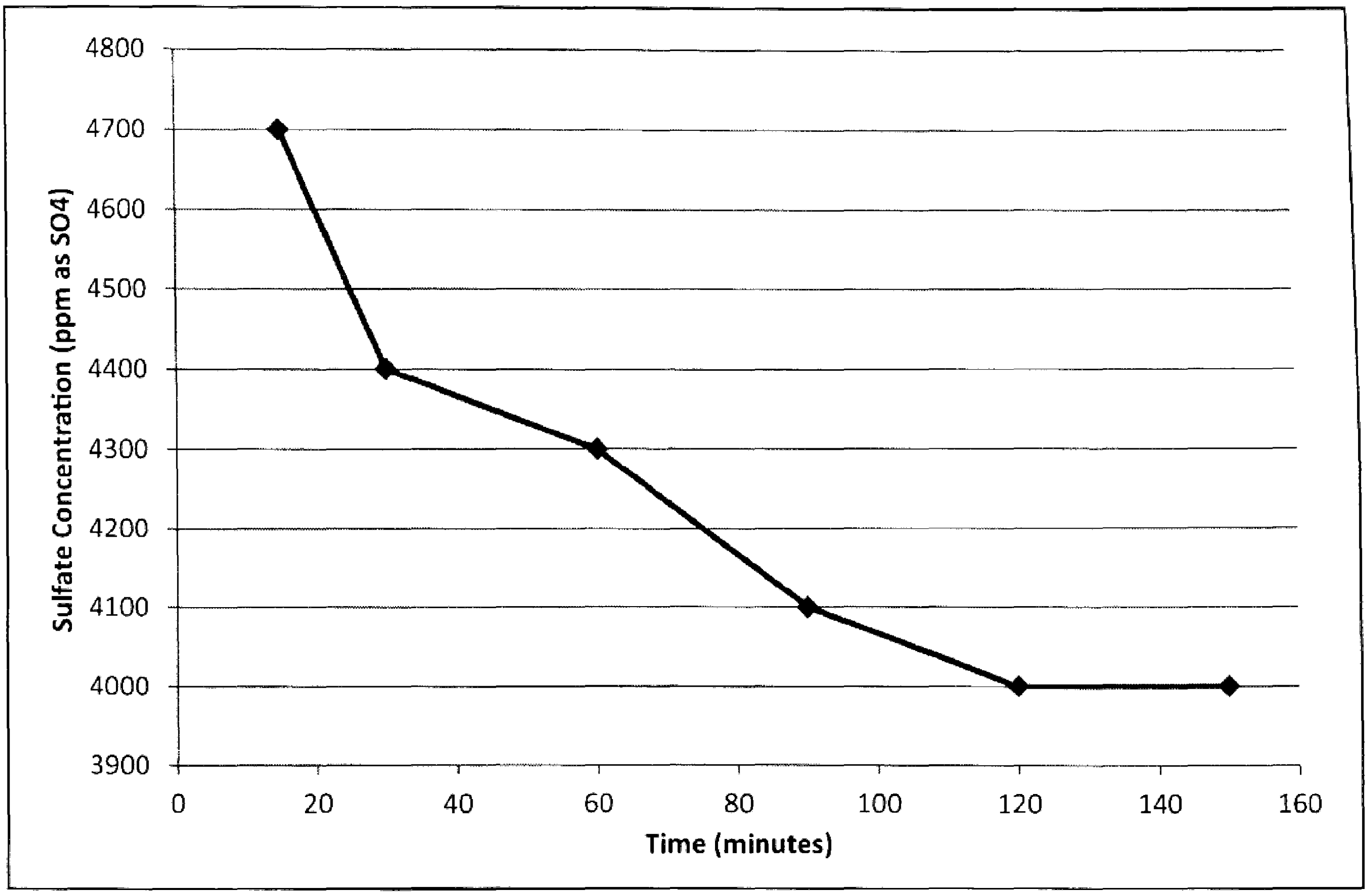

Figure 1. Gypsum precipitation kinetics at 13750 ppm total sulfate with HCl and slaked lime treatment

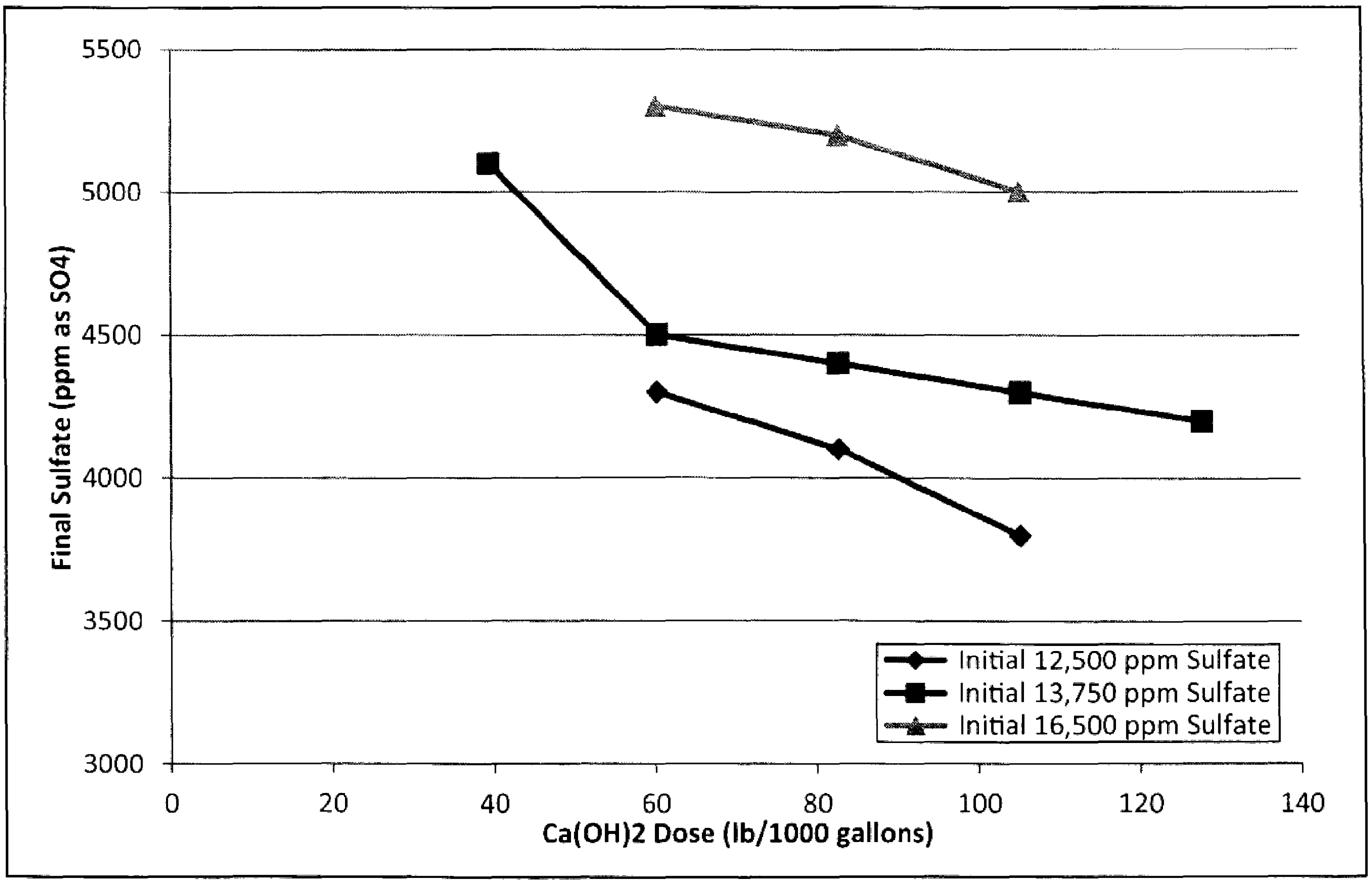

Figure 2. Sulfate removal achieved with a treatment of 46.4 pounds per 1000 gallons HCl at varying slaked lime dose

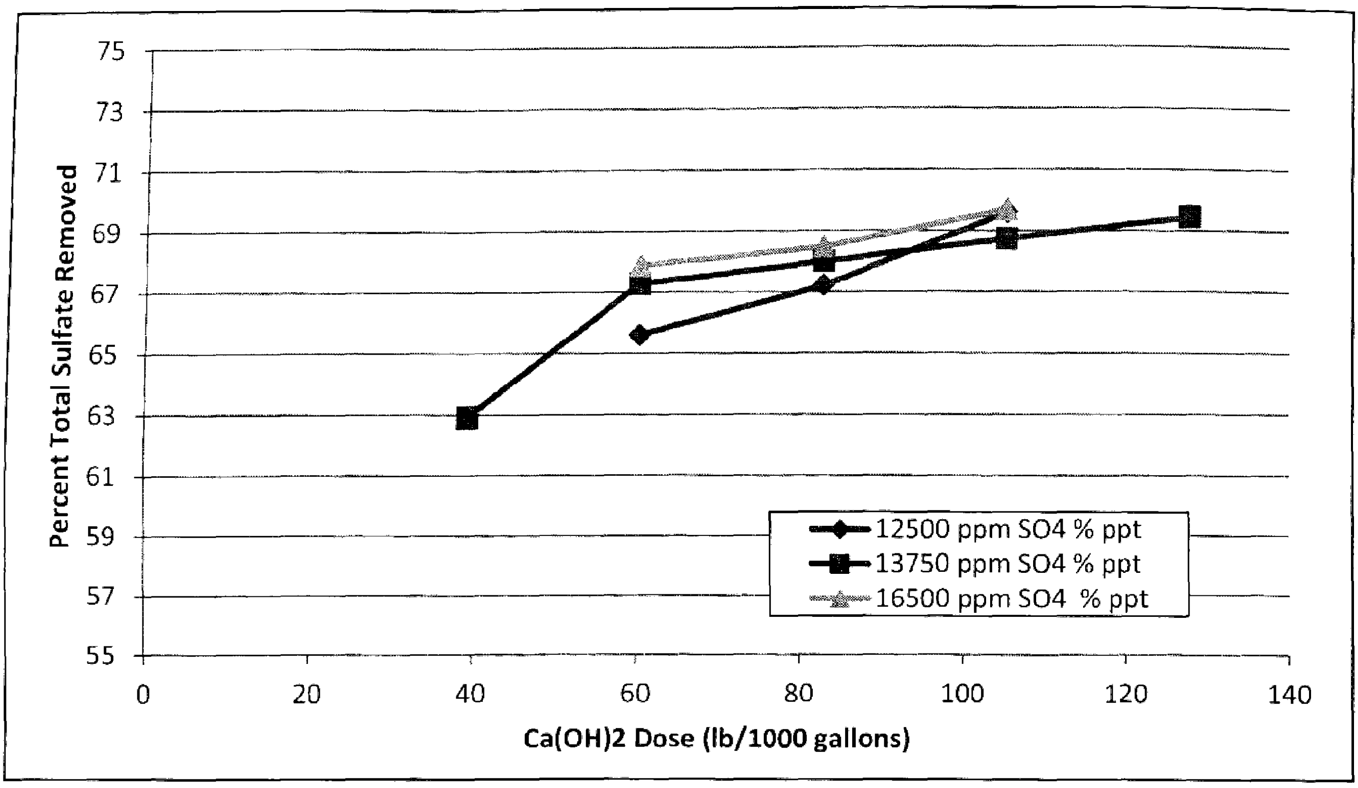

Figure 3. Percent total sulfate removed as a function of slaked lime dose at 46.4 pounds per 1000 gallons HCl treatment

the mine site RO concentrate, the treated sulfate level is less than 5000 ppm for slaked lime feed levels of 60.3 pounds per 1000 gallons and above. At the expected upper level of sulfate in the RO concentrate (16,500 ppm) the treated sulfate concentration was 5000 ppm or less only when the slaked lime feed was 105.3 pounds per 1000 gallons. Interestingly, in the case of this range of sulfate concentrations the percent total sulfate removed by this method of precipitation is about the same regardless of the initial sulfate concentration as shown in Figure 3. As seen in the figure, the percentage of total sulfate removed differs by only a few percent at each slaked lime dose level. Based on the results of these experiments the slaked lime levels needed to consistently yield a treated solution containing 5000 ppm sulfate or less at the mine site is 105.3 pounds per 1000 gallons.

The results of a series of experiments performed at varying concentrated hydrochloric acid dose at a constant slaked lime feed level of 82.8 pounds per 1000 gallons are shown in Figure 4. As seen in the figure, sulfate removal improves with addition of acid and the response is roughly linear over the range of acid levels tested.

Carbon Dioxide Neutralization Test

Neutralization of slaked lime treated RO concentrate can be readily accomplished using carbon dioxide. The lime treated concentrate contained approximately 5000 ppm sulfate. As shown in Figure 5, solution pH changes gradually between the initial value of 12.61 and 12.0. This is due to neutralization of the relatively high level of hydroxide and corresponding precipitation of calcium carbonate. Note that the dissolved calcium concentration dropped dramatically in this pH region during carbon dioxide treatment from an initial level of 1065 ppm as Ca^{2+} to 50 ppm as Ca^{2+} at pH 12.0. Approximately 98.5% of the dissolved calcium had precipitated when a pH of 11.5 was achieved. Between 12.0 and 7.5 the pH change over time is rapid. Interestingly, precipitation of calcium carbonate is associated with the removal of an additional 300 to 400 ppm sulfate from the initial slaked lime treated solution.

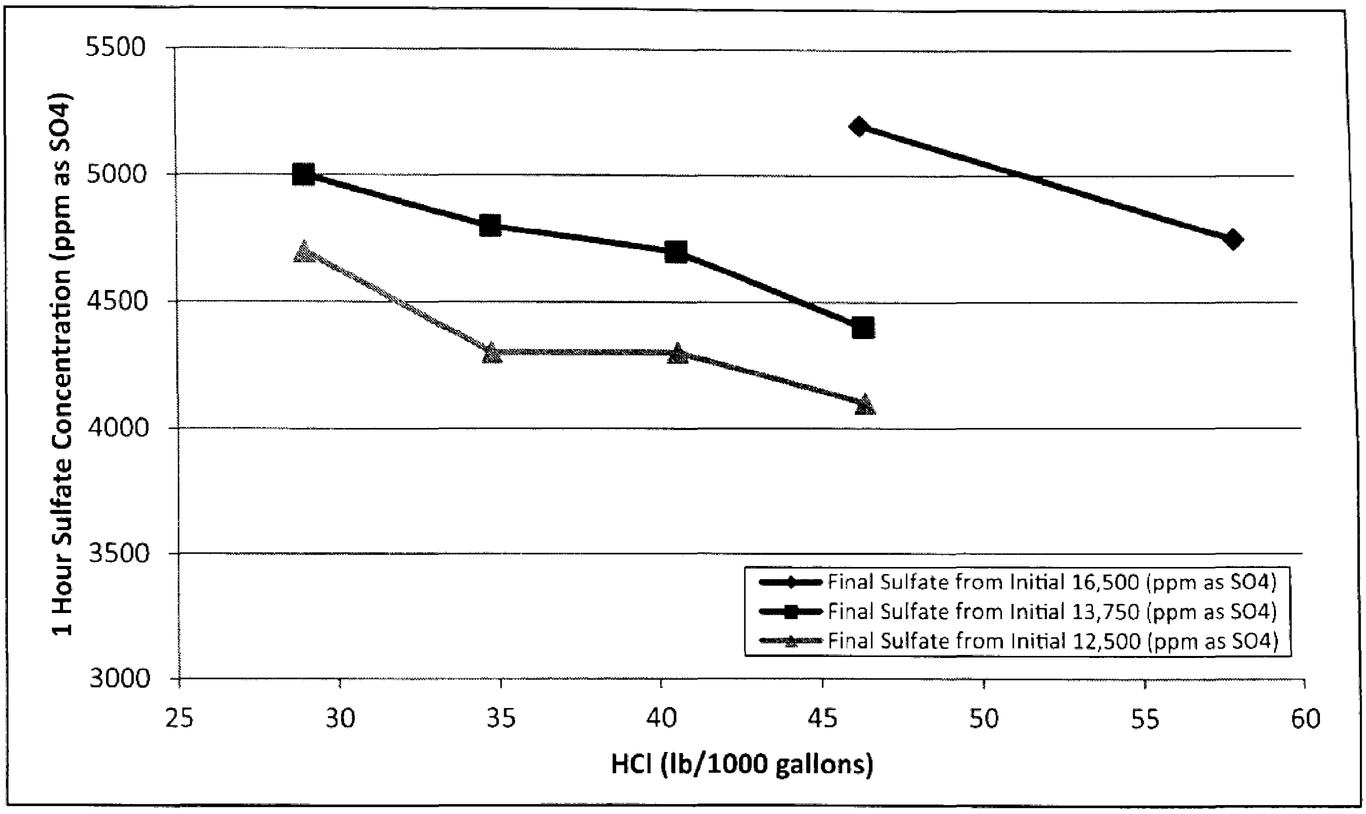

Figure 4. Sulfate removal as a function of HCl dose at 82.8 pounds per 1000 gallons slaked lime treatment

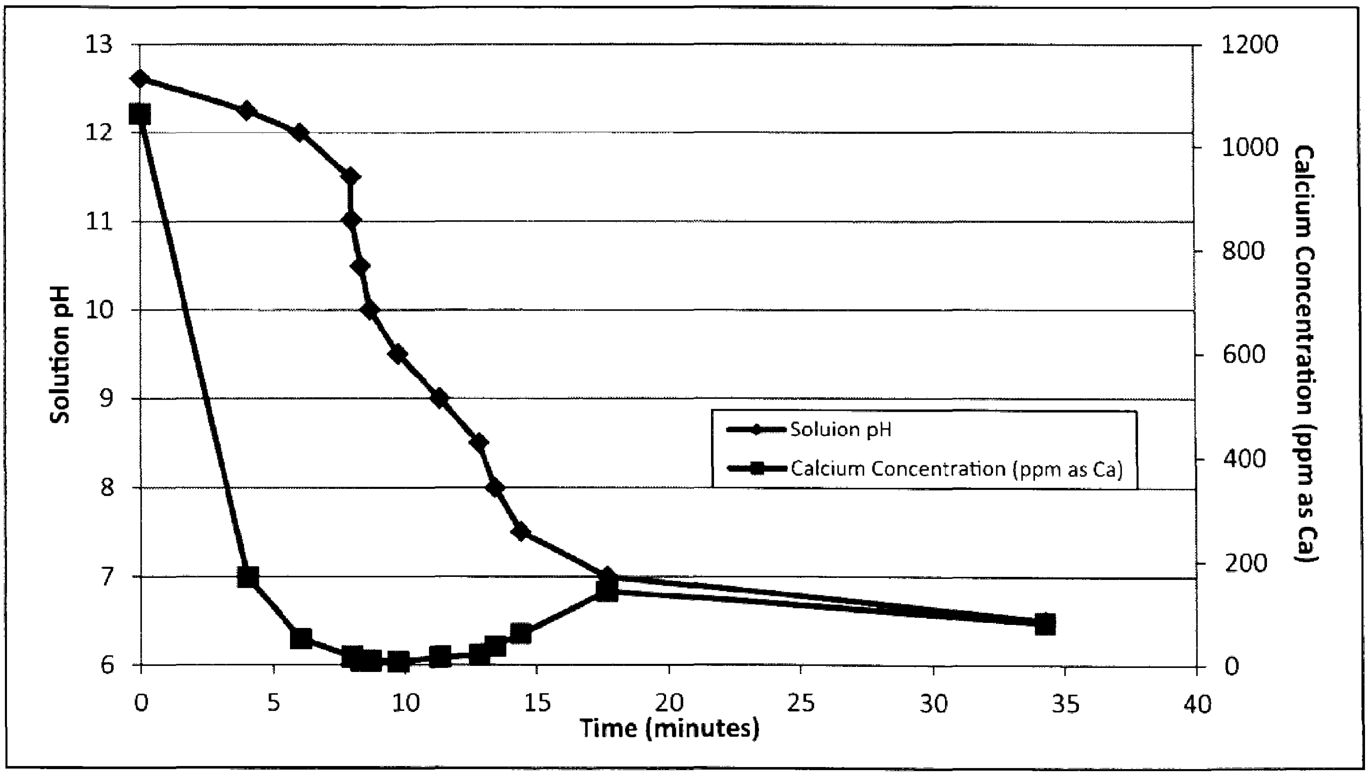

Figure 5. Carbon dioxide neutralization

Onsite Pilot Tests

The average composition of the RO influent, permeate and concentrate at the Latin American mine site are shown in Table 2. The sulfate rejection rate of the RO membrane was 99%. As seen in the table, a very high level of sulfate was produced in the RO concentrate throughout the test. Results of slaked lime treatment of the high sulfate RO concentrate followed by carbon dioxide neutralization are shown in Table 3. As seen in the table, treatment

Table 2. Average RO water parameters

Measurement	Influent	Permeate	Concentrate
pH	8.7	7	7.3
Sulfate (ppm as SO_4)	2696	27	10354
Total hardness (ppm as $CaCO_3$)	1291	79	5317

Table 3. Pilot study slaked lime treatment parameters

Measurement	Concentrate	Treated Concentrate	85/15 Effluent
pH	8.6	8.1	7.4
Sulfate (ppm as SO_4)	11909	4555	705
Chloride (ppm as Cl)	184	2269	341
Total hardness (ppm as $CaCO_3$)	6412	390	126

with slaked lime reduced the concentration of sulfate to well below 5000 ppm without exceeding the chloride limit of 2500 ppm. Prior to neutralization the solution pH was 12.7 but was readily reduced to 8.1 with carbon dioxide. Precipitation of carbonate solids lowered the total hardness to about 6% of the initial value. Blending such a treated RO concentrate with RO permeate will generate an effluent that will meet the discharge limits of the mine site.

CONCLUSIONS

- A pilot test performed at a mine site shows an RO system can operate for several months at an average recovery of 80% generating a high sulfate concentrate containing an average sulfate concentration of 10354 ppm. Blending low sulfate RO permeate with acidified slaked lime treated and carbon dioxide neutralized high sulfate RO concentrate yields a neutral solution containing less than 1000 ppm sulfate and less than 500 ppm chloride. This blend will meet mine site discharge requirements.
- Reverse Osmosis of a high sulfate mine water yields a very low sulfate permeate and a very high sulfate concentrate suitable for slaked lime treatment to remove sulfate.
- Addition of acid to neutral high sulfate water containing 12,500 to 16,500 ppm sulfate improves gypsum precipitation via slaked lime treatment. A hydrochloric acid level of 2570 ppm allows removal of 11,500 ppm sulfate from a 16,500 ppm sulfate solution in the presence of excess slaked lime.
- Reagent grade slaked lime treatment of acid treated high sulfate water containing 13,750 ppm sulfate shows 97% of the total gypsum precipitation occurs within one hour. Within two hours gypsum precipitation is complete.
- Slaked lime treatment of neutral water containing 16,500 ppm sulfate precipitates sufficient gypsum to lower the sulfate concentration to 7,500 ppm.
- Excess slaked lime improves gypsum precipitation and sulfate removal.
- Sulfate removal using slaked lime is limited by the pH achieved as gypsum precipitation occurs.

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