Active treatment of high strength acid mine drainage at a clay mine and coal refuse sites

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Extended Abstract

Acid mine drainage (AMD) with low pH and high acidity (6,000 to 12,000 mg/L) that also contain high concentrations of dissolved iron (2,000 to 6,000 mg/L) and aluminum (100 to 500 mg/L) are the focus of this presentation. Mine types that can produce this high concentration AMD include coal refuse sites, coal waste disposal sites, and refractory deep clay mines. This high strength AMD poses a number of treatment challenges including neutralization demand, iron oxidation, solids production, and coprecipitation of gypsum.

Three active treatment plants have been installed and operated over the last decade including: 1) Charles Coal Refuse (Robindale Energy); 2) Globe Clay Mine (Vesuvius, US); and 3) Laurel Coal Refuse (LCT Energy). Table 1 summarizes the influent AMD characteristics and effluent quality at each of the treatment system sites. All three treatment systems are at regulatory sites with National Pollution Discharge Elimination System (NPDES) effluent limits and have consistently achieved the NPDES effluent limits.

Iron Oxide Technologies, LLC has developed active treatment systems for this type of mine water and these systems have demonstrated long term treatment performance and cost-effective operations. The active treatment plants include: 1) lime slurry or hydrated lime storage and feed systems; 2) pH controlled operations; 3) mixing reactors that dissolve the lime; 4) aeration and mixing reactors that oxidize the ferrous iron in the AMD to produce a high-density sludge; 5) a flocculation system with polymer addition to form a settleable/filterable solid; 6) solids settling/removal systems; 7) sludge collection and dewatering components; and 8) control systems with remote cellular-based monitoring and alarms.

The mixing reactors contain mixer and tank designs that rapidly blend, disperse and dissolve either lime powder or lime slurry in the AMD. This is an important step to efficiently utilize the lime. The lime slurry is a pre-made product available from W.K. Merriman and is delivered into a mixed storage tank at approximately 35% calcium oxide.

*Table 1 Summary of Site Influent AMD and Treatment System Effluent Characteristics*

Parameter	Units	Charles Refuse		Globe Clay Mine		Laurel Refuse	
		Raw Influent	Effluent Average	Raw Influent	Effluent Average	Raw Influent	Effluent Average
pH	s.u.	2.5	7.6	3.3	7.2	2.2	7.0
Acidity	mg/L as CaCO$_3$	5,600	0	7,580	0	12,800	0
Alkalinity	mg/L as CaCO$_3$	0	25	0	20	0	10
Total Fe	mg/L	2,080	< 2.0	2,630	< 0.5	2,500	< 1.0
Total Al	mg/L	343	< 0.50	230	< 0.20	880	< 0.2
Total Mn	mg/L	14.3	< 1.5	40.0	< 1.0	76.	< 2.0
Sulfate	mg/L	7,400	4,700	10,100	3,500	13,800	2,200
Flow	gpm	10–75	NA	15–50	NA	10–150	NA
Flow	L/min	38–284	NA	57–189	NA	38–568	NA

The lime powder is hydrated lime ($Ca(OH)_2$) from Graymont, Inc., which is about 70% calcium oxide based on chemical composition and purity. Both the lime slurry and dry lime feed are regulated by pH control. The lime slurry is fed from the storage tank into the mixing reactor using a hose pump. Hydrated lime powder is fed directly from a storage silo into the mixing reactor using an auger and screw conveyor. The use of an auger and screw conveyor to directly feed hydrated lime is unique and requires mixing reactor designs that entrain the powder into the AMD where it is dispersed and rapidly dissolved.

The aeration and mixing reactor provides efficient and effective oxidation of the ferrous iron at slightly alkaline pH (7.0 to 7.5), followed rapidly by ferric iron hydrolysis and precipitation as ferric oxyhydroxides. Oxidation is frequently considered the rate limiting step in AMD treatment as homogeneous iron is typically slow. However, the process utilized in this treatment system is autocatalytic Activated Iron Solids (AIS) treatment (U.S. Patent no. 10,570,041 B2), that involves heterogeneous oxidation of the ferrous iron. Heterogeneous ferrous iron oxidation is described by the following equations:

$$Fe(III)OH + Fe(II)_{diss} \rightarrow Fe(III)OFe(II) + nH^+$$
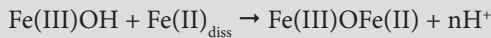
In this first equation, the ferrous iron Fe(II) is sorbed to iron oxides, which is then oxidized in the presence of oxygen to form new ferric oxide by the following generalized equation:

$$Fe(III)OFe(II) + \tfrac{1}{4}O_2 \rightarrow new(Fe(III)OH) + nH^+$$
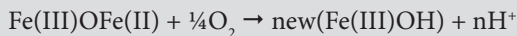
The rate of this heterogeneous reaction is determine by the concentration of Fe(III)OH (ferric oxide solids), H^+ (pH), and to a lesser extent O_2 (dissolved oxygen). In addition, temperature will affect the reaction rate based on the apparent activation energy. The aeration and mixing in the aeration and mixing reactor provides the needed dissolved oxygen for the reaction and maintains ferric oxide solids in suspension. The reactor volume and its dimensions are based on the required detention time to complete the oxidation reaction, which are estimated based on the oxidation kinetics and reactor design equations.

In addition to ferrous iron oxidation, the reactor system processes directly address dissolved aluminum removal through hydrolysis and precipitation as a hydroxide, which occurs as a result of AMD neutralization to a circumneutral pH. Dissolved manganese is indirectly addressed as a result of heterogeneous sorption of Mn(II) onto the formed iron oxide solids. Generally, manganese is effectively removed where the ratio of dissolved iron to dissolved manganese in the AMD is greater than about 40:1; estimated based on Dzombak & Morel (1990).

The final chemical process occurring in the treatment system is removal of sulfate, which can be an unwanted lime demand and precipitation reaction. The removal of sulfate occurs from the added calcium in the lime and its reaction with dissolved sulfate according to the following reaction:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

The $CaSO_4$ (or gypsum) has a solubility product (Ksp) of $10^{-4.6}$ at 25°C (Drever 1982), which generally indicates a sulfate concentration of about 2,000 mg/L is soluble at a calcium concentration of about 800 mg/L. This means sulfate can and will be removed to concentrations approaching the solubility indicated above where calcium is added from the lime neutralization. Formation of a gypsum scale can be an issue in many

treatment systems but is mitigated in the autocatalytic AIS process by the presence of high concentrations of mixed suspended solids that act as nuclei for the gypsum precipitation.

Solids collection and handling at the three systems varies depending on the final disposition (on-site or off-site landfill) of the solids. For on-site or nearby disposal, the effluent from the reactor system is directly pumped into Geotubes® where the solids are concentrated into a semi-solid and manageable sludge. The filtered water emanating from the Geotubes® is collected and discharged to polishing ponds prior to discharge. In the case of-site disposal at a landfill (Globe Mine), clarifiers are used to collect and concentrate the solids with the clarified effluent discharged into polishing ponds. The collected solids are pumped and stored in a sludge holding tank with these solids dewatered to greater than a 40% solid cake using a filter press. The dewatered solids are acceptable for landfill disposal. The filtrate from the dewatering is discharged to a polishing pond.

As shown in Table 1, the Iron Oxide Technologies designed high strength AMD treatment systems are effective at treating the AMD to acceptable levels for discharge. In addition, the designs have been shown to be cost effective in comparison to alternative treatment approaches (e,g., caustic neutralization) that are used and have been used for this type of high strength AMD.

Citations

Drever JI (1982) The Geochemistry of Natural Waters. Prentice-Hall, Inc., Englewood Cliff, NJ, USA, 388p.

Dzomback DA, Morel FMM (1990) Surface Complexation Modeling; Hydrous Ferric Oxide. John Wiley & Sons, Inc., New York, NY, USA, 393p.