



Acid Mine Drainage Active Treatment Solutions

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Abstract

Acid mine drainage (AMD) has been an environmental challenge for decades. Most of the treatment systems have been passive systems with a few taking an active treatment approach. The treatment of acid mine drainage via active treatment solutions is dependent on the flow rates of the drainage, the chemistry, types, and level of contaminants and the projected life cycle cost for a given application. The various treatment options have their advantages and disadvantages. There are a few new and improved technologies that may provide better treatment solutions with lower operating costs. There are novel solutions for selenium treatment and for rare earth element (REE) capture. Using feed water chemistry from actual AMD sites, we will review the various treatment options versus the feed water chemistry. We will evaluate the treatment options based on the projected capital costs and the projected operating costs for each option that may be used as guidelines for use in evaluating AMD for active treatment.

Introduction

Acid mine drainage and acid rock drainage (collectively herein referred to as AMD) consist of acidic and metalliferous water that either drains, seeps, leaches, or is pumped out of the strata are associated with ground from active or former coal or metal mining sites – or from the reject, refuse, or tailings materials generated from such sites. The mine water can become acidic due to metallic sulfur compounds that are solubilized and oxidized, with the primary source being pyrite (FeS_2) forming sulfuric acid. The further oxidation forms ferric hydroxide and the release of more hydrogen ions. The highly corrosive nature of sulfuric acid breaks down surrounding rock and ore strata and causes many other metals, such as Cd, Cu, Hg, Ni, Pb, Zn, Mn and Al to dissolve and enter into the mine drainage. AMD is characterized by low pH, resulting in high total dissolved solids (TDS), and high metals concentrations.

A common source of AMD at coal mining sites is coal processing waste, or refuse, that has been deposited in called “Gob Piles.” The majority of coal refuse gob piles are not lined and were subjected to varying degrees of compaction during construction. As precipitation and groundwater passes through or across on these refuse sites piles, the metals oxidation process occurs, and

high TDS and low pH water can similarly be released. This same process can also occur in underground coal mine and voids with AMD discharging from mine openings such as portals, shafts, or ventilation openings. All this water is collectively referred to as AMD is often collected in ponds or treatment basins located below mining sites. If the mine sites are abandoned or AMD is not properly treated, the AMD can enter and pollute receiving streams.

The state regulatory agencies typically try and institute passive treatment systems when applicable. Client/landowner typically does not have the staff to operate an active treatment system, nor the budget for ongoing costs for active treatment. A passive treatment system generally consists of an aerobic wetland system to raise the pH and cattails and other aquatic plants to translocate O_2 to the subsurface through their roots. The plants also help prevent channelization of the waters through the wetland. The water is generally not aesthetically pleasing, as it is often discolored orange or other colors depending on the metals being oxidized.

For very low pH situations, either an anaerobic or “Composted” wetland or anoxic limestone drain (ALD) is used. The anaerobic set up has three layers: the aerobic layer is above, an anaerobic layer of composted

organic matter in the middle, and a bed of limestone (> 90% CaCO₃) at the base. The limestone increases the alkalinity and the pH. The ALD is an airtight limestone layer with a post treatment settling pond. All these systems are gravity fed.

Active treatment may be considered for higher flow applications (>100 gpm [379 L/ min]). Several active treatment solutions can be applied to an AMD site depending on the pH and the contaminants that are in the AMD. The implementation of an active treatment systems requires active operational support and operating expenses. Therefore, the life cycle costs associated with an active AMD site along with the operational requirements need to be considered. We will look at what are the design considerations, the treatment options, projected capital costs and projected operating costs. These projections are based on specific site scenarios that would apply for each technology. This evaluation process is to be a guide to considering active treatment options.

Active Treatment Solutions Design Considerations

When evaluating a site for active treatment several key questions need to be determined and evaluated.

What is the pH?

What is the flow rate – minimum, maximum, and average?

What contaminants are in the AMD and the concentrations?

Is there Selenium?

Is there a high concentration of rare earth metals (REE)?

What is the alkalinity?

What is the oxidative reduction potential (ORP)?

What is the biological oxygen demand (BOD)?

What is the chemical oxygen demand (COD)?

What is the temperature variation?

The starting point for all active treatment solutions is determining the feed water characteristics. A complete analysis of the feed water is preferred. Table 1 is an example of a water analysis for an AMD site.

Table 1 Site A Feed Water Chemistry

Analyte	Feed Value mg/L	Analyte	Feed Value mg/L	Analyte	Feed Value mg/L
Ca	247	Cl	NR	PO ₄	NR
Mg	34.95	SO ₄	1435	SiO ₂	NR
Na	29.75	NO ₃ as N	NR	pH	2.6
K	3.77	Alkalinity	352	TSS	NR
ORP	NR	COD	NR	BOD	NR
Metals					
Al	349	Fe	1.42	Th	0.118
Be	NR	Ga	NR	Tl	ND
Cd	NR	Mn	7.145	U	0.466
Co	1.37	Ni	4.78	V	NR
Cr	NR	Nb	ND	W	ND
Cs	ND	Se	ND	Zn	NR
Cu	NR	Ti	NR	Zr	ND
Rare Earth Elements					
Ce	0.532	La	0.134	Sm	0.189
Dy	0.184	Lu	0.006	Tb	0.028
Er	0.068	Nd	0.589	Tm	0.008
Eu	0.043	Pm	NR	Yb	0.046
Gd	0.229	Pr	0.103	Y	0.917
Ho	0.0277	Sc	0.290		

NR: Not Reported ND: Not Detected

We also prefer the pH and ORP to be measured in the field to see if there is a substantial difference from the field and the lab. Based on the feed water chemistry and answers to the questions above the type of active treatment that might apply can be determined.

Active treatment option

Neutralization

Until recently active AMD treatment has been either a lime neutralization process, a high-density sludge (HDS) process or a limestone/lime neutralization process. These processes address pH, iron and aluminium, but are not effective for the treatment of selenium. The basic process is to use chemical addition to increase the pH so that the iron and aluminium form particulates that are filtered out. The neutralized water is then discharged to surface streams.

Lime Neutralization process can be used on a stream with a pH of 2 or greater with flows greater than 50 gpm (189 L/min) and high alkalinity. The contaminants other than iron and aluminium need to be below state regulations for a NPDES permit or treated in the process. This process consists of a lime slurry tank, lime reaction tank, floc tank, clarifier, and thickener with the effluent going typically to a pond for final settling and discharge.

High Density Sludge (HDS) process can be used on a stream with a pH of 2 or greater with flows greater than 50 gpm (189 L/min). Traditionally, moderate to low alkalinity is preferred. Again, the contaminants other than iron and aluminium need to be below state regulations for NPDES permit or treated in the process. This process consists of a lime slurry tank, a first stage reaction tank, a lime reaction tank, a floc tank, clarifier, and thickener with the final effluent going typically to a pond for final settling and discharge. The difference with this process is the solids recycling. The key to this process is the proper process control of the solids recycling and chemical dosing control creating a higher solids slurry, that is dewatered.

Limestone/Lime Neutralization process can be used when the pH is less than 4 and the flows greater than 50 gpm (189 L/min).

Low alkaline water is preferred. Again, the contaminants other than iron and aluminium need to be below state regulations for NPDES permit or treated in the process. This process consists of a limestone storage tank, limestone solution tank, lime slurry tank, Limestone reaction tank, lime reaction tank, floc tank, clarifier and thickener. This process involves an initial neutralization to about pH 5 with limestone and further processed with lime to pH 7 and more. Similar to the HDS process the solids are recycled to improve efficiency, but does not create the high density solids slurry.

Neutralization and Selenium Treatment

Selenium has been treated using a biological process and recently a media reduction process. Biological processes have been sequence batch reactors (SBR) or fluidized bed reactors (FBR). In this process the selenium is reduced and is incorporated into the biomass. The SBR's sometime do not have complete uptake of the selenium and some organo-selenium complexes are released resulting in higher toxicity.

The media process uses either a zerovalent iron (Ferrolock) or a sulfur modified zero valent iron media (SMI). The media is reductive. The process is up flow resulting in a partially fluidized bed. The first step is the reduction of SeO_4^{2-} to selenite (SeO_3^-). The pH must be between 4 and 6.2 for the selenate reduction, and this is the rate limiting reaction for the process. The kinetics for the reaction decreases above 5 and stops at around 8.0. Sulfate (SO_4^{2-}) is a competitive ion to selenate reduction. High ORP also affects the reduction reaction effecting the amount of empty bed contact time required and the life of the media.

The second step is adsorption of SeO_3^- to the iron (Fe) followed by reduction to ferric selenite [$\text{Fe}_2(\text{SeO}_3)_3$]. The selenium is further reduced forming ferrous selenide (FeSe). These reactions are not as sensitive to pH, but probably needs to be below 6.5. Further reduction may occur to elemental selenium (Se^0).

Water reacts with the ZVI and forms hydrogen gas (H_2) and hydroxyl ions (OH^-). The net result is the pH of the treatment

systems rises approximately 1.5 pH units. Most of the selenium laden AMD is above a pH of 4, thus the effluent of the system typically has a pH > 5.5.

If discharge is direct to a stream, the effluent of this treatment system is post treated with aeration and multimedia filter to meet NPDES permit requirements. If there is a retention settling pond available, then the effluent can go to the pond for settling of the particulate iron and aluminum prior to final discharge to a stream. Since the media is NSF-61 approved, the process can be designed to meet drinking water standards.

Neutralization and Rare Earth Element (REE) Capture

Two processes have been developed and patented for the neutralization and capture of REE. These are the University of West Virginia process, and the SMI-Solutions processes. They are different in concept, but both meet the requirements of treating the AMD to NPDES standards and capturing the REE to a high degree.

1. University of West Virginia Paul Ziemkiewicz et al. (US 10,954,582, B2) process is a modification of the HDS neutralization process. The initial unit operation is to precipitate the iron at a pH of approximately 4. The next unit operation is precipitation of a REE enriched sludge, and then finally the precipitating the aluminium. The iron and aluminium precipitates are settled in ponds prior to discharge to the stream. In addition, they have developed a method for separating and concentrating the REE in a centralized facility.
2. SMI Solutions Inc, (SMI) (Peter F. Santana, (Inventor and owner of SMI Solutions Inc., (SMI-S)) received a process patent for REE capture (US 11,230,753 B1), and subsequent international patent cooperation treaty (PCT). This novel process captures the REE within a specially modified zero-valent iron filter media and to a minor portion within a post-treatment iron sludge. In theory, the REE may form complexes with the ZVI, but will also precipitate as the pH rises within the media bed resulting in high

REE concentration levels versus the media mass. In addition to REE, other metals precipitate or complex with the media. The SMI media is NSF-61-approved and is manufactured in the USA.

Several lab trials and a current field trial have demonstrated a high capture (90+%) of the rare earth elements REE within the media bed. The process is pretreatment (total suspended solids (TSS) and total organic carbon (TOC) reduction), up flow reactor vessel followed by post treatment. The projected post water treatment for iron released during the reaction is aeration, multimedia filtration and a filter press to provide a cake for REE extraction processing. The effluent will meet typical NPDES permit standards. The spent media is an iron-rich ore with a high concentration of REE and other metals.

Life Cycle Cost Evaluation

Neutralization

For the neutralization evaluation, we will assume the following feed conditions:

Flow rate: 500 gpm	pH 3.0
Power \$0.12 kWh	Iron: 200 mg/L
Alkalinity 565 mg/L	Lime \$230/t
Aluminum 15 mg/L	Limestone \$90/t
Sulfate 663 mg/L	Polymer \$3/lb

Lime Neutralization

Lime neutralization system is simple to operated and has the least amount of capital equipment of the three neutralization systems. The projected installation cost for a lime neutralization system is \$3,153,600. The projected annual operating costs for this application are \$436,358 excluding site labor costs.

The disadvantages of this process are the precipitates are fine solids with lower suspended solids concentrations in clarifier underflow, thickener underflow and consequently, are more difficult to dewater. The lime consumption is high. Lime adsorbs to the precipitate surfaces and is lost with the sludge. Increases solids mass for disposal from lime that is either unreacted or adsorbed to particle surface (See Table 2).

High Density Sludge (HDS)

The HDS process is a bit more complicated than lime neutralization but has distinct advantages when designed and operated correctly. These advantages are:

3. Produces a denser solid resulting in lower flow of sludge in clarifier underflow and thickener underflow. The dewatered cake has a much higher solids concentration (See Table 2).
4. More efficient use of lime resulting in substantial operating savings.
5. Lower solids formed through more complete utilization of lime and formation of some FeO(OH) instead of Fe(OH)₃.

The disadvantage is there is more equipment and the projected installed cost for the HDS system is \$3,431,250. However, the projected operating cost excluding labor is \$368,484 which is about \$68,000 less per year than a conventional lime neutralization system.

Limestone/Lime Neutralization

The Limestone/lime neutralization process is for very low pH streams (2–4) where the less expensive limestone can reduce the amount of the more expensive lime required. The sludge recycle to the lime neutralization will provide slight improvements to the solids density similar to the HDS process (Table 2).

The disadvantages are there is a higher solids production from impurities in the limestone and limestone particles coating with precipitates sealing off the remaining CaCO₃. The lower sludge density is not conducive to forming denser particles. Since there is more capital equipment the capital

cost is higher. The estimated installed cost is \$5,812,700. The projected operating expenses excluding labor is \$435,901.

Selenium Treatment

Case 1 parameters are 500 gpm (1.9 m³/min) flow rate, pH 4.5, Se 30 µg/L, sulfate 500 mg/L, ORP < 300 mV. These parameters suit the use of an Advance Metals Removal system (AMRS) with SMI media. The system can be installed in a series of Connex boxes or a building. The process is simple and does not require daily operator interaction. The projected installation cost is \$2,709,651. The projected operating expense annually excluding labor is \$83,876. This assumes SMI media cost of \$8.00/lb (\$17.62/kg) and power at \$0.12/kWh.

Case 2 parameters are 500 gpm (1.9 m³/min) flow rate, pH 4.5, Se 30 µg/L, sulfate 1,500 mg/L, ORP < 300 mV. With the higher sulfate concentration, this application requires Ferrolock ZVI media and a much longer empty bed contact time than case 1. The AMRS system is simple, does not require daily operator interaction, but will need to be installed into a building due to the size of the reactor vessel. The projected installation cost is \$3,330,802. The projected operating expense annually excluding labor is \$78,190 assuming Zerlock media at \$0.92/lb (\$2.03/kg) and power at \$0.12/kWh.

REE Capture

For this evaluation the feedwater chemistry in Table 1 will be used. The AMRS-SMI system with post treatment is used in this evaluation. The system can be installed in a series of

Table 2 Neutral Treatment System Comparison

System Type	Solids Produced (Dry Wt)	Clarifier Underflow		Thickener Underflow		Dewatered Cake		Limestone Used	Lime Used
	tons	Solids %	Flow L/min	Solids %	Flow L/min	Solids %	Wet t/d	t/d	t/d
Lime	4223	2	64	5	26	25	8.21	0	3.6
HDS	2898	20	6	30	3	60	2.31	0	2.6
Lime stone/ Lime	4404	4	29	8	15	30	6.16	2.2	1.8

Table 3 Capital and Operating Expenses Comparison

System type	Projected Installed Cost	Projected Operating Expense
Lime Neutralization	\$3,153,600	\$436,358
HDS	\$3,431,250	\$368,484
Limestone/lime	\$5,812,700	\$435,091
Se-AMRS-SMI System	\$2,709,651	\$83,876
Se-AMRS ZVI System	\$3,330,802	\$78,190
REE AMRS-SMI System	\$3,827,867	\$480,512

Connex boxes or a building. The process is simple and does not require daily operator interaction. The projected installation cost is \$3,827,867. The projected REE mass on the media is 300 mg/g SMI media (Note: current trails are in progress to confirm this). The pH is raised to 3.8–4.0 with caustic prior to the media bed. Assuming SMI media cost of \$8.00/lb (\$17.62/kg), NaOH at \$1.78/gal (\$0.47/L) and power at \$0.12/kWh, the projected operating expense annually excluding labor is \$480,512.

The projected market value of the metals on the spent SMI ore is \$2,586,835 (Price of Chemical Elements en.wikipedia.org/wiki/prices_of_chemical_elements). Assuming 30% of the value of the metals can be recuperated by the operating entity, the operating cost could be offset by approximately \$776,051, resulting in \$295,539 of revenue annually. This warrants further investigation as a viable solution to AMD and the US Department of Defence (DOD), and Department of Energy (DOE) need for REE.

Conclusion

Active treatment systems are viable solutions to AMD; however, they are capital intensive and require on-going operating expenses to be covered. Table 3 below compares the various options their installation and operational costs.

The HDS process provides the lowest life cycle cost of the neutralization processes.

The use of an advanced metals removal system (AMRS) might be appropriate for a neutralization process and should provide lower operating costs. The feed water chemistry will dictate whether it is appropriate. This should be evaluated when considering an activated treatment system for neutralization.

For the treatment of selenium, the AMRS process is a viable process to achieve effluent levels less than 5 µg/L Se and meet NPDES permit requirements. Again, the system will need to be designed based on the feed water characteristics.

The use of an AMRS-SMI system for REE recovery should be examined if the total REE concentration is greater than 500 µg/L. The amount of REE and other metals retained as a spent SMI ore will have value that can offset some or all of the operating costs of the system. This is still in development but has promise to address AMD and REE capture.

References

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