Diffusive Exchange System with Internal Precipitation for Acid Mine Drainage Treatment

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ABSTRACT

Copper extraction is the principal mining activity in Chile. Acid mine drainages (AMDs) and mining effluents are characterized by high concentrations of copper, which can be recovered. Existing biochemical reactors utilize homogeneous substrates as percolation media to immobilize metals. However, microbial communities are exposed to the acid drainages within these systems and their toxicity often limits reactor reactivity.

Diffusive exchange systems on the other hand avoid direct contact of microorganisms with the AMD, significantly expanding the treatment range of biochemical reactors to include higher metal concentrations and lower pHs. A key innovation of this research is the use of vertical tubular screens to convey the AMD through the substrate while simultaneously allowing transverse diffusion of dissolved species and acting as reactors for precipitate formation and settling. This design minimizes clogging and facilitates the recovery of valuable metal. Furthermore, biochemical reactors with passive systems can be built taller and much smaller footprints can be achieved.

This work studied the performance of a 2-m long vertical diffusive exchange column with internal precipitation, allowing the simultaneous removal and recovery of copper from a synthetic AMD. Detailed insight was gained into reactions and transport processes within the tubular screen by the use of several sampling points along the column.

During the first two months the reactor was fed with increasing concentrations of sulfate and no metals, to determine its sulfate reduction potential. Then the reactor was fed with the AMD for one month; during this test effluent metals, sulfate, sulfide, acidity, alkalinity, pH, conductivity and ORP were monitored periodically. The sampling points allowed pH, ORP and metal concentrations to be measured throughout the reactor. High sulfate reduction rates of 0.2-0.6 moles/m^3-day were obtained. Also, during the first month of operation with influent metals, constant removal rates were achieved and precipitates were harvested.

Keywords: biochemical reactor; acid mine drainage; diffusion; copper; sulfate.

INTRODUCTION

Acid mine drainages (AMDs) are an environmental problem which has serious effects on the quality of both surface and ground water. These include acidification and increased concentrations of toxic metals and sulfate.

AMDs are produced by the oxidation of mineral sulfides, resulting in the dissolution of heavy metals and sulfate (Scheoran *et al*, 2010). The reaction involving the oxidation of pyrite is known and can be represented by the following equation (EPA, 1994):

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \tag{1}$$

AMD and mining operation effluents generated by the copper extraction industry contain high concentrations of copper which may in some cases be recovered. The complete oxidation of chalcopyrite can be written as (Dold, 2010):

$$CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-}. \tag{2}$$

Sulfate-reducing bioreactors or biochemical reactors (BCR) have proved to be an effective way of treating AMD (ITRC, 2012). The effectiveness of BCRs relies mainly on the activities of sulfate-reducing bacteria, which produce sulfide and bicarbonate inside the reactor. This leads to the formation of sulfides of metals such as copper, zinc and iron, which precipitate and can then be removed.

$$H_2S + M^{2+} \rightarrow MS\downarrow + 2H^+. \tag{3}$$

However, existing BCRs use a homogeneous bed as a percolation medium for immobilizing the metals in the system. This exposes the microbial communities to AMD, limiting the reactivity of the BCR.

Sulfidic diffusive exchange systems (SDES) avoid direct contact between the AMD and the microbial communities by separating the percolation medium into alternate layers or zones of high and low hydraulic conductivity (Schwarz & Rittmann, 2010). The idea of using this configuration is to separate the advecting contaminated water from the reactive material; in this way the microbial communities in a BCR are not exposed directly to the toxic metals in an AMD. This will enable the range of substrates treated in BCRs to be extended to high metal concentrations and lower pH values (Schwarz & Rittmann, 2007a).

The solutes are exchanged between the layers or zones of a SDES by diffusive processes, so solute exchange occurs because of the concentration gradient between the layers. In order for solute transport to be controlled by the diffusive processes, there should be a difference of at least two orders of magnitude between the hydraulic conductivity values of the reactive and conductive layers.

Using a SDES configuration for the substrate in a BCR allows certain disadvantages suffered by homogenous substrate BCRs to be overcome, such as: loss of organic matter reactivity due to metal crusting and precipitation; problems with blockages and preferential hydraulic flows; limitation of microbial activity due to toxic concentrations of metals; and limits on the height of the BCR because of diminished hydraulic conductivity (Schwarz & Rittmann, 2007b).

In view of the above, it would be of interest to find out whether a new prototype BCR with SDES would enable the equipment to be used to treat an AMD with a high copper concentration, which is impossible with a homogeneous bed BCR. This research developed a prototype BCR with SDES which may allow copper and other metals to be removed from an AMD by simultaneous

precipitation and sedimentation. We also evaluated whether the concentration of influent sulfate is a limiting factor for the functioning of a BCR with SDES, and determined the sulfate reduction rate.

METHODOLOGY

Design of a BCR with SDES

The proposed BCR with SDES uses vertical diffusive exchange columns as conductive zones, surrounded by the organic substrate (reactive zone). With this configuration it is expected that the majority of the metals will be removed by precipitation and accumulate at the bottom of the column.

The idea of using vertical columns as the AMD conductive zone is to promote precipitate formation and establish the exact area where the metals removed by the BCR would accumulate. The object of this is to project a BCR with SDES which would enable metals to be recovered from an AMD. Figure 1 shows the differences between a homogenous bed BCR and the proposed BCR with SDES.
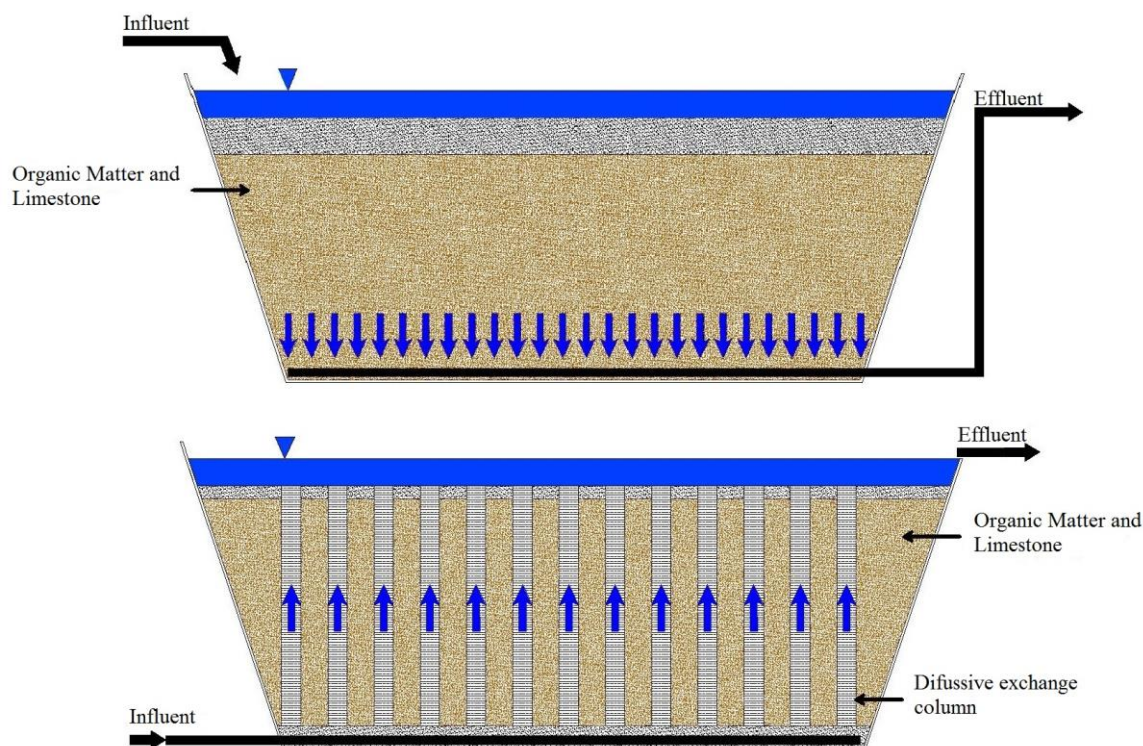

Figure 1 Diagram of a homogenous bed BCR (above) and a BCR with SDES (below). In the SDES reactor, the reactive mixture is crossed by screened tubes for the transport of fluid through the reactive bed. The screens retain the reactive mixture while allowing the lateral exchange of solutes between the advecing fluid and the bed pore space. Precipitates are expected to accumulate at the bottom of the screened tubes.

In the proposed BCR with SDES we decided to use an ascending flow to help sedimentation of the metal sulfide precipitates. The laboratory-scale BCR with SDES represents one of the several

reaction columns that may be found in a full-scale BCR with SDES. Figure 2 is a diagram of the laboratory-scale BCR with SDES constructed for the experiment.
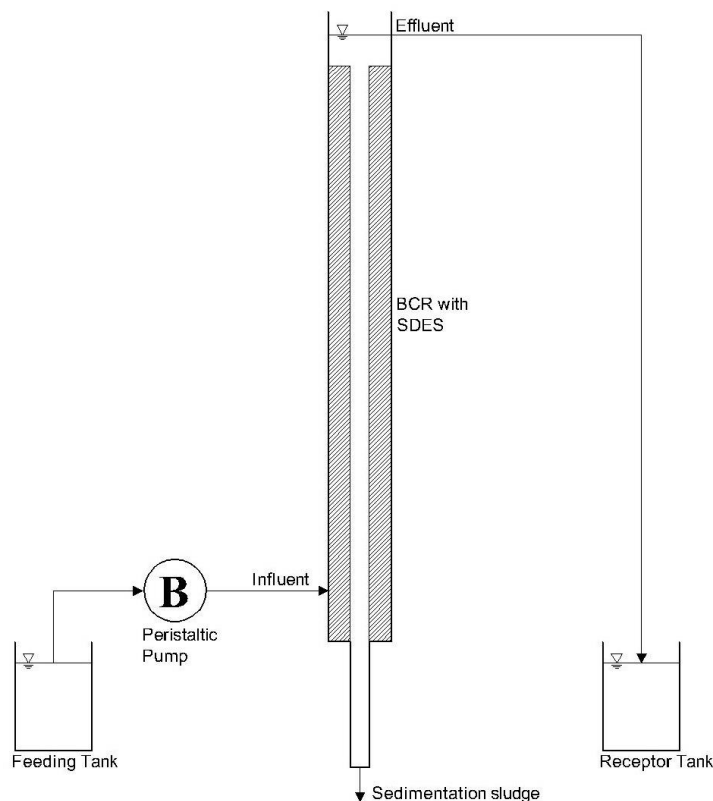

Figure 2 Diagram of the up-flow column reactor that simulates the processes that occur within a column of a BCR with SDES and its associated bed material. The reactor is made up of two concentric columns of which the interior one is screened. The reactive material is located in the inter-column space. The influent is feed into the inner column at the reactor bottom. Formed precipitates can be captured by sedimentation within the bottom extension of the screened tube.

ITRC (2012) recommends a maximum height of 1.8 m for the BCR, to avoid problems of reduced hydraulic conductivity in the lower layers of the substrate as a result of the excessive weight above. This problem does not apply to BCRs with SDES, but for practical reasons it was decided to make the laboratory-scale reactor 1.95 m high. The internal screened column is made of stainless steel, 6 cm in diameter and with aperture 0.75 mm. The outer column is made of PVC tubing, 19.3 cm in diameter. As a result, the volume occupied by the conductive central column in the reactor is 9.7%. A PVC tube 60 cm long, of the same diameter as the screened column, was placed below the column to collect the precipitates.

In order to study the reactor processes, five sampling points were fitted along the screen; these points were set at 6, 50, 100, 150 and 195 cm from the start of the reactive layer.

Organic matter

An important assumption in the choice and design of the substrate for the reactive layer was that microbial activity is sufficient to raise the pH of the AMD, because sulfate-reducing reactions produce bicarbonate and thus generate alkalinity (Scheoran, 2010). For this reason the reactive layer does not contain limestone or any other material to add alkalinity. Table 1 shows the materials used and their percentage by weight.

Table 1 Materials used in the reactive layer (% weight)

Function	Material	Percentage
Long term electron donor	Pure cellulose	50%
Short-medium electron donor	Manure	18.8%
	Leaf compost	31.2%

15 kg of organic matter were needed to fill the reactive layer in the reactor. The mixture was inoculated with 19 L of anaerobic digester content from the local sewage treatment plant. In addition, 15 L of distilled water were added to facilitate mixing and to saturate the organic matter. Figure 3 shows the organic matter used before and after mixing.

Figure 3 Organic matter utilized in the reactive mixture, before (left) and after (right) mixing

Finer organic matter can be used in BCR with SDES, since the substrate does not have to be kept permeable. The organic matter used in these reactors therefore has a larger contact area, with greater bio-availability to the microorganisms.

Experimental Tests

Four continuous experimental tests were carried out. In the first three, only the sulfate concentration in the influent was increased, while in the fourth metals were added. The purpose of

this was to study first whether sulfate is a limiting factor in the operation of a BCR with SDES. Table 2 shows the characteristics of the influent in the experimental tests.

The influent metal concentrations in the fourth test were: 568 mg Cu/L, 137 mg Zn/L, 35 mg Al/L and 0,8 mg Fe/L. These correspond to representative conditions of AMDs generated by large-scale copper mining in central Chile.

To characterize reactor functioning, samples were taken once per week from the effluent, the interior (bed pore water at a depth of 30 cm) and the five points along the screened column (numbered in the direction of flow). The sulfate and sulfide concentrations, the pH and the ORP were measured in the effluent, sampling point 5 (SP 5) and the interior. At SP 1 to SP 4, the sulfide concentration, the pH and the ORP were measured.

Table 2 Experimental tests

	Duration (weeks)	pH	Sulfate (mg/L)	Flow (L/day)
Test 1	6	5-5.5	2,218	2
Test 2	4	5-5.5	4,437	2
Test 3	4	5-5.5	6,655	2
Test 4	4	4-4.5	3,300	3

For three weeks before starting tests, 18 L of a solution with initial concentrations of 2,218 mg/L sulfate and 0.9 ml/L of lactate were recirculated through the reactor. The reactor was then fed for one week with a solution with the same initial concentrations as above, but without recirculation, at a flow of 2 L/day. This month of acclimatization is important in reactors of this type, to enable the bacteria to adapt and the communities to grow sufficiently to spread throughout the substrate.

RESULTS AND DISCUSSION

Variations in Sulfide, ORP and pH

Based on the interior screened column volume, the hydraulic residence time in the first three tests is 2.76 days, and in the fourth, 1.84 days. Table 3 shows the most important results of each test.

The results for SP 2 to SP 5 show the increase in sulfide concentrations as the contact time of the solution inside the reactor increases. All the sampling points reacted to the increased sulfate in the influent. SP 2 to SP 5, and the interior, present an increase in the average sulfide concentration as the influent sulfate increases.

At SP 2 to SP 5, when the sulfate concentration was doubled, the sulfide concentration increased on average by 51%. At these points, when the sulfate concentration was tripled, the sulfide concentration increased on average by 97%. It may therefore be concluded that the sulfide production in the reactor is limited to the influent sulfate. When the concentration of sulfate in the influent is increased, the sulfide inside the reactor also increases, in a proportion of two to one (percentage ratio).

The ORP measurements obtained during the tests at the five sampling points inside the reactor present similar behavior and appear to oscillate around the same average ORP regardless of the

sulfate concentrations in the influent. The ORP at SP 1 to SP 5 during these three tests was -108 mV on average, indicating that the reactor provides optimum conditions for anaerobic sulfate-reducing reactions, and that these conditions do not vary significantly along the reactor.

In the design it was assumed that the sulfate-reducing microbial reactions were sufficient to raise the pH of the influent. However, the average pH of the effluent during the three tests was 5.36, an average increase of only 0.06 over the pH of the influent.

Table 3 Variations in sulfide, ORP and pH during the tests with influent sulfate only (Tests 1-3)

		Sulfide average concentration	Sulfide maximum concentration	ORP	pH
		(mg/L)	(mg/L)	(mV)	
Test 1	Effluent	2.4	5.5	-14.1	
	Interior	6.7	15.1	5	
	SP 1	16.9	23.0	-120.9	
	SP 2	15.2	21.1	-112.2	
	SP 3	14.5	21.5	-112.7	
	SP 4	14.8	22.8	-113.4	
	SP 5	14.7	21.1	-115.6	
Test 2	Effluent	9.5	12.5	-86.1	5.4
	Interior	8.8	14.8	22.3	5.1
	SP 1	11.2	21.5	-93.0	5.1
	SP 2	20	28.6	-94.3	5
	SP 3	24.7	30.7	-104.3	4.9
	SP 4	22.7	24.3	-106.5	5
	SP 5	21.9	23.2	-115.3	5
Test 3	Effluent	5	11.2	-71.5	5.4
	Interior	18.9	26.1	-22.7	5
	SP 1	9.2	20.7	-98.0	5.1
	SP 2	21.8	35.6	-109.5	4.9
	SP 3	32.8	33.9	-114.6	4.8
	SP 4	30.4	35.2	-113.0	4.9
	SP 5	31.2	43.6	-112.1	5.1

Variations in the Sulfate

Figure 4 shows the sulfate concentrations obtained during the three tests in the effluent, SP 5 and inside the reactor.

In the first test it was observed that the reactor reached a state of equilibrium immediately. This was because during bacterial acclimatization the reactor was fed with the same concentrations used in

Test 1. It had therefore already reached equilibrium for the concentration used in Test 1. In Tests 2 and 3, equilibrium was reached after 15 days' operation. The interior (organic matter) never reaches equilibrium because transport in this layer is diffusive, so the test times are too short for concentrations to equalize throughout the bed material within the reactor. However it is observed that the sulfate concentration in the interior increases, and that it is dependent on the concentration in the influent.
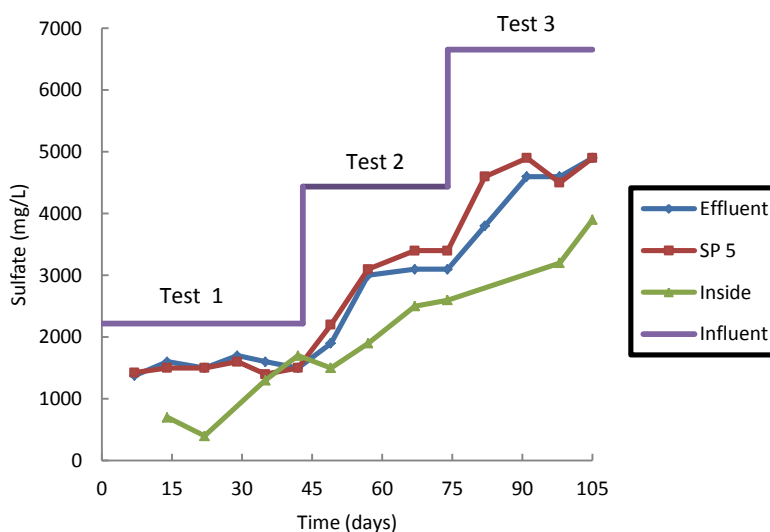

Figure 4 Variation of sulfate concentrations during the treatments with influent sulfate only (Tests 1-3). SP 5 is at the bed surface within the screened interior tube and the "inside" point is within the bed material at a depth of 30 cm.

For a homogeneous BCR, the volumetric sulfate-reduction rates are between 0.1 and 0.3 moles/m^3 of substrate/day (Gusek, 2002; ITRC, 2012; Wildeman & Schmiermund, 2004). The BCR with SDES constructed for this experiment presented average volumetric sulfate-reduction rates of 0.25, 0.5 and 0.72 moles/m^3 reactor/day for Tests 1, 2 and 3 respectively, based on total reactor volume (bed volume plus screened volume) (see Figure 5). Therefore the volumetric sulfate-reduction rate for a BCR with SDES depends on the influent sulfate concentration, and is directly proportional. In other words, if the influent sulfate concentration is doubled, the volumetric sulfate reduction rate will increase in roughly the same proportion.

The average sulfate removal percentages were 30.3, 30.9 and 29.4% in Tests 1, 2 and 3 respectively (see Figure 6). Thus the removal percentage did not vary significantly when the influent sulfate concentration was increased, remaining fairly constant at around 30%.
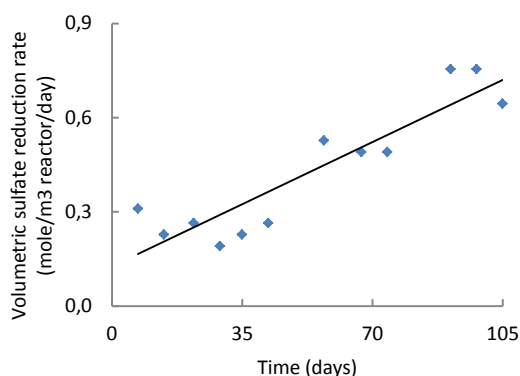
Figure 5 Volumetric sulfate reduction rates during treatment with influent sulfate only (Tests 1-3)
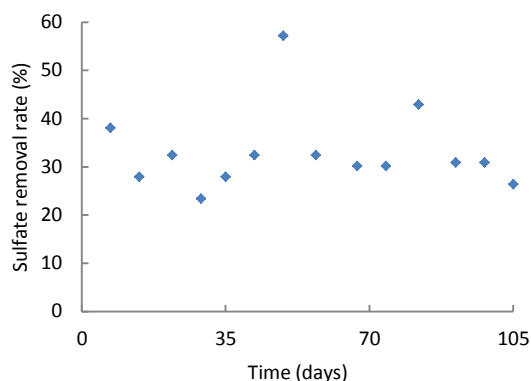

Figure 6 Sulfate removal rates during treatment with influent sulfate only (Tests 1-3)

Metal removal

In the fourth test the column was exposed to high concentrations of metals, particularly Cu and Zn, representative of AMD in central Chile. The flow was also increased by 50% to 3 L/day, to keep the reactor overloaded with metals. Under these conditions, the metal removals were 57% for Cu, 37% for Zn, and 50% for Al (Fig. 7). The overall volumetric metal removal rate was 300 mmol/m^3 reactor/day (Fig. 8). This experiment is continuing, to see whether the reactor can maintain these removal rates over time. Blackish precipitates were found in the bottom effluent, which may be mostly Covelite.

Based on sulfate reduction and metal removal rates one can compute the metal removal to sulfate removal yield, which is about two thirds or 67%. That is in average sulfate reduction would be only 67% effective in contributing to metal removal as sulfides.
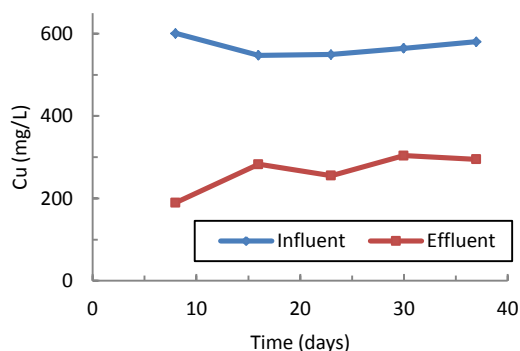

Figure 7 Influent and effluent copper concentrations during treatment with synthetic AMD (Test 4)
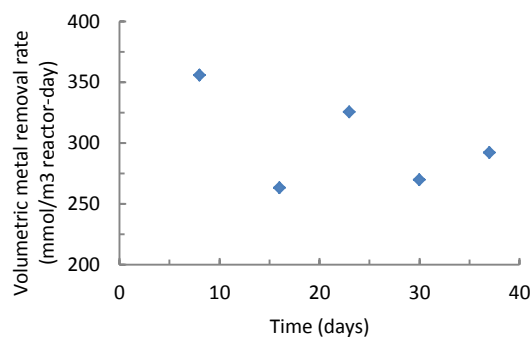

Figure 8 Overall volumetric metal removal rates during treatment with synthetic AMD (Test 4)

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CONCLUSIONS

The BCR with SDES constructed at laboratory scale presented sulfate reduction rates of up to 0.75 moles/m^3 of reactor/day. This value is 2.5 times higher than the average sulfate reduction rate found in homogeneous BCRs, showing that the use of SDES in regard to substrate, can improve BCR functioning significantly.

The BCR with SDES reacted to increases in the influent sulfate concentration. The volumetric sulfate reduction rate increased proportionally with the sulfate concentration. On the other hand the sulfide inside the reactor increased by 50% on average when the sulfate concentration was increased by 100%. Thus the sulfate concentration in an AMD is a limiting factor in the operation of a BCR with SDES.

The BCR with SDES cannot raise the pH of the influent. Thus to neutralize the pH of an AMD it may be necessary to add limestone or some other alkaline material to the mixture.

During the first month of feeding with metals, the reactor removed a significant percentage of copper and zinc; however it remains to be seen whether this removal can be maintained over time. A precipitate was recovered from the bottom of the reactor, the purity of which is to be determined for copper recovery purposes.

Hence BCR with SDES hold promise for the treatment of AMD. Biological processes and chemical reactions are separated within theses systems. This zonation allows independent optimization of key processes. The biological system can be optimized for resistance and reactivity, while de chemical system can be optimized for metal precipitation and recovery.

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