

A Tale of Two Treatment Systems: Evaluation of Active and Passive Treatment Strategies for A Legacy Mine

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Abstract

It is infrequent that the treatment possibilities for a given water chemistry and flow rate include both passive and active technologies. Usually, the solute concentrations and flow rate are too high for a passive system or too low for an active system. However, on occasion, the situation arises in which both passive and active processes are potentially viable treatment options. This is the case for a water source in the western United States where both active and passive pilot-scale systems were built and operated side-by-side in the field to assess their viability at treating historical mine seepage and identify design criteria for potential full-scale implementation. The active treatment system consisted of equipment housed within a semi-trailer and utilized a high-density sludge (HDS) process, which traditionally uses calcium hydroxide reagent to raise pH of the feed solution in order to precipitate dissolved metals. The HDS process was configurable as a single- or two-stage system depending on treatment goals. The passive bioremediation system was partially housed in a mobile 40-foot shipping container installed at the site. The bioremediation system consisted of three stages: limestone pre-treatment, primary treatment via sulfate-reducing biochemical reactors, and secondary-treatment via treatment wetlands.

The active treatment system with two-stages achieved potential discharge limits for the primary water quality standards. The bioremediation system achieved most, but not all, potential primary water quality standards during the test period and strategies for improving performance were identified. The results for each treatment system are discussed and compared to provide insight into which system might be better suited for this application.

Introduction

Various water technologies and strategies exist for treating mine-influenced waters and treatment systems can generally be categorized as either active or passive. Active treatment requires daily operational input from a person in the form of process review, set point changes, maintenance and other. Most active treatment requires chemical addition and mixing in reactors. Active treatment systems can typically handle changes in feed chemistry and flowrates. Passive systems usually rely on natural biological, geochemical, or physical processes to improve water quality. Passive treatment strategies are typically chosen for historical or remote mines because they do not generally use electricity, they operate by gravity feed, and typically require less operation, maintenance, and monitoring. The choice between active or passive strategies is critical for meeting treatment goals.

There are various factors influencing whether active or passive systems should be selected. Selection depends on considerations such as water treatment goals, regulatory requirements, flow rates, mass loading of metals requiring treatment, availability of land for a treatment system, and cost-effectiveness. Rarely does an opportunity present itself to simultaneously evaluate active and passive treatment systems side-by-side. This paper summarizes such an opportunity at a historical mine site in the Rocky Mountains of the Western U.S. The historical mine workings produce mine drainage, surface decant water, and mine tailings toe drainage. Mine drainage flow rates vary extensively over the course of the year due to precipitation primarily as snow. Several retention, settling, and surge ponds are maintained onsite to accommodate higher flows during the spring runoff and a water treatment plant (WTP) has been in operation at the site for over 40 years. Due to the age of the WTP, along with the type of treatment process in place, new treatment strategies are being evaluated including an alternative passive treatment option for some of the water requiring treatment.

Two simultaneous pilot-scale evaluations were conducted at the site in 2019. The waters targeted for treatment are characterized by low pH and elevated levels of sulfate and several metals such as aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn). Other considerations include arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and nickel (Ni), according to potential discharge water quality standards. The active treatment system consisted of calcium hydroxide addition in one- or two-stage High Density Sludge (HDS) reactors to precipitate metals. The passive treatment system consisted of a biologically-based (hereafter referred to as bioremediation) treatment system consisting of three stages: neutralization pre-treatment, primary treatment biochemical reactors, and post-treatment wetlands. The principal design objectives of the evaluations were: (1) to optimize the treatment system components under local environmental conditions; (2) evaluate the performance of locally-available bioreactor substrate materials and treatment wetland plants; and (3) provide design data for potential future implementation of full-scale treatment.

Background

High-Density Sludge

High-density sludge is a traditional active treatment technology that uses a hydroxide reagent (typically calcium) to raise the pH of the feed solution in order to precipitate the dissolved metals in water. Depending on the targeted metals to precipitate, oxidation of this solution is commonly required. The basic process flow of this system is pictured in Figure 1.

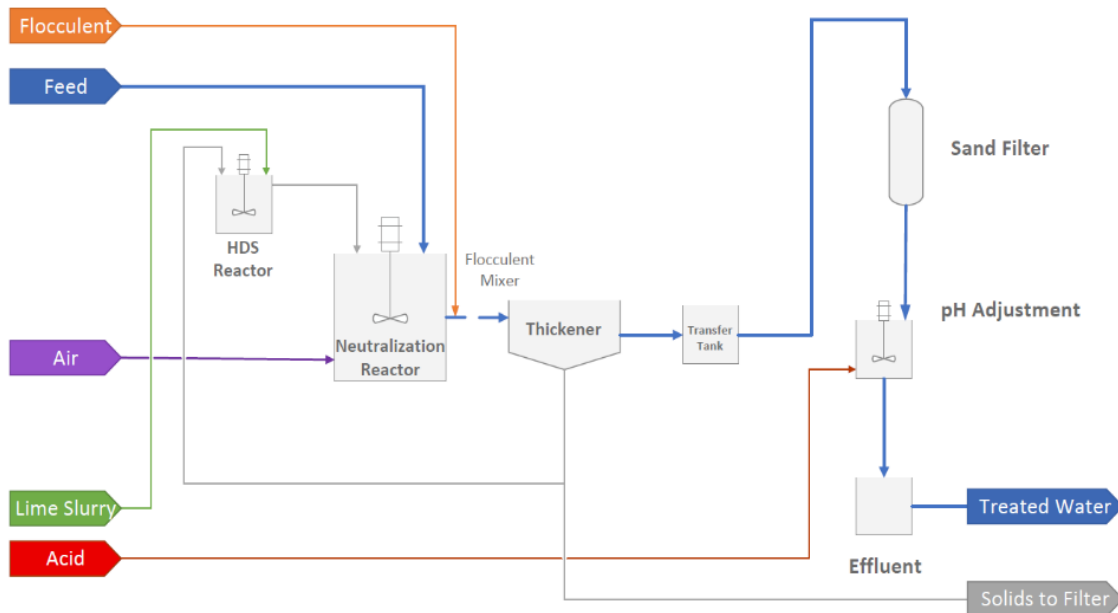


Figure 1: Single-stage HDS process flow diagram

Feed solution enters the neutralization reactor where it is oxidized with air and mixed with a hydroxide / seed slurry. Solution then leaves the neutralization reactor, mixes with flocculant and is sent to a thickener for liquid solid separation. The clarified liquid overflows the thickener weir and moves on to fine solids removal, pH adjustment and discharge. The solids settle in the thickener and are recycled to another tank (HDS reactor) where they are mixed with the hydroxide reagent. This step produces a “densifying” effect because hydroxide reagent coats the underflow or “seed” particle which effectively removes waters of hydration and produces a denser sludge. As this hydroxide / reseed slurry is then mixed with the feed solution in the neutralization reactor it raises the pH in the reactor causing dissolved metals to precipitate onto the densified particles compounding the effect. The hydroxide reagent addition is controlled by the pH of the neutralization reactor and is set based on the targeted metals to remove.

Bioremediation

The bioremediation treatment system consists of three stages as shown in Figure 2. The first stage is a basic neutralization stage using limestone to increase pH and reduce acidity. Limestone is a relatively low-cost neutralizing agent that is safe and easy to use. Limestone pre-treatment is often preferred in systems that operate semi-passively due to less maintenance required compared to chemical dosing systems. While not a remote site, using limestone also negates the need to frequently transport potentially hazardous alkaline reagents to the site and does not require additional equipment needed to operate a chemical dosing system. Increasing pH improves water quality by promoting the chemical precipitation of Al and Fe (oxy)hydroxides. Pre-treating the MIW also helps support the biological organisms required for the second treatment stage. Increasing pH improves water quality by promoting the chemical precipitation of Al and Fe (oxy)hydroxides. Pre-treating the MIW also helps support the biological organisms required for the second treatment stage.

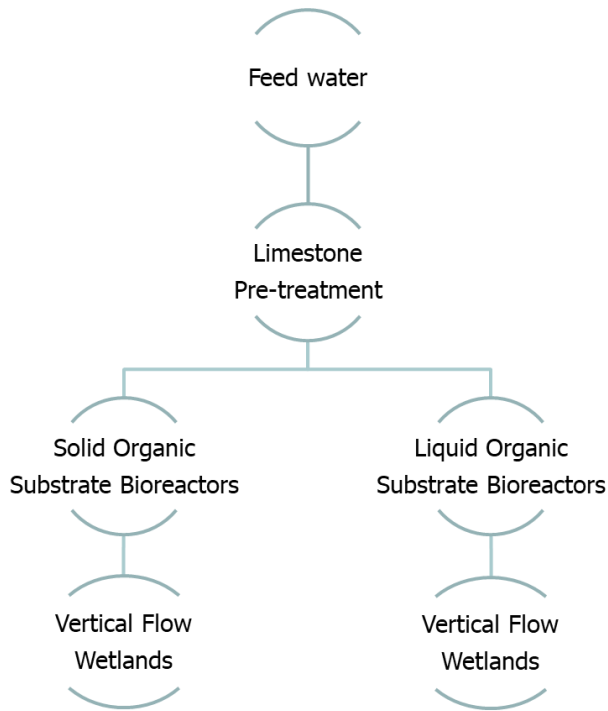


Figure 2: Three-stage bioremediation treatment process block flow diagram

Sulfate-reducing biochemical reactors (SRBRs) rely on a diverse assemblage of microbes to reduce sulfate to aqueous sulfide, which complexes with metals ions via precipitation as metal sulfides. Sulfate is reduced by sulfate-reducing bacteria while oxidizing an organic substrate. This evaluation compared the performance of two different substrates: a solid organic substrate and a liquid organic substrate. The solid substrate consisted of a mixture of readily available types of organic matter (wood chips, hay, and walnut shells). The liquid organic substrate was provided by a commercially available liquid carbohydrate-based product. The sulfate reduction process produces bicarbonate alkalinity, leading to additional metal removal

at higher pH.

The final treatment stage consists of vertical flow wetlands (VFWs) designed to promote oxic and aerobic conditions that increase dissolved oxygen, reduce biochemical oxygen demand (BOD), remove manganese as oxides; and filter out residual solids. Each treatment stage improves pH of the MIW and adds buffering capacity to the final effluent water that can be beneficial for the receiving water. The post treatment phase has the added benefit of improving the appearance of the landscape at the site.

Methods

High-Density Sludge

To perform the on-site HDS pilot, Freeport-McMoRan designed and constructed a portable pilot plant within a semi-trailer. The plant was configurable as a single- or two-stage system with the option to run two single-stage tests congruently. Major equipment included: hose pumps, transfer tanks, solids reactors, thickeners and a sand filter. All process equipment was housed within the trailer, with the exception of bulk reagent storage and potable water totes. Figure 3 shows an inside look of some of the equipment used in the pilot plant.



Figure 3: Two-stage HDS pilot plant

The trailer control system included a PLC, HMI, and historian to trend and store key operating parameters over the course of the test work. The HDS control strategy was designed to be fully automated and operate the plant overnight without the need for night-shift intervention. Level indicators and switches monitored tank levels and triggered a safe shutdown of the plant if any plugging was detected. This level of automation minimized the chance of tank overflows, which preserved the integrity of the tests by limiting process upsets and solids lost into the secondary containment. The plant was designed with enough residence time in the reactors to test up to five gallons per minutes (gpm). Flocculant, chelate, and lime were all monitored and dosed as part of the control system. The primary control function was a neutralization reactor pH control loop in each stage, with a steady dosage of flocculant based on the feed flowrate. The solids recycle flowrate in each stage was varied to maintain a set point based on the solids sampling from the previous day or current solids density as measured by a Marci scale.

Whether the HDS process is configured as a single- or two-stage system depends on the targeted metals and level of removal for each. For the testing, dissolved Al was a key factor in determining the plant configuration. Since no final Al target had been determined at the time of the pilot both single- and two-stage configurations were tested. Below are the configurations tested on-site:

- Single-stage HDS operated at a pH set point of 10.5
- Single-stage HDS operated at a pH set point of 10.3
- Single-stage HDS operated at a pH set point of 10.0
- Two-stage HDS, stage 1 operated at a pH of 7.0, stage 2 operated at a pH of 10.5
- Two-stage HDS, stage 1 operated at a pH of 7.0, stage 2 operated at a pH of 10.5 with chelate addition after stage 2

Three different pH set points were chosen for single-stage operation to determine if pH solubility was a primary means of precipitation for aluminum. Aluminum is more soluble at higher and lower pH but less soluble in the near neutral range. Improved aluminum removal was expected with a lower pH setpoint. However, pH is also a significant driver for Mn removal. Optimum pH for abiotic Mn precipitation is around 10.5, so a balance between Al and Mn removal had to be achieved.

Bioremediation

The pre-treatment stage consisted of four 55-gallon drums filled with limestone (ca. 3-inch diameter) and connected in series. Due to the relatively low pH of the water to be treated and elevated levels of Al and Fe, a pre-treatment phase is needed to improve the water quality prior to contact with the sulfate-reducing bacteria. From the dissolution of calcium carbonate (CaCO_3), calcium ions are formed along with bicarbonate. This increases pH and allows the formation of low solubility metal hydroxides. Above a pH of 3.4, ferric Fe readily forms insoluble Fe hydroxides. Above a pH of 5.6, Al begins forming insoluble Al

hydroxides. These solids were encouraged to settle out with the limestone and immediately after the limestone beds within a 55-gallon barrel settling tank. This reduces the suspended solids load that could enter the primary treatment and cause plugging issues.

The primary treatment stage for MIW is the SRBR. Sulfate reduction by bacteria produces sulfide ions along with additional alkalinity. Free sulfide combines with metals susceptible to sulfide precipitation (e.g., Fe, Cu, Zn, and Cd). These sulfides are relatively insoluble at circum-neutral pH. The additional alkalinity promotes increases in pH and further removal of metals, such as aluminum, that form insoluble hydroxide precipitates. The sulfate-reducing bioreactors were constructed using 120-gallon tanks (Figure 4). Two organic substrates were used as the source of organic carbon: a solid organic substrate (SOS) and liquid organic substrate (LOS). In this pilot plant, the SOS contained a mixture of wood chips (39% wt), alfalfa hay (10% wt), pecan shells (20% wt), and limestone sand (29% wt). The latter for additional neutralization capacity, particularly during start-up. The LOS was provided by dosing a non-reactive aggregate-filled reactor with MicroC ® 1000 (EOSi, Pocasset, MA, USA), a proprietary carbohydrate-based liquid providing organic carbon.



Figure 4: Primary treatment sulfate reducing bioreactors

The wetlands treatment stage was designed to polish SRBR effluent and improve water quality prior to discharge. A vertical flow wetland was selected for evaluation as the most likely to continue operating year-round in an extremely cold climate. In a vertical flow wetland, water is treated as it percolates downward through the root zone of plants and through the 24-inch-deep layered sand and gravel bed (Figure 5). The unsaturated sand and gravel promotes an aerobic environment that returns oxygen back to the SRBR

effluent, which is anoxic. The microbial community and plants also consume the high organic load (i.e., BOD) present in SRBR effluent. While not listed as a primary Water Quality Standard, it is indicated as a secondary standard for basic water quality. Mn-oxidizing bacteria drive the biotically-mediated oxidation of Mn, which can occur much faster and at a lower pH (ca. 6.5) than abiotic Mn oxidation.

Water samples were routinely collected from each stage of the treatment system to monitor performance. Field chemistry parameters (pH, dissolved oxygen, electrical conductance, oxidation-reduction potential, and temperature) were recorded weekly. Aqueous samples were collected every two weeks for quantifying metals (total and dissolved), anions, and acidity / alkalinity. The evaluation was conducted from mid-July to late-October 2019, until freezing conditions impacted operation of the pilot study.



Figure 5: Vertical flow wetland as the final treatment stage

Results

High-Density Sludge

Five different HDS configurations were completed on-site from September through November 2019. Each single stage configuration had four days of sampling while the two-stage configuration had six total days of sampling, four with chelate addition and two without. Given that the final water quality standards are yet to be determined this pilot was judged by the lowest potential discharge limits available.

All the primary WQS were met in each configuration with the exceptions of Cd and Al. As expected, neither the single- nor two-stage configurations alone achieved the lowest potential Cd target. Only the addition of the chelate to the second stage effluent followed by filtration through a 0.45-micron filter achieved a final effluent concentration significantly below the target. Chelate could be added to either the single- or two-stage configurations if needed. Also as expected, the Al target was only achieved in the two-stage configurations. The Al standard is important to understand, as it changes the scope of a future treatment system. Table 1 shows the results from the various configurations.

Table 1: HDS pilot test results summary

Test Summary	Reactor 1 pH	Reactor 2 pH	Passing status for selected water quality standards					
			Al	Cd	Cu	Fe	Mn	Zn
1 Stage -pH 10.5	10.5	NA	Fail	Fail	Pass	Pass	Pass	Pass
1 Stage -pH 10.5	10.3	NA	Fail	Fail	Pass	Pass	Pass	Pass
1 Stage -pH 10.5	10.1	NA	Fail	Fail	Pass	Pass	Pass	Pass
2 Stage -without chelate	7	10.5	Pass	Fail	Pass	Pass	Pass	Pass
2 Stage -with chelate	7	10.5	Pass	Pass	Pass	Pass	Pass	Pass

Bioremediation

Improvements in pH were observed at each stage of treatment, with a final effluent pH within WQS. The pH increased from an average of 2.9 to an average of pH 6.4 following pre-treatment and this level was maintained through the SRBRs. In addition to improving pH of the MIW, limestone pre-treatment is advantageous for removal of Al and Fe prior to the solution entering the SRBRs. This reduces plugging and subsequent flow restrictions through the SRBRs. Total recoverable Fe was removed 99% while 44% of the Al was removed in pre-treatment. Al removal was lower than expected but continued to be removed further downstream in subsequent treatment phases.

Performance of the SRBRs met expectations up to the flow rate evaluated. As the bioreactors required an acclimatization period ranging from 30 to 75 days, the target flow rate was not achieved during this evaluation. Regardless, the SRBRs exhibited metal sulfide precipitation and alkalinity generation. Average metal removal rates were comparable between reactor types (i.e., LOS vs. SOS), with the exception of Al removal. The SOS reactor exhibited continual removal of Al potentially due more effective filtration of Al hydroxide particulates. Total Al concentrations in the SOS reactors continued to be removed below the pre-treatment effluent levels to just above the WQS. LOS reactors did not appreciably remove additional aluminum and maintained levels approximately the same as the pre-treatment effluent level.

Total recoverable Fe levels exiting the SRBRs were slightly higher than the pre-treatment effluent levels, potentially due to release of Fe from the substrate materials, e.g., woodchips and sawdust or lava

rock. Dissolved Cu concentrations were removed by both types of reactors below WQS. The LOS reactors were able achieved the low level nearly from start-up. As expected, Mn concentrations were relatively unchanged within the SRBRs because Mn does not typically precipitate in reducing environments. There was an initial decrease in SRBR Mn concentrations likely due to adsorption of Mn with the organic matter or the formation of Mn carbonates, but this is not sustained and Mn returned to pre-treatment effluent levels. Zn levels were reduced by both types of SRBRs to levels just above WQS. Dissolved Cd concentrations were similarly reduced by both reactor types to just below WQS by the end of the evaluation.

The vertical flow wetlands provided final polishing to the effluent from the SRBRs and generally improved water quality. DO and pH were improved by the VFWs and increased to approximately 4 mg O₂ /L and pH 7.5, respectively. ORP increased as it passed through the VFWs indicating the desired shift from anoxic to oxic conditions necessary for Mn oxidation. With the exception of Fe and Mn, COCs were removed below the benchmarked WQS. VFWs removed additional Al, Cd, and Zn below WQS from the SRBR effluent. Fe was further removed by VFWs, but not consistently below WQS. Mn removal rate was removed approximately 90% but was not sufficient achieve potential WQS. Further removal would be expected as the wetland plant communities mature and develop a more extensive root zone and associated rhizosphere, but this had not occurred by the end of this test period. BOD, while not a specific WQS, was improved by the VFWs with an average of 86-89% of incoming BOD removed. The reduction of additional COCs through the VFWs supports the need for any potential large-scale treatment system to include a polishing step to achieve treatment below WQS for discharge. However, any treatment wetland will require more time to mature to maximize the biological removal mechanisms targeted.

Conclusion

As expected, results from this side-by-side evaluation of MIW treatment strategies reinforce some of the widely-recognized characteristic differences between active and passive treatment systems. The active treatment system using high-density sludge was able to meet the WQSs for aluminum, cadmium, copper, iron, manganese, and zinc during the relatively short evaluation period. Alternatively, the passive bioremediation system achieved WQSs only for aluminum, cadmium, and zinc, but not copper, iron, and manganese. Relative to the active system, the bioreactors took longer to achieve steady state conditions necessary for sulfate reduction while the wetlands needed additional time to mature. Opportunities exist for improving the performance of the bioremediation system and they warrant further consideration. For example, careful selection of bioremediation substrates would mitigate the potential leaching of metals into the treated water. Ultimately, these two treatment strategies are not competing against each other but rather should be viewed as complementary tools, each with their own ideal applications.

