4.0 Active Treatment Technologies

Active treatment systems involve treating mine drainage with alkaline chemicals to raise water pH, neutralize acidity and precipitate metals. Although effective, active treatment is expensive when the cost of equipment, chemicals, and manpower are considered (Skousen et al. 1990). Chemical treatment may also be a long term, and possibly never-ending liability. If AMD problems develop during mining or after reclamation, a plan to treat the discharge must be developed. Treatment of AMD includes neutralization of acidity and precipitation of metal ions to meet the relevant effluent limits (U.S. Environmental Protection Agency 1982). A variety of alternative treatment methods can be employed to meet the limits specified.

In order for an operator to make a selection of an active treatment system, he must determine the raw water's flow rate, pH, total suspended solids, acidity/alkalinity in mg/L as $CaCO_3$, Fe and Mn concentrations, the receiving stream's flow and designated use, availability of electrical power, the distance from chemical addition to where the water enters a settling pond, and the volume and configuration of a settling pond. After evaluating these variables over a period of time, the operator can consider the economics of different chemicals and alternative active treatment systems. Most active chemical treatment systems consist of an inflow pipe or ditch (sometimes a raw water storage pond and aerator for large flows), a storage tank or bin to hold the treatment chemical, a means of controlling the chemical application, a settling pond to capture precipitated metal oxyhydroxides, and a discharge point (Figure 4.1). The latter is the point at which NPDES compliance is monitored. The amount of $CaCO_3$ (tons/yr) needed for neutralization can be calculated by multiplying the flow (gpm), the AMD's acidity (mg/L as $CaCO_3$), and a factor of 0.0022 (conversion of units to get acid load in tons/yr). The product is the tons of $CaCO_3$ required to neutralize the acid load per year. This value (tons of $CaCO_3$/yr) can then be multiplied by a conversion factor for each chemical to determine the amount of chemical needed (Table 4.1).

4.1 Aeration/Oxidation

Aeration is the process of introducing air into water. Oxidation occurs when oxygen in air combines with metals in the water. If the water is oxidized, metals generally will

precipitate at lower pH values. However, only about 10 mg/L O_2 can dissolve in water, thereby limiting the oxidizing effects of water not directly exposed to air. For this reason, aeration of water can promote oxidation in many water treatment systems. If aeration and oxidation were incorporated or improved in the treatment system, chemical treatment efficiency would increase and costs could be reduced.

Mechanical surface aeration introduces atmospheric oxygen into water by rotating blades positioned below the water in an aeration basin (U.S. Environmental Protection Agency 1983). The turbulence created by the aerator disperses air bubbles and keeps the iron floc in suspension. Oxygen is absorbed by the water and can then react with ferrous iron and other reduced compounds in the water. Different kinds of aerators may be used. Mechanical surface aerators are the most common and are frequently found at large hydrated lime treatment plants where large volumes of highly acidic and reduced water are treated. In-line aerators use high velocity spray nozzles to improve air contact with water. Simpler aeration systems use gravity to cascade water over rocks (falls or stairsteps) or splash blocks may be installed in open channels or flumes. The effectiveness of aeration in oxidizing Fe^{2+} can depend on pH because the inorganic oxidation reaction is slow below about pH 5. Therefore, oxidation is usually combined with addition of base to neutralize pH. Some waters may have net alkalinity and high enough pH that only aeration is needed to precipitate Fe and produce a near-neutral solution.

Acid Mine Drainage Treatment System

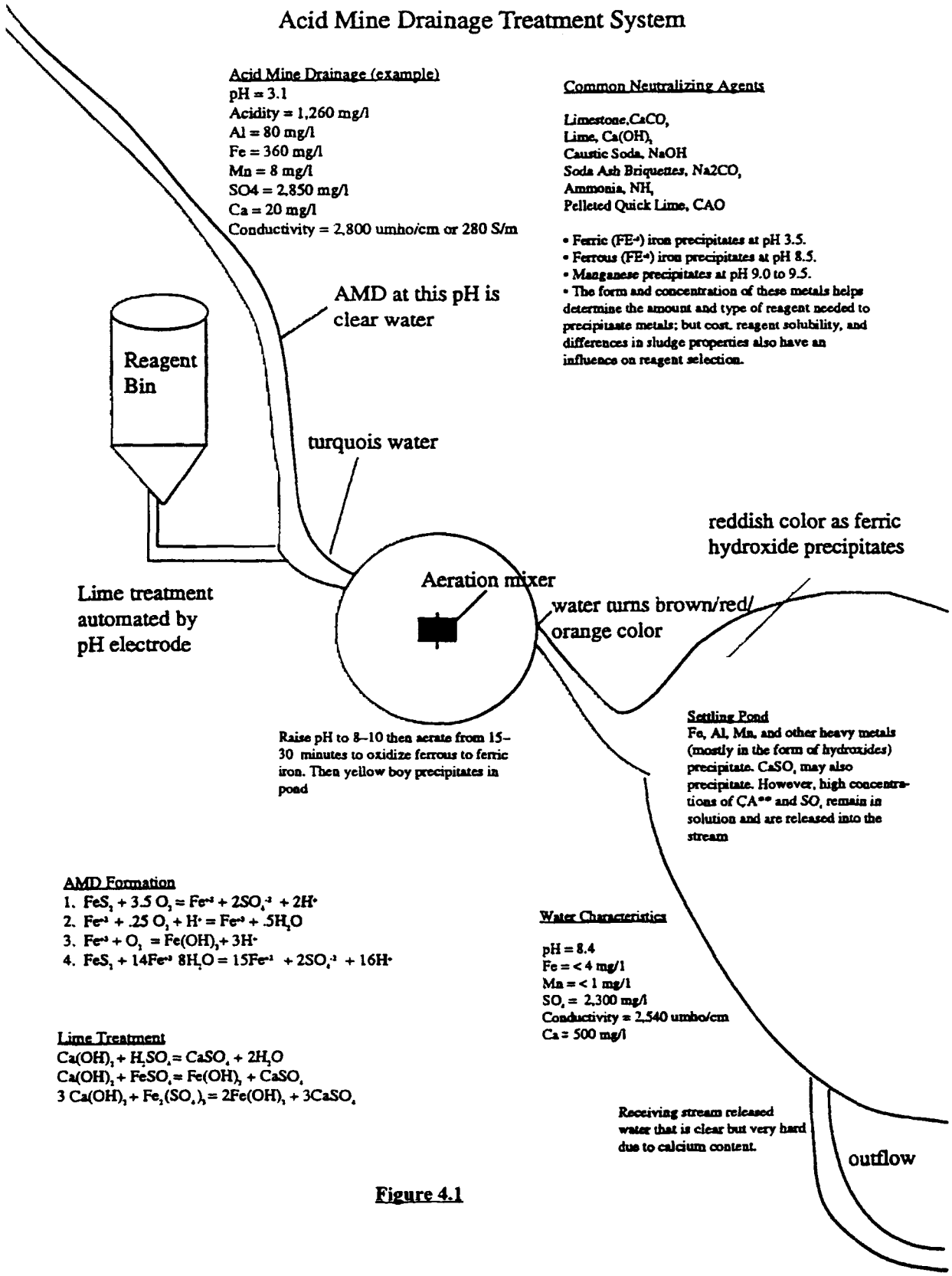

Figure 4.1

Table 4.1. Chemical compounds used in AMD treatment.

Common Name	Chemical Name	Formula	Conversion Factor[1]	Neutralization Efficiency[2]	1996 Cost[3] $ per ton or gal. Bulk	<Bulk
Limestone	Calcium carbonate	$CaCO_3$	1.00	50%	$ 10	$ 15
Hydrated Lime	Calcium hydroxide	$Ca(OH)_2$	0.74	95%	$ 60	$100
Pebble Quicklime	Calcium oxide	CaO	0.56	90%	$ 80	$240
Soda Ash	Sodium carbonate	Na_2CO_3	1.06	60%	$200	$320
Caustic Soda (solid)	Sodium hydroxide	NaOH	0.80	100%	$680	$880
20% Liquid Caustic	Sodium hydroxide	NaOH	784	100%	$0.46	$0.60
50% Liquid Caustic	Sodium hydroxide	NaOH	256	100%	$1.10	$1.25
Ammonia	Anhydrous ammonia	NH_3	0.34	100%	$300	$680

[1] The conversion factor may be multiplied by the estimated tons of acid/yr to get tons of chemical needed for neutralization per year. For liquid caustic, the conversion factor gives gallons needed for neutralization.

[2] Neutralization Efficiency estimates the relative effectiveness of the chemical in neutralizing AMD acidity. For example, if 100 tons of acid/yr was the amount of acid to be neutralized, then it can be estimated that 78 tons of hydrated lime would be needed to neutralize the acidity in the water (100(0.74)/0.95).

[3] Price of chemical depends on the quantity being delivered. Bulk means delivery of chemical in a large truck, whereas <Bulk means purchased in small quantities. Liquid caustic prices are for gallons. Others are in tons.

Oxidants (Table 4.2) are sometimes used to aid in the completion of the oxidation process to enhance metal hydroxide precipitation and reduce metal floc volume. The hypochlorite products, hydrogen peroxide, and potassium permanganate are used in AMD situations and have demonstrated very effective oxidation. Calcium peroxide (Trapzene) has been shown to oxygenate AMD as well as neutralize acidity (Lilly and Ziemkiewicz 1992).

Table 4.2. Chemicals for acid neutralization, coagulation/flocculation, and oxidation

NAME	CHEMICAL FORMULA	COMMENTS
Acid Neutralization		
Limestone	$CaCO_3$	Used in anoxic limestone drains and open limestone channels.
Hydrated Lime	$Ca(OH)_2$	Cost effective reagent, but requires mixing.
Pebble Quick Lime	CaO	Very reactive, needs metering equipment.
Soda Ash Briquettes	Na_2CO_3	System for remote locations, but expensive.
Caustic Soda	$NaOH$	Very soluble, comes as a solid in drums, beads, or flakes, or as a 20% or 50% liquid. Cheaper in the liquid form.
Ammonia	NH_3 or NH_4OH	Very reactive and soluble; also purchased as aqua ammonia.
Potassium Hydroxide	KOH	Similar to caustic.
Magnesium Hydroxide	$Mg(OH)_2$	Similar to hydrated lime.
Magna Lime	MgO	Similar to pebble quicklime.
Calcium Peroxide	CaO_2	Used as a neutralizer and oxidant; either powder or 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/Flocculants		
Alum (aluminum sulfate)	$Al_2(SO_4)_3$	Acidic material, forms $Al(OH)_3$.
Copperas (ferrous sulfate)	$FeSO_4$	Acidic material, usually slower reacting than alum.
Ferric Sulfate	$Fe_2(SO_4)_3$	Ferric products react faster than ferrous.
Sodium Aluminate	$NaAlO_2$	Alkaline coagulant.
Anionic Flocculants		Negatively-charged surface.
Cationic Flocculants		Positively-charged surface.
Polyampholytes		Both positive and negative charges on surface based on pH.
Oxidants		
Calcium Hypochlorite	$Ca(ClO)_2$	Strong oxidant.
Sodium Hypochlorite	$NaClO$	Also a strong oxidant.
Calcium Peroxide	CaO_2	Trapzene, an acid neutralizer.
Hydrogen Peroxide	H_2O_2	Strong oxidant.
Potassium Permanganate	$KMnO_4$	Very effective, commonly used.

Case Studies:

Documented case studies are unknown at this time.

4.2 Neutralizers

Six primary chemicals have been used to treat AMD (Table 4.1). Each chemical has characteristics that make it more or less appropriate for a specific condition. The best choice among alternatives depends on both technical and economic factors. The technical factors include acidity levels, flow rate, the specific types and concentrations of metals in the water, the rate and degree of chemical treatment needed, and the desired final water quality. The economic factors include prices of reagents, labor, machinery and equipment, the number of years that treatment will be needed, sludge removal and disposal, the interest rate, and risk factors. Costs for five primary chemicals under conditions of designated flows and acidity values are presented in Table 4.3.

Enough alkalinity must be added to neutralize acid and to raise water pH to the level that dissolved metals in the water will form insoluble metal hydroxides and settle out of the water. The pH required to precipitate most metals from water ranges from pH 6 to 9. However, ferric hydroxide precipitates at about pH 3.5 and aluminum hydroxide precipitates at pH 4.5. The types and amounts of metals in the water therefore heavily influence the selection of an AMD treatment system. Ferrous iron (Fe^{2+}) precipitates as solid bluish-green ferrous hydroxide at pH $\geq$8.5. In the presence of oxygen, ferrous iron oxidizes to ferric iron (Fe^{3+}), and ferric hydroxide forms a yellowish-orange solid (commonly called yellow boy), which precipitates at pH $\geq$3.5. A more efficient way of treating high ferrous AMD is to first aerate the water (also outgassing CO_2), causing Fe to convert from ferrous to ferric, and then adding a neutralizing chemical to raise the pH to 8 to form ferric hydroxide. Aeration after chemical addition is also beneficial because ferrous iron conversion to ferric iron is pH dependent and is much more rapid at a pH of 8. Aeration before and after treatment usually reduces the amount of neutralizing reagent necessary to precipitate Fe from AMD. Aluminum hydroxide generally precipitates at pH $\geq$5.0 but also enters solution again at a pH of 9.0. Manganese hydroxide precipitation is variable due to its many oxidation states, but will generally precipitate at a pH of 9.0 to 9.5. However, a solution pH of 10.5 is sometimes necessary for complete removal of Mn. In some cases, complete Mn removal is very difficult

to attain. This high pH for Mn removal can cause Al to enter solution again. For waters with high Mn and Al, a two phase treatment system may be required. As this discussion demonstrates, the appropriate treatment chemical can depend on both the oxidation state and concentrations of metals in the AMD (U.S. Environmental Protection Agency 1983).

Interactions among metals also influence the rate and degree to which metals precipitate. For example, ferric hydroxide precipitation will largely remove Mn from the water at pH 8 due to co-precipitation, but only if the Fe concentration in the water is much greater than the Mn content (about 4 times more or greater). If the Fe concentration in the AMD is less than four times the Mn content, Mn may not be removed by co-precipitation and a solution pH of ≥ 9 is necessary to remove the Mn. Because AMD contains multiple combinations of acidity and metals, each AMD is unique and its treatment by these chemicals varies widely from site to site. For example, the AMD from one site may be completely neutralized and contain no dissolved metals at a pH of 8.0, while another site may still have metal concentrations that do not meet effluent limits even after the pH has been raised to 10.

Costs have been developed for five AMD treatment chemicals under four sets of flow (gpm) and acidity concentration (mg/L as $CaCO_3$) conditions (Table 4.3). These conditions are: (1) 50 gpm and 100 mg/L; (2) 1000 gpm and 100 mg/L; (3) 250 gpm and 500 mg/L; (4) 1000 gpm and 2500 mg/L. These conditions represent a sufficiently wide range for valid comparison of the treatment systems.

The costs for each technology were divided into two broad categories: installation cost and variable cost. Each of these can be broken down into several sub-categories. For example, installation cost includes materials, equipment, and labor. Materials consist of piping, extra material for the system foundation, and additional site preparation. Equipment includes conventional machinery and/or actual system hardware. Labor costs are based on man hours at a current union wage scale of $27 an hour. Variable cost includes reagent cost, annual labor, and maintenance. The amount of reagent was computed using acid neutralization formulas presented in Skousen and Ziemkiewicz (1996), but neutralization efficiencies were not included in the reagent calculation. Annual labor is estimated man-hours to run the system for one year multiplied by the current union scale of $27 an hour.

Other variable costs include repair costs and electricity (Phipps et al. 1991).

The prices for the reagents, equipment, and labor were based on actual costs to mining operators in West Virginia in May 1996. All dollar values are in 1996 U.S. dollars. The net present value (NPV) is the value of the total treatment system plus annual operating and chemical expenses over the specified duration of treatment. A rate of 6% per year was used to devalue the dollar during future years of the treatment period. The annualized cost was obtained by converting the total system cost (NPV) to an equivalent annual cost so that each system could be compared equally on an annual basis. The parameters used in the analysis were entered in a spreadsheet and can be varied to conform to local conditions.

Use of soda ash has the highest labor requirements (10 hours per week) because the dispensers must be filled by hand and inspected frequently (Table 4.3). Caustic soda has the highest reagent cost per mole of acid-neutralizing capacity and soda ash has the second highest. But remember, soda ash is much less efficient in treating water than caustic. Hydrated lime treatment systems have the highest installation costs of the five technologies because of the need to construct a lime treatment plant and install a pond aerator. However, the cost of hydrated lime is low. The combination of high installation costs and low reagent cost make hydrated lime systems particularly appropriate for long term treatment of high flow (>100 gpm) and high acid situations.

For a five-year treatment period, ammonia has the lowest annualized costs for the low flow/low acid situation (Table 4.3). Pebble quicklime is similar to ammonia in cost, and caustic is third. Soda ash is fourth because of its high labor and reagent costs, and hydrated lime is last because of its high installation costs. With the intermediate flow and acid cases, ammonia is the most cost effective, with pebble quicklime second. Hydrated lime and soda ash were next. Caustic soda is the most expensive alternative with these intermediate conditions. In the highest flow/acidity category, pebble quicklime and hydrated lime are clearly the least costly treatment systems, with an annualized cost of $260,000 less than ammonia, the next best alternative. The use of soda ash and caustic is prohibitively expensive at high flow and high acidity.

Table 4.3. Costs in 1996 of five chemicals to treat acid mine drainage in West Virginia. The analysis is based on a five-year operation period and includes chemical reagent costs, installation and maintenance of equipment, and annual operating costs. The "<Bulk" chemical prices in Table 1 were used to calculate the reagent costs for only the 50 gpm flow. The "Bulk" prices were used for higher flows. Neutralization efficiencies were not included in the reagent cost calculation.

Flow and Acidity Conditions				
Flow, gpm (L/min)	50 (189L)	1000 (3780L)	250 (945L)	1000 (3780L)
Acidity, mg/L as $CaCO_3$	100	100	500	2500
Chemical				
Soda Ash				
reagent costs	$3,731	$44,000	$58,300	$1,166,000
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
Net present value	75,052	244,679	245,774	4,911,804
Annualized cost	**$17,817**	**$58,086**	**$58,346**	**$1,166,046**
Ammonia				
reagent costs	$2,543	$22,440	$28,050	$561,000
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	1,936	6,357	6,357	6,357
salvage value	0	0	0	0
Net present value	48,547	139,117	162,749	2,407,725
Annualized cost	**$11,525**	**$33,026**	**$38,636**	**$571,586**
Caustic Soda (20% Liquid)				
reagent costs	$5,174	$79,341	$99,176	$1,983,520
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
Net present value	51,601	368,398	451,950	8,389,433
Annualized cost	**$12,250**	**$87,457**	**$107,292**	**$1,991,636**

Pebble Quicklime				
reagent costs	$1,478	$9,856	$12,320	$246,400
repair costs	500	2,500	2,500	10,000
annual labor	6,500	11,200	11,200	11,200
electricity	0	0	0	0
installation costs	16,000	80,000	80,000	120,000
salvage value	0	5,000	5,000	20,000
Net present value	49,192	162,412	172,790	1,127,220
Annualized cost	**$11,678**	**$38,556**	**$41,020**	**$267,600**
Hydrated Lime				
reagent costs	$814	$9,768	$12,210	$244,200
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	58,400	102,000	106,000	200,000
salvage value	5,750	6,500	7,500	25,000
Net present value	94,120	228,310	242,809	1,313,970
Annualized cost	**$22,344**	**$54,200**	**$57,642**	**$311,932**

4.2.1 Calcium Carbonate

Limestone ($CaCO_3$) has been used for decades to raise pH and precipitate metals in AMD. It has the lowest material cost and is the safest, easiest to handle of the AMD chemicals, and produces the most compact and easy to handle sludge material. Unfortunately, its successful application has been limited because of its low solubility especially in cold weather, its tendency to develop an external coating, or armor, of ferric hydroxide when added to AMD, and its inability to raise pH to sufficient levels for Mn removal. In cases where pH is low and mineral acidity is also relatively low (low metal concentrations), finely-ground limestone may be dumped in streams directly or the limestone may be ground by water-powered rotating drums and metered into the stream. Limestone has also been used to treat AMD in anaerobic (anoxic limestone drains, section 5.3) and aerobic environments (open limestone channels, section 5.6). These latter two techniques are especially useful where compliance with NPDES discharge limits is not required during all times of the year (like Fe and Mn removal to <2 mg/L). They are both being utilized by specialists in abandoned mine land reclamation projects and by operators wishing to reduce chemical treatment costs and improve compliance (Faulkner 1996).

Case Studies:

Rotary drum stations have been used to grind limestone into a powder before introduction into streams and have been constructed in West Virginia for treating AMD streams (Zurbuch 1984). A six-drum station was constructed in 1994 on the Blackwater River at a cost of $900,000, and it introduces about 90 grams/sec of ground limestone to the stream or about 8.6 Mg/day (9.5 tons/day), at a dosage of 28 grams per cubic meter water flow (28 mg/L). The drum station uses about 1800 Mg (2,000 tons) of limestone in an average river flow year at a cost of $12.60/Mg ($14/ton) of limestone delivered. Limestone introduction into the river by rotary drums has restored 22 km (14 miles) of the Blackwater River below the drum station and maintained the pH above 6.0. A fish survey in 1995 showed 17 species, including rainbow and brown trout, inhabiting the river.

The diversion well (see section 5.8) uses water action to aid limestone dissolution. The flow rate must be rapid enough to agitate the bed of limestone particles and the acid water dissolves the limestone for alkalinity generation. Metal flocs produced by hydrolysis and neutralization reactions are flushed through the system by water flow out the top of the well and the churning action of the fluidized limestone also helps remove Fe oxide coatings so that fresh limestone surfaces are always exposed. Metal flocs suspended in the water are settled in a downstream pond.

Introduction of limestone sand into the stream channel to treat AMD has also been used in West Virginia (see section 5.9).

4.2.2 Calcium Oxide

Pebble quicklime, CaO, has been recently used in conjunction with a water wheel application system (Jenkins and Skousen 1993). The amount of chemical applied is dictated by the movement of the water wheel, which causes a screw feeder to dispense the chemical. The hopper and feeder can be installed in less than an hour. This system was initially used for small and/or periodic flows of high acidity because calcium oxide is very reactive. Recently, however, water wheels have been attached to large bins or silos for continuous treatment of high flow/high acidity situations. To estimate the potential treatment cost of using pelleted quicklime on a site, about two pounds of quicklime (CaO) neutralizes the same acidity as one gallon of 20% caustic (NaOH), or one pound of ammonia.

Case Studies:

One operator in northern West Virginia calculated a water wheel unit paid for itself in just 105 days of operation at their site. This calculation included the cost of the machine, labor, installation, and purchasing and transporting the material. Caustic soda was used previously to treat an average flow of 100 L/min and 1100 mg/L of acidity (as $CaCO_3$) at a cost of $245 per day, or about $80,000 per year. With the water wheel, the same water was treated at a cost of about $75 per day or about $28,000 per year, a cost savings of 70%. Three other sites showed between 62 and 82% cost savings when using quicklime vs caustic (Jenkins and Skousen 1993).

4.2.3 Kiln Dust

See section 2.2.4.

4.2.4 Trapzene

Trapzene (CaO_2) is the trade name for a specially formulated compound of calcium peroxide. It is used as an oxidant as well as an acid neutralizer. It seems to be especially useful for Mn oxidation and removal (Lovett and Ziemkiewicz 1991).

Case Studies:

Lilly and Ziemkiewicz (1992) report successful treatment of Mn at several sites. Water pH was raised from 3.5 to 7.5 with Trapzene application and metals (Fe, Mn, and Al) were removed at a lower pH than had been achieved with liquid NaOH. Sludge volumes were also reduced using Trapzene compared to NaOH.

4.2.5 Calcium Hydroxide

Hydrated lime, $Ca(OH)_2$, is the most commonly-used chemical for treating AMD. It is sold as a powder that tends to be hydrophobic, and extensive mechanical mixing is required to disperse it in water. Hydrated lime is particularly useful and cost effective in large flow, high acidity situations where a lime treatment plant with a mixer/aerator is constructed to help aerate the water and mix the chemical with the water (Skousen and Ziemkiewicz 1996).

Hydrated lime can be purchased in 22-kg (50-pound) bags or in bulk. Bulk lime is preferred by mine operators due to cost and handling advantages. It can be delivered by barge, truck, or train to many sites and handled pneumatically. Proper storage of hydrated

lime is important in order to maintain its flow characteristics and thus ensure efficient use. The appropriate silo volume depends on the daily lime requirement, but should be large enough to hold the amount of hydrate needed to last between scheduled deliveries with a safety margin to cover periodic unexpected delivery delays. The length of time that the system will be in operation is a critical factor in determining the annual cost of a lime treatment system due to the large initial capital expenditure that can be amortized over time. The topography of the site is also an important cost factor with design and structural costs increasing as the slope of the site increases.

Case Studies:

Central Ohio Coal Company switched from a 20% caustic solution to high calcium $Ca(OH)_2$. The raw water (3800 L/min, pH 2.6, Fe 750 mg/L, Mn 10 mg/L, acidity 2500 mg/L as $CaCO_3$, sulfate 4,400 mg/L) is treated with $Ca(OH)_2$, then aerated, and the solids are settled in a sedimentation basin. The resulting lime sludge settles relatively quickly and the final settled volume is less than that of the caustic sludge. Final water quality is within effluent limits and can be discharged. Approximately $220,000 per yr is saved by using $Ca(OH)_2$ vs 20% caustic, and this cost savings include the price of chemical, maintenance costs, and sludge disposal (Colson 1997).

4.2.6 Magna Lime

This chemical, a mixture of calcium and magnesium oxide, is dispensed with a water wheel similar to pebble quicklime. Kinetics of dissolution for calcium-magnesium oxide is slightly slower than straight CaO. Depending on the source of the material, purchase of magna lime may be economical and may provide similar or better treatment efficiency for some AMD sources. It may also be used as an alkaline amendment to acid-producing materials (see section 2.2.2).

4.2.7 Caustic Soda

Caustic soda (NaOH) is often used in remote locations (e.g., where electricity is unavailable), and in low flow (<100 gpm), high acidity situations. It is commonly the chemical of choice if Mn concentrations in the AMD are high because caustic can raise water pH to 13.0. The system can be gravity fed by dripping liquid caustic directly into the AMD. Caustic is very soluble in water, disperses rapidly, and raises the pH of the water quickly. Caustic

should be applied at the surface of ponded water because the chemical is more dense than water and sinks. Mixing the chemical with AMD tends to improve its neutralization slightly. The major drawbacks of using liquid caustic for AMD treatment are high cost, dangers in handling the chemical, and high sludge volumes.

Tanks housing caustic soda can range in volume from 1900 to 30,000 L (500 to 8,000 gallons). Large tanks are usually placed on a cement platform to limit the tendency for the tank to slip or twist as the ground swells and contracts with temperature changes. The discharge line is fixed at the bottom of the tank and transports the caustic solution to the seep, ditch, or pond. The rate of flow is controlled by a gate valve placed at the end of the discharge line.

Liquid caustic can freeze during winter months, but there are several options available to deal with the freezing problem. These include burying the caustic tank, installing a tank heater, switching from a 50% to a 20% caustic solution, using a freeze-proof solution containing some potassium hydroxide (KOH), and utilizing solid caustic. Burying a caustic tank is expensive because the operator must then comply with stringent EPA underground storage tank regulations. Heaters must be replaced often because of the corrosive effects of caustic. Of these options, the three most economical solutions are switching to the 20% caustic solution, adding some KOH, and switching to solid caustic. Switching from a 50% to a 20% caustic solution lowers the freezing point from 12°C (54°F) to about -37°C (-25°F). The addition of KOH (35% of the solution) also lowers the freezing point. Solid caustic, which may be delivered in 32-kg (70-pound) drums, beads, or flakes, has been used with good success. It is possible to regulate the rate at which solid caustic dissolves by metering the flow of water into the drum. Solid caustic can be used to make liquid caustic. A 20% solution of caustic requires 0.22 kg of solid caustic to be dissolved in a L of water (1.8 pounds per gallon). Making a liquid solution from solid caustic is not cost effective when liquid caustic can be purchased, but the use of solid caustic for treating AMD is cost effective when compared to soda ash briquettes.

Case Studies:

Southern Ohio Coal Company uses a 50% caustic solution to treat AMD that is eventually recycled to its preparation plant after solids are settled (Colson 1997). Concerns

about the use of lime and gypsum precipitation in the return water makes caustic treatment the preferred choice over lime treatment. The raw water (11,300 L/min, pH 3.5, Fe 289 mg/L, acidity 688 mg/L as $CaCO_3$) is treated with 50% liquid NaOH, then aerated by floating aerators, and a flocculant is added to aid in solids settlement. After flocculant addition, the water and solids enter a large thickener designed to receive the high flow of water. Approximately 10% of the water treated is removed as sludge. The sludge is raked to the center of the thickener and pumped to an impoundment. Final water quality meets effluent limits (less than 1 mg/L Fe at flow rates less than 3500 L/min, and between 1 and 3 mg/L Fe at flows between 3500 to 11,500 L/min).

4.2.8 Soda Ash Briquettes

Soda ash, Na_2CO_3, is generally used to treat AMD in remote areas with low flow and low amounts of acidity and metals, but its use is declining. Selection of soda ash for treating AMD is usually based on convenience rather than chemical cost. Soda ash comes as solid briquettes and is gravity fed into water by the use of hoppers mounted over a basket or barrel. The number of briquettes to be used each day is determined by the flow and quality of water to be treated. One problem with the basket-hopper system is that the briquettes absorb moisture, causing them to expand and stick to the corners of the hopper. This hinders the briquettes from dropping into the AMD stream. For short term treatment at isolated sites, some operators use a much simpler system employing a box or barrel with holes to allow water inflow and outflow. The operator fills the box or barrel with briquettes on a regular basis and places the box or barrel in the flowing water. This system offers less control of the amount of chemical used.

Case Studies:

Numbers have not been generated on specific sites.

4.2.9 Ammonia

Ammonia, the common term for anhydrous ammonia (NH_3), is a material that must be handled carefully (Hilton 1990). A gas at ambient temperatures, ammonia is compressed and stored as a liquid. It dissolves readily when released into water. It behaves as a strong base and can easily raise the pH of receiving water to 9.2. At pH 9.2, it buffers the solution to further pH increases. Injection of ammonia into AMD is one of the quickest ways to raise

water pH. It should be injected into flowing water at the entrance of the pond to ensure good mixing because ammonia is lighter than water. The most promising aspect of using ammonia for AMD treatment is its cost, especially compared to caustic soda. A cost reduction of 50% to 70% can be realized when ammonia is substituted for caustic if the target pH for metal precipitation is <9.2 (Skousen et al. 1990).

Major disadvantages of using ammonia include: 1) hazards associated with handling the chemical, 2) potential increases of nitrate and acid downstream due to biological reactions, and 3) the consequences of excessive application rates (Faulkner 1990). Specialized training and experience are important for the safe use of ammonia. Operators using ammonia are required to conduct additional analyses of discharge water where it is released into the stream and to monitor the biological conditions downstream. The extra analyses include temperature, total ammonia-N, and total acidity.

Operators must be careful to inject the appropriate amount of ammonia due to the potential consequences of excessive ammonia application. While ammonia can be effective for Mn removal in many cases, this requires careful monitoring and attention. Therefore, in situations where Mn is the ion of primary concern (low Fe, high Mn water), a different chemical may be more appropriate. Low flow in the receiving stream may also require the substitution of another neutralizing chemical during dry seasons due to high levels of ammonia in the stream (Faulkner 1990).

Case Studies:

Skousen et al. (1990) found a 73% reduction in cost when switching from 20% NaOH to ammonia. This figure was based on a 950-L flow (250-gpm) with an acidity concentration of 500 mg/L as $CaCO_3$. The annual cost to treat this drainage with ammonia was $32,000 compared to $121,000 with 20% NaOH.

4.3 Flocculants / Coagulants

Other chemicals used sparingly in AMD treatment include flocculants or coagulants, which increase particle settling efficiency (Table 4.2). These materials are usually limited to cases where unique metal compositions require a specialized treatment system, or where aeration and residence time in settling ponds are insufficient for complete metal precipitation. Coagulants reduce the net electrical repulsive forces at particle surfaces, thereby promoting

consolidation of small particles into larger particles. Flocculation aggregates or combines particles by bridging the space between particles with chemicals. Bridging occurs when segments of a polymer chain absorb suspended particles creating larger particles (Skousen et al. 1993).

The most common coagulants/flocculants used in water treatment are aluminum sulfate (alum) and ferric sulfate. These materials are also called polyelectrolytes and produce highly-charged ions when dissolved in water. Anionic polymers dissolve to form negatively-charged ions that are used to remove positively-charged solids. The reverse occurs with cationic flocculants. Polyampholytes are neutral, but when dissolved in water release both positively- and negatively-charged ions. Flocculants may be added to water as a liquid, or more commonly, placed in water as a gelatinous solid ("floc" logs).

Case Studies:

Specific case studies are not available at this time.

4.4 Reverse Osmosis

Osmosis occurs if two solutions of different concentrations in a common solvent are separated from one another by a membrane. If the membrane is semi-permeable (i.e., permeable to the solvent and not to the solute), then the solvent will flow from the more dilute solution to the more concentrated solution until an equilibrium concentration is reached. In reverse osmosis, the direction of solvent flow is reversed by applying pressure to the more concentrated solution (U.S. Environmental Protection Agency 1983). The solvent flows through the semi-permeable membrane, leaving the solutes behind. The concentrated solution then becomes more concentrated with solute. The solvent is thereby cleaned of solutes by passage through the membrane.

While semi-permeable membranes have been used to separate solvents from solutes, the concentrated solution (also called brine or sludge in AMD terminology) contains high concentrations of metals or other pollutants. Disposal of this brine is problematic because no neutralization of acidity has occurred and no metal hydroxides have been formed (Mason and Gupta 1972, Wilmoth 1973).

The process produces a high quality effluent water suitable directly for potable and industrial use. The concentrated brine solution is high in acid, Fe, and sulfate.

Case Studies

Case studies are not available at this time.

4.5 Ion Exchange Resins

Ion exchange in water treatment is defined as the reversible interchange of ions between a solid medium and the aqueous solution. The most common ion exchange example is the softening of "hard" water for domestic use. The hard water (caused by Ca^{2+} and Mg^{2+} ions in solution) is passed through a bed of ion exchange material, which is charged with monovalent cations, usually sodium. The divalent calcium and magnesium cations are exchanged for sodium ions (U.S. Environmental Protection Agency 1983). Ion exchange resins or materials consist of a chemically-inert polymer matrix with functional groups attached for exchange. The functional groups may be anionic or cationic. In current ion exchange technology, the resins available can be classified as strong-acid cation, weak-acid cation, strong-base anion, and weak-base anion types. Combinations of available resins have been used in systems for treatment of different waters for specific purposes.

Case Studies:

Case studies are not available at this time as noted by Hubbard et al. (1994).

4.6 Electrodialysis

An electrodialysis unit consists of a number of narrow compartments separated by closely spaced membranes. Each compartment is separated by both cation and anion membranes. Positive and negative electrodes are located at opposite ends of the unit. The solution fills the channels between the membranes, and when the electrodes are energized, the ions in solution migrate toward the positive or negative poles and are collected on the membranes (Skelly and Loy 1973).

Case Studies:

Hilton (1989) found that electrodialysis worked well in ponds of acid mine drainage, but found the membranes to clog very quickly with metal ions. Iron quickly fouls the membranes and causes problems for disposal (Powell and Vickland 1968).

4.7 Natural Zeolites

Natural zeolites are hydrous aluminosilicates that may be used to exchange ions for treatment of AMD. The sodium ion, naturally occurring in zeolites, is preferentially

exchanged for metal cations. Once the zeolites were loaded and filled with exchanged metal cations, the material must necessarily be regenerated using a sodium chloride solution to remove the metal cations from the aluminosilicate matrix.

Case Studies:

The U.S. Bureau of Mines conducted several laboratory studies which demonstrated natural zeolites were successful in reducing metal concentrations in AMD to drinking water standards (Schultze et al. 1994), but no field tests were initiated.

4.8 Metal Recovery from AMD Sludge

AMD treatment by chemicals causes the formation and precipitation of metal hydroxides in ponds. Passive treatment of AMD also accumulates metal hydroxide sludges into discrete areas. This sludge contains various concentrations of metals corresponding to the amounts in the source water. Since most mine drainage contains some level of Fe, the possible recovery and utilization of Fe hydroxides, oxyhydroxides, or oxides as sources of Fe for pigments, coatings, catalysts, and foundry sands. Other metals, if sufficient in quantity in the source AMD, may also be recoverable for industrial and commercial uses.

Case Studies:

Fish et al. (1996) found Fe oxides from alkaline wetland sludges to be similar or slightly inferior in comparison to natural and synthetic Fe oxide products. Rao et al. (1994) showed Fe and Zn could be recovered from AMD, but that a three-step process was needed for separation of metals.

References

Colson, A. 1997. Unpublished case study for ADTI project. Southern Ohio Coal Company, Columbus, OH.

Faulkner, B.B. 1990. Handbook for the use of ammonia in treating mine waters. West Virginia Mining and Reclamation Association. Charleston, WV.

Faulkner, B.B. 1996. Acid mine drainage treatment recommendations. Unpublished report for the West Virginia Mining and Reclamation Association, Charleston, WV.

Fish, C.L., R.S. Hedin, and J.M. Partezana. 1996. Chemical characterization of iron oxide precipitates from wetlands constructed to treat polluted mine drainage. p. 541-549. In:

Proceedings, 1996 National Meeting of the American Society for Surface Mining and Reclamation, May 18-23, 1996, Knoxville, TN.

Hilton, T. 1989. The magic of water treatment. In: Proceedings, Ninth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 25-26, 1989, Morgantown, WV.

Hilton, T. 1990. Handbook - Short Course for Taking A Responsible Environmental Approach towards Treating Acid Mine Drainage with Anhydrous Ammonia. West Virginia Mining and Reclamation Association. Charleston, WV.

Hubbard, K.L., G.D. Darling, S.R. Rao, and J.A. Finch. 1994. New functional polymers as sorbents for the selective recovery of toxic heavy metals from acid mine drainage. p. 273-280. In: Proceedings, International Land Reclamation and Mine Drainage Conference, April 24-29, 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.

Jenkins, M., and J. Skousen. 1993. Acid mine drainage treatment with the Aquafix System. In: Proceedings, Fourteenth Annual West Virginia Surface Mine Drainage Task Force Symposium. April 27-28, 1993, West Virginia University, Morgantown, WV.

Lilly, R., and P. Ziemkiewicz. 1992. Manganese removal at a lower pH with calcium peroxide: results of field trials. In: Proceedings, Thirteenth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 8-9, 1992, West Virginia University, Morgantown, WV.

Lovett, R., and P. Ziemkiewicz. 1991. Calcium peroxide for treatment of acid mine drainage. p. 35-46. In: Proceedings, Second International Conference on the Abatement of Acidic Drainage. September 16-18, 1991, MEND, CANMET, Montreal, CAN.

Mason, D.G., and M.K. Gupta. 1972. Reverse osmosis demineralization of acid mine drainage. Water Pollution Control Research Series. Project 14010 FQR, U.S. Environmental Protection Agency, Washington, DC.

Phipps, T.T., J. Fletcher, B. Fiske, and J. Skousen. 1991. A method for evaluating the costs of alternative AMD treatment systems. In: Proceedings, Twelfth Annual West Virginia Surface Mine Drainage Task Force Symposium, April 3-4, 1991, West Virginia University, Morgantown, WV.

Powell, J.H., and H.I. Vickland. 1968. Preliminary evaluation of the electrodialysis process for treatment of acid mine drainage waters. Final Report to the Office of Saline Water, Contract 14-01-001-1187. Unpublished report.

Rao, S.R., N. Kuyucak, T. Sheremata, M. Leroux, J.A. Finch, and K.G. Wheeland. 1994. Prospect of metal recovery / recycle from acid mine drainage. p. 223-232. In: Proceedings, International Land Reclamation and Mine Drainage Conference, April 24-29, 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.

Schultze, L.E., M.J. Zamzow, and P.R. Bremner. 1994. AMD cleanup using natural zeolites. p. 341-347. In: Proceedings, International Land Reclamation and Mine Drainage Conference, April 24-29, 1994, USDI, Bureau of Mines SP 06B-94, Pittsburgh, PA.

Skelly and Loy. 1973. Processes, procedures, and methods to control pollution from mining activities. EPA-430/9-73-011, U.S. Environmental Protection Agency, Washington, DC.

Skousen, J., R. Lilly, and T. Hilton. 1993. Special chemicals for treating acid mine drainage. Green Lands 23(3): 34-41.

Skousen, J., K. Politan, T. Hilton, and A. Meek. 1990. Acid mine drainage treatment systems: chemicals and costs. Green Lands 20(4): 31-37.

Skousen, J., and P. Ziemkiewicz. 1996. Acid mine drainage control and treatment. Second Ed. National Research Center for Coal and Energy, National Mine Land Reclamation Center, West Virginia University, Morgantown, WV. 362 pp.

U.S. Environmental Protection Agency. 1982. Development document for effluent limitations guidelines and standards for the coal mining point source category. USEPA 440/1-82/057, Cincinnati, OH.

U.S. Environmental Protection Agency. 1983. Neutralization of acid mine drainage, design manual. USEPA 600/2-83-001, Cincinnati, OH.

Wilmoth, R.C. 1973. Applications of reverse osmosis to acid mine drainage treatment. EPA-670/2-73-100, Environmental Protection Technology Series, Cincinnati, OH.

Zurbuch, P.E. 1984. Neutralization of acidified streams in West Virginia. Fisheries 9:42-47.