Special Chemicals for Treating Acid Mine Drainage

By Jeff Skousen, Ron Lilly and Tiff Hilton

Introduction

In 1990, a paper was published in *Green Lands* entitled "Acid Mine Drainage Treatment Systems: Chemicals and Costs" (Skousen et al., 1990). In that paper we described four commonly-used chemicals in neutralizing acid mine drainage (AMD). Hydrated lime (calcium hydroxide), soda ash briquettes (sodium carbonate), caustic soda (sodium hydroxide), and ammonia (anhydrous ammonia) were related to situations, both in terms of water flow and metal composition, where they were best suited. Costs for each chemical treatment system were broken down into equipment installation, repair, and salvage costs, along with annual chemical reagent costs over four AMD flow and acid concentration cases. These tables were recently updated with 1992 costs and projected over 5- and 20-year operation periods (Fletcher, Phipps and Skousen, 1992).

As shown in Table 1, caustic had the lowest annualized costs during the 5-year time period for the low flow (50 gpm) and low acidity (100 mg/l acidity) situation, even though it had the highest reagent cost. Ammonia had the next lowest annualized costs, soda ash was third because of its high labor and reagent costs, and hydrated lime was fourth because of its high installation costs. In the intermediate flow and acidity cases, ammonia became the most cost effective, with hydrated lime second. Soda ash and caustic soda were the most expensive alternatives for all but the low flow and acidity case. In the highest flow and acidity category, hydrated lime was clearly the least costly treatment system, with an annualized cost $230,000 less than ammonia, the next best alternative.

Over a 20-year operation period (Table 2), caustic soda and ammonia were still the least expensive choices for the low flow and acidity situation, and hydrated lime was still clearly the least expensive alternative for the high flow and acidity condition. Ammonia, as in the 5-year budgets, was the cheapest treatment system for the intermediate flow and acidity conditions and was second for the highest flow and acidity combination.

Special AMD Treatment Methods

Since AMD treatment began, most companies simply used one of the above chemical treatment systems for acid neutralization and metal precipitation. Raising the pH of the water usually caused precipitation of the metals and if the metals did not precipitate adequately to meet effluent limits, more chemical was added.

While the same four acid neutralization chemical treatment systems are still predominately used by the coal industry, several other chemicals have become available during the past five years (Table 3). Limestone was found to successfully treat AMD in anaerobic (oxygen-free) environments such as anoxic limestone drains where the limestone does not armor with metal hydroxide deposits. (Faulkner and Skousen, 1993; Skousen, 1991). Pebble quick lime (calcium oxide) has been recently used in conjunction with the Aquafix Water Treatment System utilizing a water wheel concept (Jenkins and Skousen, 1993).

Several operators have used potassium hydroxide, magnesium hydroxide, and magna lime with good success. These products behave similarly to the calcium-type products and their use depends on the price. Ammonia is used in many locations in West Virginia with good success and cost savings. Some problems and cautions associated with its use were outlined in Faulkner and Skousen (1991). Trapzene has been tried at several AMD treatment sites (Lilly and Ziemkiewicz, 1992). Trapzene is a calcium peroxide material which oxidizes the water as well as neutralizes the acidity. Kiln dust and fly ash have been used less often because of impurities in each material which creates more sludge.

Today's AMD treatment situations often require more than one chemical or system in order to find the most cost effective method, and in order to meet more stringent effluent limits. Some sites have an array of hoses and valves connected to drums and tanks with several chemical products being dispensed (Figure 1).

Figure 1. Sometimes several chemicals are necessary for suitable treatment of AMD. This site required the addition of an acid neutralizing reagent and also a flocculant to aid in precipitation of the metals.

Numerous products are available for water treatment and the selection of the appropriate product, its specific role or function, and its cost should be considered carefully.

Metal Sludge Precipitation

Once metal sludges are formed by the addition of alkaline reagents, adequate retention time in a settling basin is necessary for metal hydroxide precipitation. In areas where water retention time in a pond is insufficient due to high flow or pond size constraints, a variety of chemicals (coagulants, flocculants and oxidants) are available to improve the settling efficiency of metal flocs in retention ponds.

Coagulation and Flocculation

Coagulation and flocculation are terms that refer to two different processes to facilitate colloid settling in water. Coagulation reduces the net electrical repulsive forces at particle surfaces, thereby promoting consolidation of small particles into larger particles. These larger particles are then able to settle.

Flocculation aggregates or combines small particles by bridging the space between particles with chemicals. Bridging occurs when segments of a polymer chain adsorb suspended particles causing larger particles. Both processes result in the formation of larger particles which promote precipitation (Figure 2).

Aluminum sulfate (alum) is the standard coagulant used in water treatment. It reacts with alkalinity in the water to form aluminum hydroxide flocs which attract other metals for precipitation. Ferrous sulfate also reacts with alkalinity but is slower reacting than alum. Ferric sulfate coagulates particles over a larger pH range than ferrous sulfate and the precipitate is a heavy, quick-settling floc. Ferric chloride is more frequently used as an oxidant but reacts similarly as ferrous sulfate. Sodium aluminate is alkaline instead of acidic like the other coagulants. The limited use of sodium aluminate is due to its high cost.

Activated silica has been used as a flocculant since the 1930's to strengthen flocs and to reduce the potential of deterioration. The resulting floc with silica is larger, denser, faster-settling, and more stable. Clays and metal hydroxides are also called weighing agents so when added to water they add bulk to the water enhancing floc formation.

Naturant flocculants are used only in specialized situations. They are expensive and usually used when specific water parameters or effluent limits must be met. They have not been used in AMD treatment situations to this date.

Synthetic flocculants are a recent and popular addition to the field of water treatment. These flocculants are also sometimes called polyelectrolytes and are extremely large molecules that, when dissolved in water, produce highly-charged ions. Anionic polymers dissolve to form negatively-charged ions, and are used to remove positively-charged solids. The reverse occurs with cationic flocculants. Nonionic polymers or polyampholytes are neutral but when dissolved in water release both positively- and negatively-charged ions. Compared with other mineral and natural flocculants, the synthetic polymers are needed in much smaller quantities. Synthetic flocculants may be added to water as a liquid, or more commonly, placed in water as a solid ("floc" logs).

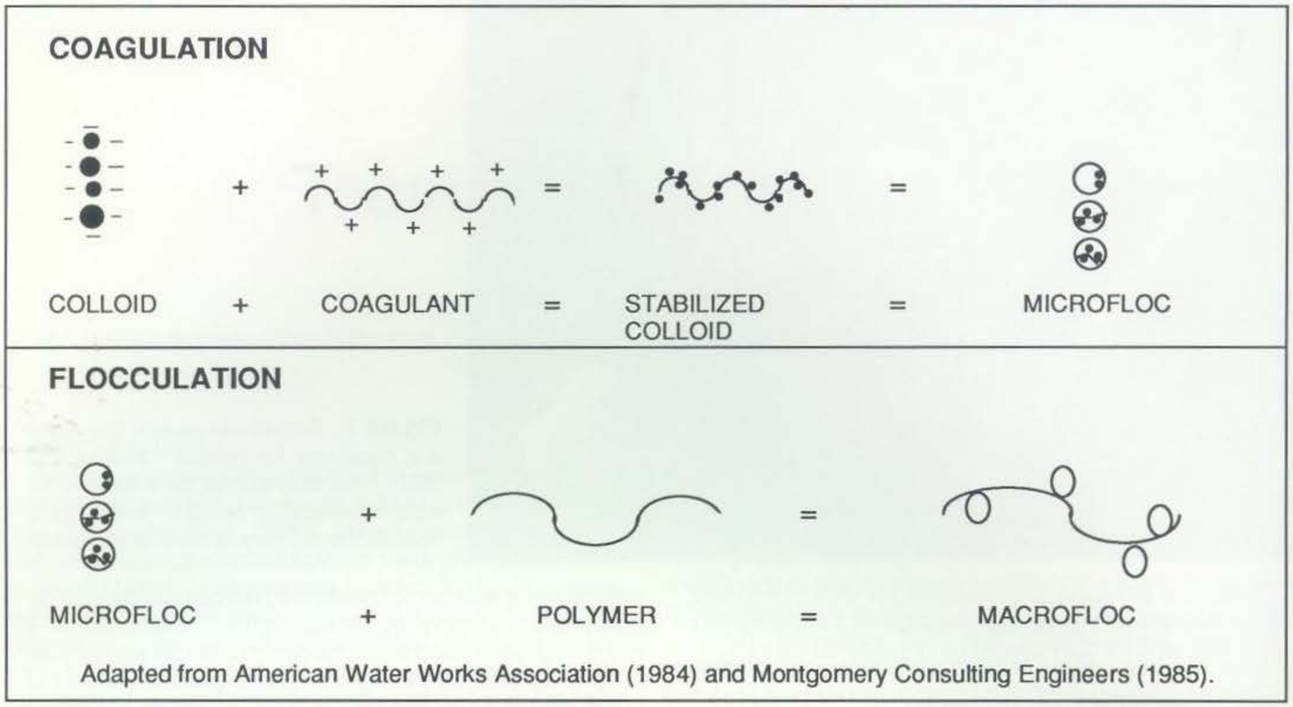

Figure 2. Coagulation is the process of reducing the net electrical repulsive forces at particle surfaces causing consolidation into larger particles. Flocculation is the process of bridging small particles into larger particles. Both processes promote larger particle formation to enhance settling efficiency.

Figure 3. Ultrion is a product that oxidizes metals and also promotes coagulation of particles for settling.

Oxidants

Aeration is the process of introducing air into water. Oxidation occurs when oxygen in air combines with metals in the water. Once oxidized, substances such as iron and manganese come out of solution and precipitate at neutral pH (7 to 8) versus higher water pH (9 to 12) when oxidation levels are lower. For this reason, oxidation is a major limiting factor in the efficiency of many AMD treatment systems. In most cases, chemical treatment costs could be reduced substantially if aeration and oxidation were incorporated or improved in the treatment system.

Oxidants aid in the completion of the oxidation process to enhance metal hydroxide precipitation and reduce sludge volume. Oxygen can be used as an oxidant but we are unaware of anyone actually bubbling oxygen into AMD. More commonly, the hypochlorite products and hydrogen peroxide are used and have demonstrated very effective oxidation. Potassium permanganate is also an effective oxidant and used on many sites where extra oxidation is needed. Ultrion oxidizes metals and speeds up coagulation of metal hydroxides (Figure 3).

Case Studies

Case #1 - A mine in northern West Virginia originally used only anhydrous ammonia for acid neutralization and metal precipitation. The water being treated has a flow of 125 to 400 gpm, 2.5 pH, 4,000 mg/l acidity, and 3,200 mg/l iron. Using only anhydrous, the cost of water treatment averaged $12,000 per month. Also the ponds had to be pumped and cleaned 5 days a week.

The company later decided to use anhydrous and hydrogen peroxide together. Currently, the total cost of both chemicals is $11,000 per month and the ponds are only pumped 2 or 3 days per week. Using both chemicals reduced overall chemical usage, and pond cleaning frequency and associated labor costs were decreased (cost estimates are not available for sludge removal). The metal flocs currently produced with both products precipitate faster and are denser. Dissolved iron (reduced Fe) is less than 3 mg/l after peroxide treatment.

Case #2 - A sealed deep mine in southern West Virginia produces a drainage of 200 to 500 gpm, 6.5 pH, no acidity, and 30 to 50 mg/l iron in the ferric form. Raising the pH to higher levels had little effect on ferric iron precipitation and pond retention time was insufficient for the iron to precipitate on its own. A coagulant and flocculant mixture was selected (NALCO's 7883 (Ultrion) or Stockhausen's 190 coagulant along with NALCO's 8877 or Stockhausen's 262 flocculant) in order to meet the iron effluent limitation.

A cost evaluation showed that ferrous iron treated by acid neutralization chemicals vs ferric iron treated by coagulants/flocculants were almost equivalent (with costs of ammonia at $.28/lb. and 20% sodium hydroxide at $.50/gal). A positive aspect with regard to the coagulant/flocculant treatment was a reduction in sludge volume. Conversely, higher costs were associated with increased labor for mixing two products and maintaining chemicals during winter.

Summary

As can be seen from Tables 3 and 4, many chemicals are available for treatment of AMD. Bench testing in a laboratory will indicate the level of treatment that a certain chemical may induce on a specific AMD. The Jar Test is also an effective way of determining the right chemical or combination of chemicals which will treat the water and settle the flocs. Jar tests can be done very simply with quart canning jars and stirring devices. Experiments may be conducted to determine the effectiveness of various acid neutralizers and coagulants/flocculants, optimum dosage for precipitation, optimum pH for floc generation, and the most effective order in which to add various chemicals. However, a field trial is recommended to demonstrate treatment during real conditions. A product may look expensive on paper but it may be diluted in the field or modified by physical application to enhance treatment and greatly reduce costs associated with water treatment.

Contacts

American Cyanamid (CYTEC)	304-744-3454
Dubois Chemical Co.	800-438-2647
Dupont Chemical Co.	919-282-9772
Envirotech	304-855-4437
FMC Corp.	800-523-5005
MineTek, Inc.	304-253-2923
Nalco Chemical Co.	304-768-7388
Stockhausen Chemical Co.	800-768-7388

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Table 1. Costs of alternative technologies to treat acid mine drainage in West Virginia, 5-year operation period.

Flow and Acidity Conditions				
Flow (gpm)	**50**	**1000**	**250**	**1000**
Acidity (mg/l)	**100**	**100**	**500**	**2500**
Chemical				
Soda Ash				
reagent costs	$ 3,248	$64,955	$ 81,194	$1,623,876
repair costs	0	0	0	0
annual labor	14,040	14,040	14,040	14,040
installation costs	229	229	229	229
salvage value	0	0	0	0
NPV	73,051	332,985	401,3886,	899,728
Annualized cost	**$ 17,343**	**$ 79,049**	**$ 95,288**	**$1,637,971**
Ammonia				
reagent costs	$ 1,116	$ 22,323	$ 27,904	$ 558,071
repair costs	495	495	495	495
tank rental	480	1,200	1,200	1,200
annual labor	7,020	7,020	7,020	7,020
electricity	600	600	600	600
installation costs	5,936	6,357	6,357	6,357
salvage value	0	0	0	0
NPV	46,843	139,627	163,135	2,396,392
Annualized cost	**$ 11,120**	**$ 33,147**	**$ 38,728**	**$ 568,895**
Caustic Soda				
reagent costs	$ 3,852	$ 77,036	$ 96,295	$1,925,891
repair costs	0	0	0	0
annual labor	7,020	7,020	7,020	7,020
installation costs	283	5,478	5,478	5,478
salvage value	0	0	0	0
NPV	46,079	359,551	440,676	8,147,602
Annualized cost	**$ 10,939**	**$ 85,356**	**$104,615**	**$1,934,211**
Hydrated Lime				
reagent costs	$ 526	$ 10,527	$ 13,158	$ 263,169
repair costs	1,000	3,100	3,500	10,500
annual labor	6,500	11,232	11,232	11,232
electricity	3,500	11,000	11,000	11,000
installation costs	38,400	102,000	106,000	204,000
salvage value	5,750	6,500	7,500	25,000
NPV	82,656	248,193	264,216	1,431,760
Annualized cost	**$ 19,622**	**$ 58,920**	**$ 62,724**	**$ 339,895**

Table 2. Costs of alternative technologies to treat acid mine drainage in West Virginia, 20-year operation period.

Flow and Acidity Conditions				
Flow (gpm)	**50**	**1000**	**250**	**1000**
Acidity (mg/l)	**100**	**100**	**500**	**2500**
Chemical				
Soda Ash				
reagent costs	$ 3,248	$ 64,955	$ 81,194	$1,623,876
repair costs	0	0	0	0
annual labor	14,040	14,040	14,040	14,040
installation costs	229	229	229	229
salvage value	0	0	0	0
NPV	198,518	906,296	1,092,553	18,787,000
Annualized cost	**$ 17,308**	**$ 79,015**	**$ 95,254**	**$1,637,936**
Ammonia				
reagent costs	$ 1,116	$ 22,323	$ 27,904	$ 558,071
repair costs	495	495	495	495
tank rental	480	1,200	1,200	1,200
annual labor	7,020	7,020	7,020	7,020
electricity	600	600	600	600
installation costs	5,936	6,357	6,357	6,357
salvage value	0	0	0	0
NPV	119,397	371,316	435,326	6,516,302
Annualized cost	**$ 10,410**	**$ 32,373**	**$ 37,954**	**$ 568,121**
Caustic Soda				
reagent costs	$ 3,852	$ 77,036	$ 96,295	$1,925,891
repair costs	0	0	0	0
annual labor	7,020	7,020	7,020	7,020
installation costs	283	5,478	5,478	5,478
salvage value	0	0	0	0
NPV	124,981	969,590	1,190,488	22,175,851
Annualized cost	**$ 10,896**	**$ 84,533**	**$103,792**	**$1,933,389**
Hydrated Lime				
reagent costs	$ 526	$ 10,527	$ 13,158	$ 263,169
repair costs	1,000	3,100	3,500	10,500
annual labor	6,500	11,232	11,232	11,232
electricity	3,500	11,000	11,000	11,000
installation costs	38,400	102,000	106,000	204,000
salvage value	0	0	0	0
NPV	170,606	513,297	552,070	3,597,957
Annualized cost	**$ 14,874**	**$ 44,752**	**$ 48,132**	**$ 313,686**

Table 3. Chemicals for acid neutralization and chemicals used for coagulation, flocculation, and oxidation.

NAME	CHEMICAL FORMULA	COMMENTS
Acid Netralization		
Limestone	$CaCO_3$	Used in anaerobic situations (anoxic limestone drains).
Hydrated Lime	$Ca(OH)_2$	Requires extensive mixing.
Pebble Quick Lime	CaO	Very reactive, needs metering equipment.
Soda Ash Briquettes	Na_2CO_3	System for remote locations.
Caustic Soda	$NaOH$	Very soluble, comes as a solid in drums or briquettes, or as a 20% or 50% liquid.
Potassium Hydroxide	KOH	Similar to caustic.
Magnesium Hydroxide	$Mg(OH)_2$	Similar to hydrated lime.
Magna Lime	MgO	Similar to Pebble lime.
Ammonia	NH_3 or NH_4OH	Very reactive and soluble. Can be also purchased as aqua ammonia.
Trapzene	CaO_2	Used as a neutralizer and oxidant. Available as a powder or as briquettes.
Kiln Dust	CaO, $Ca(OH)_2$	Waste product of limestone industry. Active ingredient is CaO with various amounts of other constituents.
Fly Ash	$CaCO_3$, $Ca(OH)_2$	Neutralization value varies with each product.
Coagulants		
Alum (aluminum sulfate)	$Al_2(SO_4)_3$	Acidic, forms $Al(OH)_3$.
Copperas (ferrous sulfate)	$FeSO_4$	Acidic, usually slower reacting than alum.
Ferric Sulfate	$Fe_2(SO_4)_3$	Ferric products react faster than ferrous.
Ferric Chloride*	$FeCl_3$	Also used as an oxidant.
Sodium Aluminate	$NaAlO_2$	Alkaline coagulant.

*Other coagulants are magnesium chloride, aluminum chloride, calcium chloride. These chloride compounds are also oxidants.

NAME	CHEMICAL FORMULA	COMMENTS
Flocculants		
Mineral Flocculants		
- Activated Silica	Na_4SiO_4	A negative charge on surface. Attracts cations and metal hydroxides.
- Clays	bentonite	Negatively-charged surface.
- Metal Hydroxides	$Al(OH)_x$, $Fe(OH)_x$	Usually a positively-charged surface.
Natural Flocculants		
- Starch Derivatives	corn starches	Gelatinous materials.
- Polysaccharides	Guar gums	Sticky substances.
- Sodium Alginates	$C_6H_7O_6Na$	Food thickeners.
Synthetic Flocculants		
- Anionic		Negatively-charged surface.
- Cationic		Positively-charged surface.
- Polyampholytes		Have both positive and negative charges on surface based on pH.
Oxidants		
Oxygen	O_2	The ultimate oxidant.
Chlorine Compounds	Cl_2	
- Calcium Hypochlorite	$Ca(ClO)_2$	Strong oxidant.
- Sodium Hypochlorite	$NaClO$	Strong oxidant.
- Calcium Chloride	$CaCl_2$	Also a coagulant.
- Sodium Chloride	$NaCl$	Rock salt.
- Ferric Chloride	$FeCl_2$	Also a coagulant.
Peroxide Materials		
- Calcium Peroxide	CaO_2	Trapzene, an acid neutralizer.
- Hydrogen Peroxide	H_2O_2	Strong oxidant.
Potassium permanganate	$KMnO_4$	Very effective, commonly used.

Table 4. Some brand name chemical products with their classification used in AMD treatment.

	Name	Classification	Comments
NALCO	Ultrion (7883)	Oxidizer/Coagulant	Settles clays/solids.
	7884, 7885, 8887	Flocculants	Settles metal flocs.
	7886	Neutralizer/Coagulant	Applied to alkaline water with Fe
Stockhausen	CM-190, CM-191	Oxidizer/Coagulant	Settles metal flocs.
	CM-196	Flocculant	Settles flocs and clays.
MineTek	Gelfloc	Flocculant	Log-type, settles floc and solids.
DuBois	Mine Guard 200	Neutralizer	NaOH and KOH, freezeproof.
	Coagulite 200, 222, 300	Coagulants	Settles solids.
	Floculite 551, 552	Flocculants	Anionic, settles flocs.
American Cyamamid	1203, 1206	Flocculants	Anionic, settles flocs.
FMC	Calcium peroxide	Oxidant/Neutralizer	Removes metals.
FMC and DuPont	Hydrogen peroxide	Oxidant	
	Calcium/Sodium Hypochlorite	Oxidant	
	Calcium/Ferric/Sodium Chloride	Oxidant/Coagulant	
	Potassium Permanganate	Oxidant	

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