BIOLOGICAL SULFATE REMOVAL

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Introduction

Water is a necessary component of mining operations worldwide and requires careful management. Sulfate impacted waters are often encountered at mining operations. This water may require treatment if the water cannot be reused in mining processes. Freeport-McMoRan has invested in a water treatment test facility at Sierrita, AZ to evaluate alternative water treatment technologies for sulfate removal. A demonstration scale, active biological sulfate removal plant is being evaluated at this facility.

The main objective of plant is to demonstrate the performance of this process to obtain effluent sulfate concentrations below 500 ppm, determine the financials of a full scale facility and evaluate potential byproducts that could be achieved as a calcium/sulfur cake or sulfide source for other water treatment.

Methodology

The biological sulfate removal plant consists of two processes: 1) Anaerobic and 2) Aerobic.

The anaerobic process consists of sulfate reducing bacteria that obtain energy for metabolic activity by facilitating electron transfer from electron donors to electron acceptors. In this case hydrogen gas is used as the electron donor while sulfate acts as electron acceptor and is reduced to hydrogen sulfide. Other electron donors such as organic wastes or alcohols like ethanol could potentially be utilized.

$$Ca^{2+} + SO_4^{2-} + 4H_2 + CO_2 \rightarrow Ca^{2+} + HS^- + HCO_3^- + 3H_2O$$

The sulfate reduction produces alkalinity and about 45% of the total calcium precipitates as calcium carbonate. Addition of carbon dioxide gas controls the pH within working range of the reactor. The resultant solution from the anaerobic process, containing a high concentration of hydrogen sulfide, overflows into the aerobic reactor.

The aerobic process consists of a consortium of sulfide oxidizing bacteria. Under oxygen limited conditions, solution containing hydrosulfide from the anaerobic process is converted into elemental sulfur. Aerobic process control is maintained by operating within an optimal rH range (a function of pH and ORP).

$$Ca^{2+} + HS^- + HCO_3^- + 0.5O_2 \rightarrow S\downarrow + CaCO_3\downarrow + H_2O$$

This reaction again increases the pH of the solution and carbon dioxide gas is used to control the pH of the reactor; about 52% of the total calcium precipitates as calcium carbonate. The overall reaction of the process is:

$$Ca^{2+} + SO_4^{2-} + 4H_2 + CO_2 + 0.5O_2 \rightarrow S\downarrow + CaCO_3\downarrow + 4H_2O$$

Solids formed in the aerobic reactor are removed in post treatment settler tanks. It is necessary to remove the calcium carbonate solids that form in the anaerobic reactor by bleeding out a small flow from the reactor periodically. Figure1 shows a basic process flow.

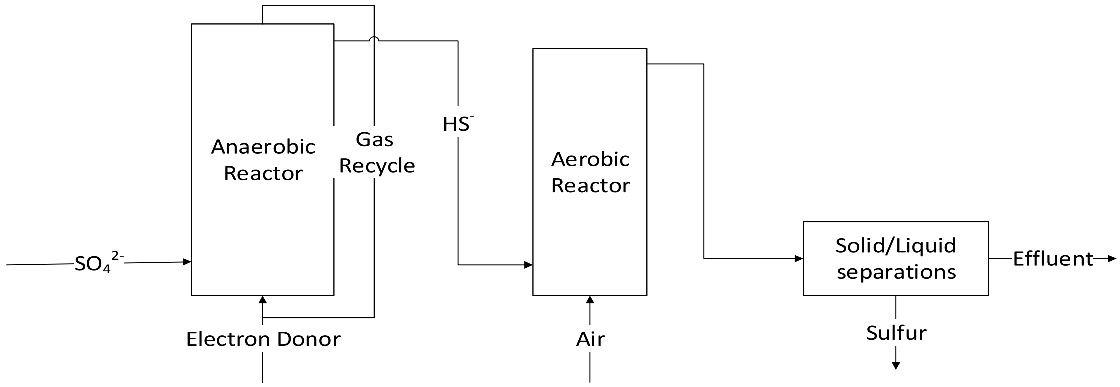

Figure1. Process Flow

Results

The effluent for this process is near neutral pH. Demonstration plant operations have consistently resulted in less than 500 ppm sulfate (average 72% reduction) and 15 ppm calcium (approximately 97% reduction). This compares to an average feed concentrations of 1500 ppm sulfate and 450 ppm calcium. The solids removed in the process consist of approximately 30% sulfur, 69% calcium carbonate and about 1% gypsum. The biological startup duration required by the anaerobic and aerobic bacteria is less than a week. At Sierrita, biological activity for sulfide and sulfur production started within a few hours of inoculation and reached full capacity within a week.

Discussion

The Anaerobic process performance is controlled by the amount of hydrogen added to the system. The performance of the reactor is always limited to 95% sulfate reduction to ensure sufficient sulfate is present in the reactor to prevent methanogenesis. During a situation when sulfate is completely reduced to sulfide, the electron donor would promote the growth of unwanted acetate or methane producing bacteria.

Aerobic performance is controlled by the amount of oxygen added to the reactor. Excess air added to the aerobic bacteria over oxidizes sulfide to sulfate and produces acidity. Too little oxygen would result in the bacteria becoming inhibited and release hydrogen sulfide gas in downstream vessels.

Conclusions

The main objective was to demonstrate stable operation and good performance of the technology. The Sierrita Bio-Sulfate removal demonstration plant continues to be successfully operated to meet the less than 500 ppm effluent sulfate objective. Initial financial data gathered indicates higher costs for treating 1000 gal of water compared with other technologies like reverse osmosis and ion exchange. However, Bio-Sulfate has advantages of being able to obtain effluent sulfate concentrations of 250 ppm or less with no pretreatment. The hydrogen sulfide produced in the intermediate stage can be used for precipitating metals when combined with a metal extraction plant.

References

Arie Pronk, Dijkman Henk, 2008, Basic Process Description SULFATEQ sulphate removal demonstration plant for treating interceptor well water

Arie Pronk, Dijkman Henk, 2008, Basic operating manual, maintenance & start-up procedure