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## Overview of Acid Mine Drainage Treatment with Chemicals

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## Acid Mine Drainage Formation

- Acid mine drainage (AMD) forms when sulfide minerals in rocks are exposed to oxidizing conditions in coal and metal mining, highway construction, and other large-scale excavations. There are many types of sulfide minerals, but iron sulfides common in coal regions, pyrite and marcasite ( $\text{FeS}_2$ ), are the predominant AMD producers. Upon exposure to water and oxygen, pyritic minerals oxidize to form acidic, iron and sulfate-rich drainage. The drainage quality emanating from underground mines or backfills of surface mines is dependent on the acid-producing and alkaline minerals contained in the disturbed rock.
- In general, sulfide-rich and carbonate-poor materials are expected to produce acidic drainage. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline conditions in water.



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## Acid Mine Drainage Formation

- Acidity in AMD is comprised of **mineral acidity** (iron, aluminum, manganese, and other metals depending on the specific geologic setting and metal sulfide) and **hydrogen ion acidity**. Approximately 20,000 km of streams and rivers in the United States are degraded by AMD. About 90% of the AMD reaching streams originates in abandoned surface and deep mines.
- Since no company or individual claims responsibility for reclaiming abandoned mine lands (AML), no treatment of the AMD occurs and continual contamination of surface and groundwater resources results. In a previous Green Lands article (Winter 1996 edition), Ziemkiewicz and Skousen reviewed strategies used to control AMD at its source. In this presentation, chemical treatment alternatives are discussed.



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## Acid Mine Drainage



The source of the acid mine drainage at Manila Creek, West Virginia. The mine sediment over the years has collected over an area 3 feet thick, 6 feet wide, and 12 feet long. The pH of the water at the source is 3.5, the iron content is 567 mg/l, and the flow from the abandoned mine is 42 GPM.



## The Oxidation of Pyrite

- Pyrite oxidation creates sulfuric acid and ferrous and ferric sulfates. The method by which pyrite oxidizes to form sulfuric acid and ferric hydroxide proceeds as follows:



- Equation 1 describes the oxidation of pyrite that occurs abiotically with catalysis by *Thiobacillus ferrooxidans* (Forstner, Salomons 1988). Equations 2 and 3 represent the oxidation of ferrous iron to ferric iron and the consequent precipitation of ferric iron as ferric hydroxide. The two reactions account for the characteristic reddish-brown color of sediments contaminated by acid drainage. The three reactions combine to form the **fourth** stoichiometric equation, describing the **complete reaction** of pyrite and  $\text{H}_2\text{SO}_4$  formation (Hadley, Snow 1974).



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## What Factors Influence the Quality of Mine Drainage?

- Primary, secondary, tertiary and downstream factors influence the quality and quantity of mine drainage.
- **Primary factors** influencing the amount and quality of acidic water are the relative amount of water and oxygen in the environment. In order for pyrite to oxidize, both oxygen and water must be present. Water serves not only as a reactant, but also as a reaction medium and a product-transport solvent (Forstner, Salomons 1988).
- A **secondary factor** is the neutralization of acids by the alkalinity released from the carbonate minerals in the mine waste and surrounding stratum (Forstner, Salomons 1988).
- **Tertiary factors** include the physical characteristics of mining waste, the spatial relationship between wastes, and the hydrologic regime.
- The physical characteristics of importance are **particle size, physical weathering tendency, and permeability**. The particle size relates to the amount of surface area that is exposed to oxidation. The smaller the particle size, the more total surface area is exposed, and the greater potential for oxidation. Weathering increases the surface area of the material. The increase in surface area and the physical weathering and fracturing of strata increase the permeability of the waste material.



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## What Factors Influence the Quality of Mine Drainage?

- The **sequence of stacking different wastes** may affect the water quality of mine drainage. By contributing to the alkalinity of the percolating water, calcareous material placed atop pyritic material will reduce both the potential for oxidation and the acidity generated (Forstner, Salomons 1988).
- The **hydrologic regime** of a mine can influence the quality of mine drainage. Because waste inundation limits the transfer of oxygen, significant acid generation in a saturated zone may not occur. A fluctuating water table induces pyrite oxidation during declines in the water table (Forstner, Salomons 1988).
- **Downstream factors** may impact the quality and quantity of acid drainage. Physical processes such as dilution and precipitation and chemical processes such as neutralization will permit a stream to assimilate acid drainage, but not without incurring a great deal of acid damage to the preceding stream (Forstner, Salomons 1988).



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## Chemical Treatment of Acid Mine Drainage

- Since the passage of the Surface Mining Control and Reclamation Act (SMCRA) in 1977, coal mine operators have been required to meet environmental land reclamation performance standards. Operators must also meet water quality standards established in the Clean Water Act of 1972 (CWA), which regulates discharges into waters of the U.S. Control of AMD is a requirement imposed on operators by both SMCRA and CWA.
- In addition to the surface mining permit, each mining operation must be issued a National Pollutant Discharge Elimination System (NPDES) permit under CWA. Allowable pollutant discharge levels are usually determined by the US EPA technology-based standards, or the discharge levels may be based on the more stringent water quality-based standards where discharges are being released into streams with designated uses.
- **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. In most cases, a variety of alternative treatment methods can be employed to meet the limits specified.



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## Chemical Treatment of Acid Mine Drainage

- NPDES permits on surface mines usually require **monitoring of pH, total suspended solids (TSS), and iron and manganese concentrations**. Other parameters may be requested by the regulatory authority in a particular mining situation. However, in order for an operator to make a selection of an AMD treatment system, one must determine (in addition to the above parameters) the flow rate, the receiving stream's flow and quality, availability of electrical power, the distance from chemical addition to where the water enters a settling pond, and the pond's volume for water retention time.
- After evaluating these variables over a period of time, the operator can consider the economics of different chemicals and alternative AMD treatment systems. Most **AMD chemical treatment systems consist of an inflow pipe or ditch, a storage tank or bin holding the treatment chemical, a means of controlling its application rate, a settling pond to capture precipitated metal oxyhydroxides, and a discharge point**. The latter is the point at which NPDES compliance is monitored. The amount of chemical needed for neutralization can be calculated by multiplying the flow (gpm), the AMD's acidity (mg/l), and a factor of .0022. The product is the tons of acid that require neutralization per year (calcium carbonate eq.). This value (tons of acid/yr) can then be multiplied by a conversion factor for each chemical to get the amount needed.



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## Overview of Chemicals Available to Treat AMD

- **Six primary** chemicals have been used to treat AMD (Table 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, the 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, the interest rate, and risk factors.



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## Chemical Compounds Used

Table 1. Chemical Compounds used in AMD treatment.

Common Name	Chemical Name	Formula	Conversion Factor <sup>1</sup>	Neutralization Efficiency <sup>2</sup>	1999 Cost <sup>3</sup>	
					Bulk	<Bulk
Limestone	Calcium carbonate	CaCO <sub>3</sub>	1	30%	\$10	\$15
Hydrated Lime	Calcium hydroxide	Ca(OH) <sub>2</sub>	0.74	90%	\$60	\$100
Pebble Quicklime	Calcium oxide	CaO	0.56	90%	\$80	\$240
Soda Ash	Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	1.06	60%	\$200	\$320
Caustic Soda (solid)	Sodium hydroxide	NaOH	0.8	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 <sub>3</sub>	0.34	100%	\$300	\$680

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

<sup>2</sup> 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 82 tons of hydrated lime would be needed to neutralize the acidity in the water (100(0.74)/0.90).

<sup>3</sup> 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 in tons.



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## Metal Precipitation and pH

- Enough **alkalinity must be added to raise water pH and supply hydroxides ( $\text{OH}^-$ ) so 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 (except ferric iron which precipitates at about pH 3.5). The types and amounts of metals in the water therefore heavily influence the selection of an AMD treatment system. Ferrous iron converts to a solid bluish-green ferrous hydroxide at  $\text{pH} \geq 8.5$ . In the presence of oxygen, ferrous iron oxidizes to ferric iron, and ferric hydroxide forms a yellowish-orange solid (commonly called yellow boy), which precipitates at  $\text{pH} \geq 3.5$ .
- **In oxygen-poor AMD, where iron is primarily in the ferrous form, enough alkalinity must be added to raise the solution pH to 8.5 before ferrous hydroxide precipitates.** A more efficient way of treating high ferrous AMD is to first aerate the water (also outgassing  $\text{CO}_2$ ), causing the iron to convert from ferrous to ferric, and then adding a neutralizing chemical to raise the pH to 6 or 7 to form ferric hydroxide. Aeration after chemical addition is also beneficial. Aeration before and after treatment usually reduces the amount of neutralizing reagent necessary to precipitate iron from AMD. Aluminum (Al) hydroxide generally precipitates at  $\text{pH} \geq 5.0$  but also enters solution again at a pH of 9.0. Manganese precipitation is variable due to its many oxidation states, but will generally precipitate at a pH of 9.0 to 9.5.



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## Metal Precipitation and pH

- Sometimes, however, a **pH of 10.5 is necessary for complete removal of Mn**. As this discussion demonstrates, the appropriate treatment chemical can depend on both the oxidation state and concentrations of metals in the AMD (U.S. EPA, 1983). **Interactions among metals** also influence the rate and degree to which metals precipitate.
- For example, **iron precipitation will largely remove manganese from the water at pH 8** due to co-precipitation, but only if the iron conc. is much greater than the manganese conc. (~ 4 times more or greater). If the iron conc. in the AMD is less than four times the manganese content, manganese may not be removed by co-precipitation and a solution pH of  $\geq 9$  is necessary to remove it.
- **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 pH of 8.0, while another site may still have metal concs. that do not meet effluent limits even after the pH has been raised to 10.



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## Chemicals

- **Limestone**

Limestone has been used for decades to raise pH and precipitate metals in AMD. It has the lowest material cost and is the safest and easiest to handle of the AMD chemicals.

Unfortunately, its successful application has been limited due to its **low solubility and tendency to develop an external coating**, or armor, **of ferric hydroxide** when added to AMD.

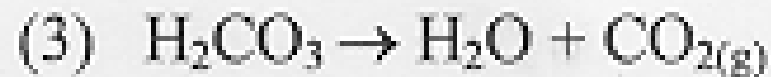
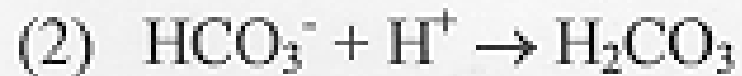
- In cases where pH is low and mineral acidity is also relatively low (low metal concentrations), **finely-ground limestone** may be dumped in streams directly or the limestone may be ground by water-powered rotating drums and metered into the stream.
- These applications have been tried in West Virginia in AMD-impacted streams with great success. Limestone has also been used to treat AMD in anaerobic (anoxic limestone drains) and aerobic environments (open limestone channels). These latter two techniques are especially useful in situations where specific discharge limits do not have to be met.
- They are both being installed on abandoned mine land reclamation projects and by operators wishing to reduce chemical treatment costs and improve compliance (Faulkner 1996).



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## Limestone Reactions





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## Chemicals

- **Hydrated Lime**

Hydrated lime is a **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 dispense and mix the chemical with the water (Skousen and Ziemkiewicz 1995).

- However, due to the kinetics of lime dissolution and its neutralization efficiency, increasing the lime rate above that required for acid neutralization increases the volume of unreacted lime that enters the metal floc settling pond.
- 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 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.



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## Hydrated Lime Installation





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## Chemicals

- **Pebble Quicklime**  
**CaO**, has been recently used in conjunction with the **Aquafix Pebble quicklime**, Water Treatment System utilizing a water wheel concept (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 high flow/high acidity situations. Preliminary tests show an average of **75% cost savings** over caustic systems and **about 20 to 40% savings** over ammonia systems.





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## Chemicals

- **Soda Ash**

**Soda ash 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 is determined by the flow and quality of AMD.



- **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. For short-term treatment at isolated sites, some operators use a much simpler system employing a box or barrel with holes that allows 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.



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## Chemicals

- **Caustic Soda**

Caustic soda is often used in remote locations (e.g., where electricity is unavailable), and in low flow, high acidity situations. It is commonly the chemical of choice if manganese concentrations in the AMD are high. 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. Caustic should be applied at the surface of ponded water because the chemical is more dense than water and sinks. The major drawbacks of using liquid caustic for AMD are high cost and dangers in handling.

- Tanks housing caustic soda can range from 500 to 8,000 gals. 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 Temp. The discharge line is fixed at the bottom of the tank and transports the caustic to the seep, ditch, or pond. The flow is controlled by a gate valve 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 percent to a 20 percent caustic solution, using a freeze-proof solution containing some potassium hydroxide (KOH), and utilizing solid caustic. Burying a caustic tank is expensive because the operation 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 percent caustic solution, adding some KOH, and switching to solid caustic. Switching from a 50 percent to a 20 percent caustic solution lowers the freezing point from 0°C to about -37°C.
- **The addition of KOH also lowers the freezing point.** Solid caustic, which may be delivered in 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. 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.





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## Chemicals

- **Ammonia**

Ammonia is a material that must be handled carefully (Hilton 1990). A gas at ambient temperatures, ammonia is compressed and stored as a liquid but returns to the gaseous state when released into water. In the gaseous state, ammonia is extremely soluble and reacts rapidly. 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, and

therefore large amounts of ammonia must be added to raise the pH above 9.2. Injection of ammonia into AMD is one of the quickest ways to raise 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 figure of 50% to 70% can be realized when ammonia is substituted for caustic if the target pH for metal precipitation is <9.8 (Skousen et al. 1990).
- **Major disadvantages of using ammonia** include: 1) hazards associated with handling the chemical, 2) potential biological implications, and 3) the consequences of excessive application rates (Faulkner 1990). Specialized training and experience are important for its safe use. Operators using ammonia are required to conduct analyses of discharge water where it is released into the stream and to monitor the biological conditions downstream. These include temp., 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 manganese removal in many cases**, this requires careful monitoring and attention. Therefore, in situations where manganese is the ion of primary concern (low iron, high manganese 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 conditions due to ammonia's toxic un-ionized state under these conditions (Faulkner 1990).





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## Costs of Treating AMD

- Costs have been developed for five AMD treatment chemicals under four sets of flow (gpm) and acid concentration (mg/l) conditions (Table 2). 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 (1995), 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 eastern USA in around year 2000.** All dollar values are from that year. 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 per annum. The parameters used in the analysis were entered in a spreadsheet and can be varied to conform to local conditions.



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## Costs of Treating AMD

- **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 2). 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 more inefficient in treating water than caustic. Hydrated lime treatment systems have the highest installation costs of the four 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/high acid situations.
- **For a five-year treatment period, ammonia has the lowest annualized costs** for the low flow/low acid situation (Table 2). Pebble quicklime was similar to ammonia in cost, and caustic was third. Soda ash is fourth because of its high labor and reagent costs, and hydrated lime is fourth 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 very expensive at high flow and high acidity.



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## Other Aspects of AMD Treatment Technologies

- **Other Neutralizing Chemicals**

While the primary AMD chemicals and applications have been discussed, particular circumstances may require a different chemical, a combination of chemicals, particular management patterns to implement the most cost effective method, or to meet more stringent effluent limits. Several operators have used potassium hydroxide, magnesium hydroxide, and magna lime with good results (Table 3).

- Potassium hydroxide is used because it is safer to use than caustic and reduces the potential for over treatment, but it is more expensive than caustic. **Magnesium hydroxide and magna lime** are dispensed in a manner similar to and behave like calcium hydroxide, but tend to be more expensive.
- The **table below compares costs in 1996 of six 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.

# Cost Comparison (Table 2)

## Flow and Acidity Conditions

Flow (gpm)	50	1000	250	1000
Acidity (mg/l)	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

## Flocculants and Coagulants

- Other chemicals used sparingly in AMD treatment include flocculants or coagulants, which increase particle settling efficiency (Table 3). These materials are usually limited to cases where unique metal compositions require a specialized treatment system, or where aeration and/or 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 electrolytes and upon polymerization 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.
- Flocculants may be added to water as a liquid, or more commonly, placed in water as a gelatinous solid ("floc" logs).



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## Oxidants

- 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.** For this reason, aeration of water can be a limiting factor 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.
- **Oxidants (Table 3) 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 has been shown to oxygenate AMD as well as neutralize acidity (Lilly and Ziemkiewicz 1992).



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## Residence Time in Ponds and Floc Generation

- After chemical treatment, the treated water flows into sedimentation ponds so metals in the water can precipitate. Dissolved metals precipitate from AMD as a loose, open-structured mass of tiny grains called "floc". **All chemicals currently used in AMD treatment cause the formation of metal hydroxide sludge or floc.** Sufficient residence time of the water, which is dictated by pond size and depth, is important for adequate metal precipitation. Hilton (1993) found pond size to be too small on most AMD treatment sites to result in complete treatment of the water and precipitation of dissolved metals. The amount of metal floc generated by AMD neutralization depends on the quality and quantity of water being treated, which in turn determines how often the ponds must be cleaned. Knowing the chemical and AMD being treated will help determine the general floc properties & provide an estimate of the stability of the various compounds in the floc.
- Ackman (1982) **investigated the chemical and physical characteristics of AMD floc and concluded that each floc varied depending on the nature of the AMD,** the neutralization chemical, and the mechanical mixing or aeration device used during chemical treatment. He stated the most important physical property is the floc's settleability, which includes both the settling rate and final floc volume. Ackman found that calcium hydroxide and sodium carbonate produced a granular, dense floc versus a more gelatinous, loose floc generated by sodium hydroxide and ammonia. The chemical compositions of flocs were generally composed of hydrated ferrous or ferric oxyhydroxides, gypsum, hydrated aluminum oxides, calcium carbonate and bicarbonate, with trace amounts of silica, phosphate, manganese, copper, and zinc.
- Payette et al. (1991) found that **AMD neutralized by calcium hydroxide resulted in the formation of crystalline gypsum** as well as various amorphous metal hydroxides. AMD floc was mostly amorphous at 1 hour after formation, while crystals were observed in the floc 24 hours after formation. In a series of experiments on floc generation and stability, Brown et al. (1994 a, b, c) found.



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## Residence Time in Ponds and Floc Generation

1. More floc was produced as the pH of the AMD solution was increased by chemical addition.
2. Using 4 AMD types, each was unique in its reaction to four neutralization chemicals.
3. The amount of floc produced as a function of the amount of chemical added (termed its "efficiency") remained about the same across all pH ranges for calcium hydroxide, sodium hydroxide, and sodium carbonate. Ammonia became less efficient at high pH.
4. **Sodium carbonate was needed in the highest amount** to raise water pH to 7.5 or greater.
5. Floc volumes were lowest with sodium carbonate and highest with calcium hydroxide after 1 week of settling.
6. Greater settling time caused floc consolidation.
7. Flocs were composed of metals in ratios similar to the metal ratios of the AMD from which it was generated.
8. **Flocs were primarily amorphous** (having no crystalline structure), except for sodium carbonate flocs.
9. Flocs collected from ponds on mined areas showed little similarity in composition to flocs generated with the same AMD and chemical in the laboratory. The field flocs had soil particles mixed with the chemical floc.
10. Aging of AMD flocs caused them to be more stable, thereby decreasing their likelihood of releasing metals (Watzlaf and Casson 1990). The greater stability of aged flocs remained even after re-introducing the flocs into acidic solutions. Aging in a dry environment resulted in better floc stability than flocs aged under water. Aging also caused floc consolidation.



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## Residence Time in Ponds and Floc Generation

- Floc disposal options include: 1) leaving the floc submerged in a pond indefinitely, 2) pumping or hauling floc from ponds to abandoned deep mines or to pits dug on surface mines, and 3) dumping floc into refuse piles. Flocs pumped or dumped onto the surface of land or mixed with overburden during backfilling and allowed to age and dry is a good strategy for disposal. **In its oxidized and dried condition, AMD flocs can become crystalline and become part of the soil.** Injecting stable floc containing excess alkalinity into acidic deep mine pools has the potential to improve the quality of discharge from the pools. Injection into abandoned mine works is cost-effective where conditions allow its safe disposal.
- Lovett and Ziemkiewicz (1991) estimated ammonia chemical costs for a site in West Virginia at \$72,000 per year and floc handling costs of \$486,000 per year. Based on a flow of 100 gpm for this site, Brown et al. (1994b) estimated that this site generated approximately 77,900 cubic yards of floc per year. Dividing \$486,000 by 77,900 cubic yards of floc yields a cost of \$6.25 per cubic yard for floc handling and disposal on this site. Several mine operators observed that floc handling and disposal may cost up to \$15 per cubic yard. Due to their high water content and the sheer volume of material, floc handling costs frequently exceed chemical costs by several times.
- **Each AMD is unique and the chemical treatment of any particular AMD source is site specific.** Each AMD source should be tested with various chemicals by titration tests to evaluate the most effective chemical for precipitation of the metals. The costs of each AMD treatment system based on neutralization (in terms of the reagent cost and capital investment and maintenance of the dispensing system) and floc volumes and disposal should be evaluated to determine the most cost effective system.

<b>NAME</b>	<b>CHEMICAL FORMULA</b>	<b>COMMENTS</b>
<b>Acid Neutralization</b>		
Limestone	CaCO <sub>3</sub>	Used in anoxic limestone drains and open limestone channels.
Hydrated Lime	Ca(OH) <sub>2</sub>	Cost effective reagent, but requires mixing.
Pebble Quick Lime	CaO	Very reactive, needs metering equipment.
Soda Ash Briquettes	Na <sub>2</sub> CO <sub>3</sub>	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 <sub>3</sub> or NH <sub>4</sub> OH	Very reactive and soluble; also purchased as aqua ammonia.
Potassium Hydroxide	KOH	Similar to caustic.
Magnesium Hydroxide	Mg(OH) <sub>2</sub>	Similar to hydrated lime.
Magna Lime	MgO	Similar to pebble quicklime.
Calcium Peroxide	CaO <sub>2</sub>	Used as a neutralizer and oxidant; either powder or briquettes.
Kiln Dust	CaO, Ca(OH) <sub>2</sub>	Waste product of limestone industry. Active ingredient is CaO with various amounts of other constituents.
Fly Ash	CaCO <sub>3</sub> , Ca(OH) <sub>2</sub>	Neutralization value varies with each product.
<b>Coagulants/Flocculants</b>		
Alum (aluminum sulfate)	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Acidic material, forms Al(OH) <sub>3</sub> .
Copperas (ferrous sulfate)	FeSO <sub>4</sub>	Acidic material, usually slower reacting than alum.
Ferric Sulfate	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Ferric products react faster than ferrous.
Sodium Aluminate	NaAlO <sub>2</sub>	Alkaline coagulant.
Anionic Flocculants		Negatively-charged surface.
Cationic Flocculants		Positively-charged surface.
Polyampholytes		Both positive and negative charges on surface based on pH.
<b>Oxidants</b>		
Calcium Hypochlorite	Ca(ClO) <sub>2</sub>	Strong oxidant.
Sodium Hypochlorite	NaClO	Also a strong oxidant.
Calcium Peroxide	CaO <sub>2</sub>	Trapzene, an acid neutralizer.
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	Strong oxidant.
Potassium permanganate	KMnO <sub>4</sub>	Very effective, commonly used.



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## Summary

- Acid mine drainage occurs when geologic materials containing metal sulfides are exposed to oxidizing conditions. Subsequent leaching of reaction products into surface waters pollute over 20,000 km of streams in the U.S. Chemicals used for treating AMD after formation are hydrated lime, pebble quicklime, caustic soda, soda ash briquettes, and ammonia. Each chemical has advantages for certain water conditions and treatment.
- **Under low flow situations, pebble quicklime and ammonia are the most cost effective.** Under high flow situations, hydrated lime and pebble quicklime are the most cost effective due to their low reagent cost compared to the other chemicals. Each chemical reacts differently with a specific AMD. Therefore, it is essential that each AMD source be treated and evaluated with each chemical to determine which is most environmentally sound, efficient and cost effective.
- **Coagulants and flocculants may be used in water treatment where retention time in sedimentation ponds is insufficient for metal precipitation.** Oxidants can be used to meet more stringent effluent limits and to make chemical treatment more efficient. Floc, the metal hydroxides collected in ponds after chemical treatment, are disposed of in abandoned deep mines, refuse piles, or left in collection ponds. Studies show that flocs are relatively stable materials and metals contained therein do not resolubilize after disposal, especially if aged and dried.



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## Passive Treatment

- **Constructed Wetlands**

Wetlands are passive systems, a relatively new treatment technology. Constructed wetlands use soil-borne and water-borne microbes associated with wetland plants to remove dissolved metals from mine drainage. Wetlands are generally more effective in removing iron than manganese. Wetlands are most useful in the treatment of small flows of a few gallons per minute. Initial design and construction costs may exceed tens of thousands of dollars. Optimum sizing and configuration criteria are still under study. Seasonal variations in metal removal efficiency occur, with lesser amounts removed in cold weather.

- **Open Limestone Channels/Anoxic Limestone Drains**

This simply constructed passive treatment method uses open ditches filled with limestone (anoxic drains are covered). The dissolution of limestone adds alkalinity and raises pH, but a coating of limestone by iron and aluminum precipitates affects the performance of this treatment method.

- **Diversion Wells**

Acidic water is diverted to a well containing crushed limestone. Iron precipitate coating is prevented by the turbulence of the flow through the well. The system works well, but needs periodic replenishment of limestone.



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## **A Case Study**

### **TREATMENT OF ACID MINE WATER BY USE OF HEAVY METAL PRECIPITATION AND ION EXCHANGE**

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## Acid Mine Water Properties

**TABLE 1 Properties of acid mine water obtained from a South African gold mine**

pH	Turbidity NTU	Suspended solids, %	TDS,%	Al <sup>3+</sup> ppm	Ba <sup>2+</sup> ppm	Ca <sup>2+</sup> ppm	Cr <sup>3+</sup> ppm
1.65	92.9	2.9	1.31	249	0.0749	300	4.85
Cu <sup>2+</sup> ppm	Fe <sup>+</sup> Ppm	K <sup>+</sup> Ppm	Mg <sup>2+</sup> Ppm	Mn* ppm	Na <sup>+</sup> Ppm	Ni <sup>2+</sup> ppm	Fe <sup>2+</sup> ppm
1.80	942	558	359	113	345	5.75	154
Pb <sup>2+</sup> ppm	Si <sup>2+</sup> Ppm	Sr <sup>2+</sup> Ppm	Ti <sup>2+</sup> Ppm	Zn <sup>2+</sup> ppm	Zr <sup>2+</sup> ppm	Cd <sup>2+</sup> ppm	Co <sup>2+</sup> ppm
0.349	23.8	1.77	3.55	10.1	0.0719	0.26	1.94
Cl <sup>-</sup> ppm	Br <sup>-</sup> Ppm	NO <sub>3</sub> <sup>2-</sup> Ppm	F <sup>-</sup> Ppm	SO <sub>4</sub> <sup>2-</sup> ppm	PO <sub>4</sub> <sup>3-</sup> ppm		
954	280	0	431	6305	337		

\* Total concentration



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## After Oxidation and Precipitation

**TABLE 3 Precipitation after H<sub>2</sub>O<sub>2</sub> oxidation**

Parameters	After oxidation	Lime precipitation			Target
pH	1.45	5.70	6.90	8.10	6.0–8.5
Cr <sup>2+</sup> (ppm)	4.85	2.31	0.0045	0.0001	0.001
Cu <sup>2+</sup> (ppm)	1.80	0.955	0.0292	0.0058	0.003–0.006
Fe (ppm)	942	322	18.5	0.452	> 0.2
Mn (ppm)	112	16.6	0.520	0.0898	0.1
Ni <sup>2+</sup> (ppm)	5.75	4.90	2.27	0.0899	0.01–0.05
Pb <sup>2+</sup> (ppm)	0.349	0.011	0.0048	0.0012	0.02–0.1
Ti <sup>2+</sup> (ppm)	3.55	0.0287	0.0180	0.0049	0.005
Zn <sup>2+</sup> (ppm)	10.1	4.88	0.541	0.0001	0.05–0.005
Zr <sup>2+</sup> (ppm)	0.0920	0.0597	0.0544	0.0512	—
Cd <sup>2+</sup> (ppm)	0.260	0.238	0.180	0.121	0.001–0.002
Co <sup>2+</sup> (ppm)	1.94	1.80	1.033	0.0600	0.005



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## Combined Precipitation

TABLE 4 Precipitation by combination of lime and Na<sub>2</sub>S

Species	After oxidation	Lime + Na <sub>2</sub> S precipitation			Target
		0.6x Na <sub>2</sub> S	0.8x Na <sub>2</sub> S	1.0x Na <sub>2</sub> S	
PH	1.45	8.0	8.0	8.0	6.0 – 8.5
Cr <sup>2+</sup> (ppm)	4.85	0.0001	0.0001	0.0001	0.001
Cu <sup>2+</sup> (ppm)	1.80	0.0020	0.0018	0.0015	0.003 – 0.006
Fe (ppm)	942	0.2142	0.2142	0.2141	> 0.2
Mn (ppm)	112	0.0899	0.0873	0.0789	0.1
Ni <sup>2+</sup> (ppm)	5.75	0.0441	0.0364	0.0342	0.01 – 0.05
Pb <sup>2+</sup> (ppm)	0.349	0.0015	0.0011	0.0010	0.02 – 0.1
Ti <sup>2+</sup> (ppm)	3.549	0.005	0.0049	0.0048	0.005
Zn <sup>2+</sup> (ppm)	10.1	0.0001	0.0001	0.0001	0.05 – 0.005
Zr <sup>2+</sup> (ppm)	0.0919	0.0500	0.0498	0.0495	–
Cd <sup>2+</sup> (ppm)	0.260	0.0018	0.0013	0.0009	0.001 – 0.002
Co <sup>2+</sup> (ppm)	1.94	0.005	0.0048	0.0042	0.005



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## Settling Characteristics

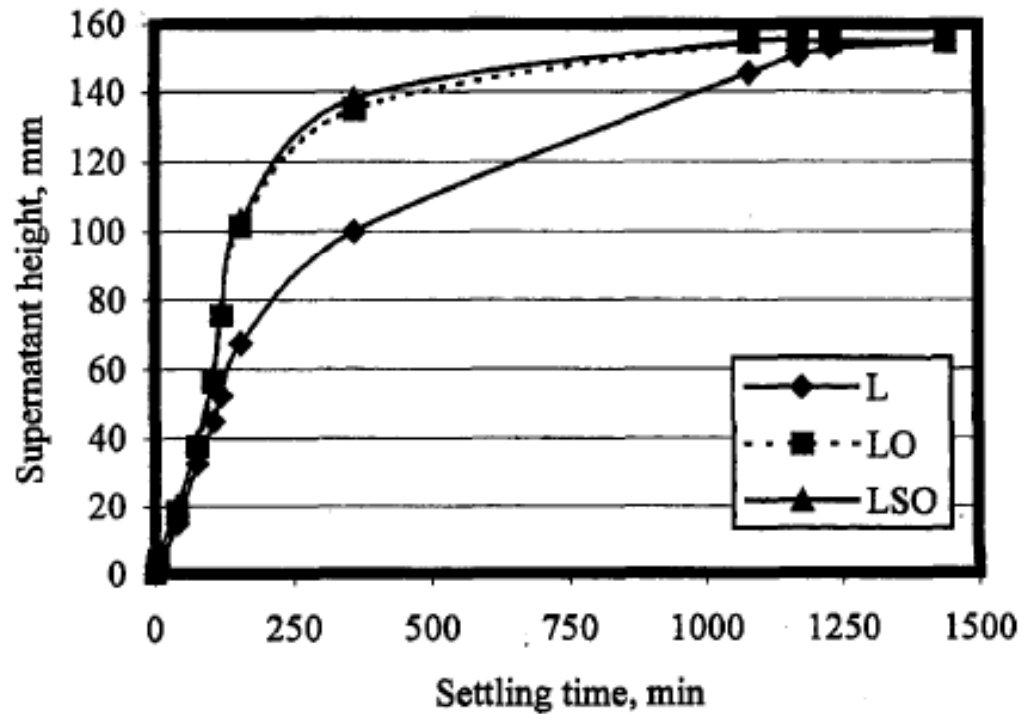


Fig.1 Settling characteristics of precipitates under different precipitation conditions, as indicated by the height of the supernatant liquid in the vessel.

**TABLE 5 Properties of the effluent from the proposed precipitation process**

Properties	Feed	After treatment	Target
PH	1.65	8.0	6.0–8.5
Turbidity	92.9	1.8	<4
Al <sup>3+</sup> (ppm)	249	0.267	>0.1
Ba <sup>2+</sup> (ppm)	0.0749	0.0281	>0.5
Ca <sup>2+</sup> (ppm)	300	823	400
Cr <sup>3+</sup> (ppm)	4.85	0.0001	0.001
K <sup>+</sup> (ppm)	558	556	—
Na <sup>+</sup> (ppm)	345	345	230
Cu <sup>2+</sup> (ppm)	1.80	0.0020	0.003–0.006
Fe* (ppm)	942	0.214	>0.2
Mg <sup>2+</sup> (ppm)	359	348	200
Mn* (ppm)	113	0.0899	0.1
Ni <sup>2+</sup> (ppm)	5.75	0.0441	0.01–0.05
Pb <sup>2+</sup> (ppm)	0.349	0.0015	0.02–0.1
Si <sup>2+</sup> (ppm)	23.8	0.919	—
Sr <sup>2+</sup> (ppm)	1.77	1.06	—
Ti <sup>2+</sup> (ppm)	3.55	0.005	0.005
Zn <sup>2+</sup> (ppm)	10.1	0.0001	0.05–0.005
Zr <sup>2+</sup> (ppm)	0.0919	0.0500	—
Cd <sup>2+</sup> (ppm)	0.260	0.0018	0.001–0.002
Co <sup>2+</sup> (ppm)	1.94	0.005	0.005
F <sup>-</sup> (ppm)	431	44.0	1.0
Cl <sup>-</sup> (ppm)	954	478	—
Br <sup>-</sup> (ppm)	280	258	—
SO <sub>4</sub> <sup>2-</sup> (ppm)	6305	3353	1000
PO <sub>4</sub> <sup>3-</sup> (ppm)	337	0.0005	—

\* Total concentration

## Effluent Properties



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## SEM Image



Fig.2 SEM image of the aggregate magnetite-hydroxide-sulphide precipitates.



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## Precipitation Process

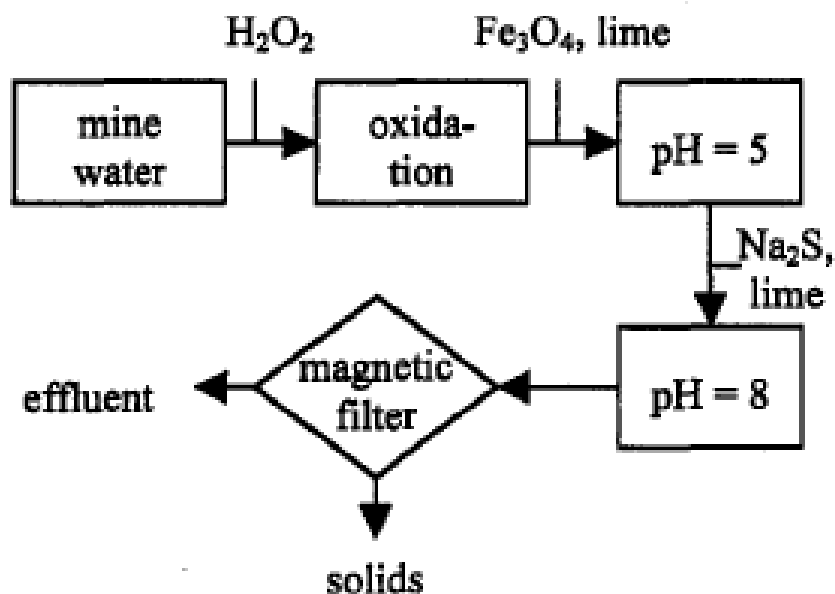


Fig.3 Flowsheet of the proposed precipitation process.



## Ion Exchange Portion

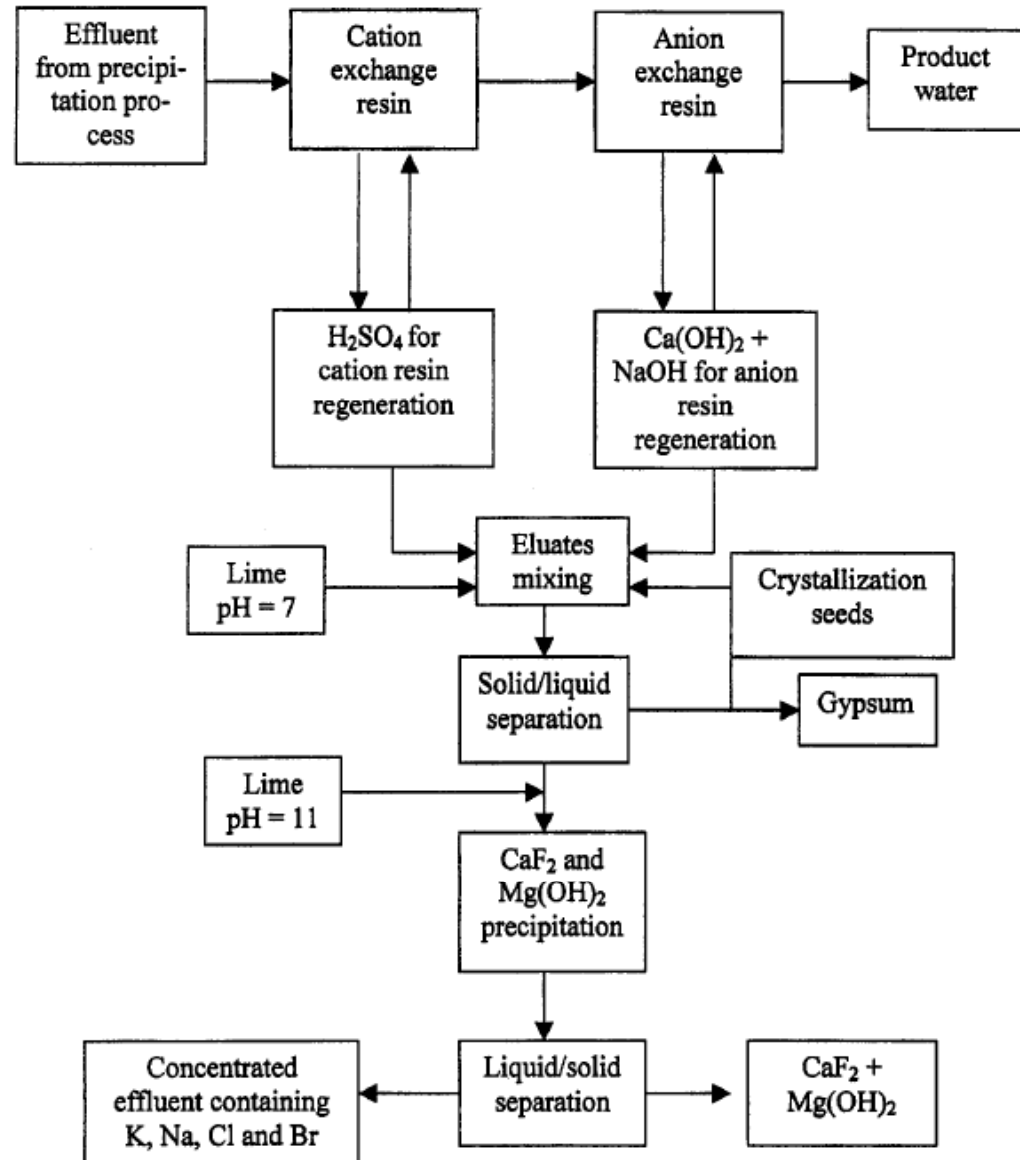


Fig.16 Proposed process for desalination of the effluent from precipitation process.



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# Ion Exchange for Desalination

## ION EXCHANGE FOR DESALINATION

### Removal of cations

The cations were removed with Amberlite IR120H. Calcium was selected as the model ion to investigate the sorption and elution characteristics of the resin.

### Adsorption

Figure 4 shows a typical sorption isotherm of  $\text{Ca}^{2+}$  on the IR120H resin. The adsorption occurred at a pH of 6.5 and required 12 hours to reach equilibrium. The concentration of  $\text{Ca}^{2+}$  in the resin phase was calculated by use of equation (1):

$$q = (C_0 - C)V_1/V_r \quad (1)$$

where  $C_0$  and  $C$  denote the initial and equilibrium concentrations of the metals in the aqueous phase, while  $V_1$  and  $V_r$  are the volumes of the aqueous phase and the resin respectively. Sorption isotherms were obtained by plotting the metal adsorbed (mg) per mL of resin against concentration of metal remaining in solution at equilibrium.



## Sorption Isotherm

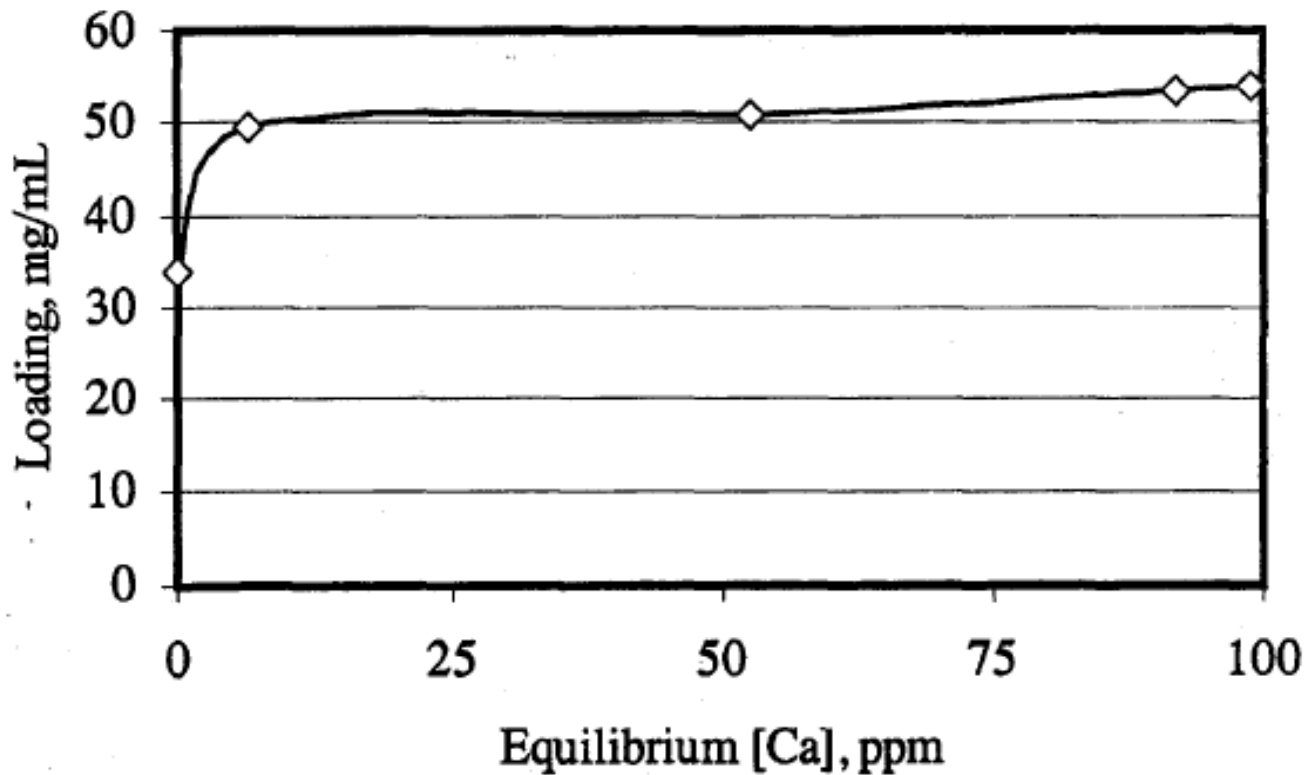


Fig.4 Sorption isotherm of  $\text{Ca}^{2+}$  on IR120H.



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## Microbiological Treatment Example

### TREATMENT OF ACID MINE WATER BY SULFATE-REDUCING BACTERIA; RESULTS FROM A BENCH SCALE EXPERIMENT

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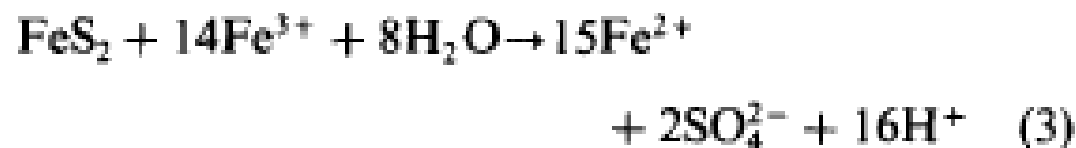
*Wat. Res. Vol. 30, No. 7, pp. 1617-1624, 1996*



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## Reaction Scheme





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## Experimental Setup

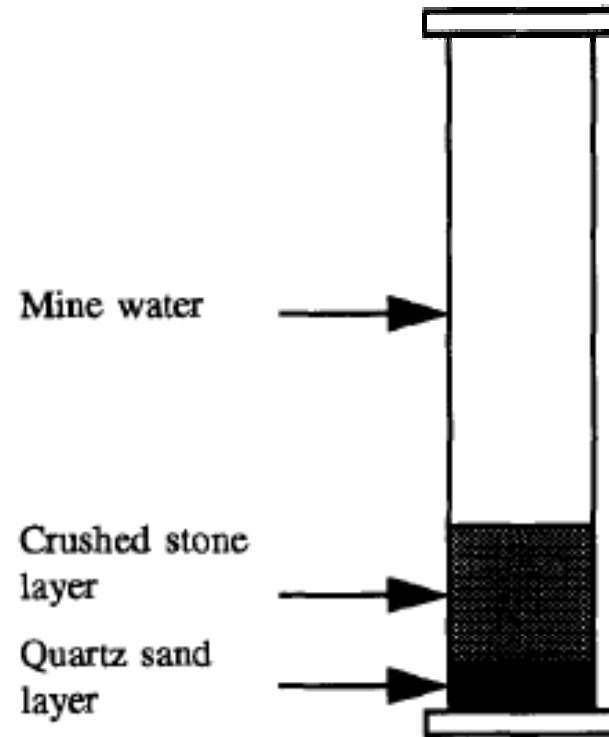


Fig. 1. Polyacrylate cylinder used in mine water treatment experiment.



## Mine Water Composition

Table 2. Water chemical parameters measured in mine water from Wallenberg mine and Gammelgruva, and start concentrations (theoretical and measured) in cylinders supplied with whey (W), whey low dosage (WLD), whey + cow manure (WCM) and whey + SRB (WSRB). Theoretical start concentrations were estimated from individual mine water concentrations and the mixing ratio, omitting a possible precipitation. Measured concentrations were determined two hours after set-up. All concentrations are in  $\text{mg l}^{-1}$

Parameter	Concentrations in mine waters			Start concentrations in cylinders after mixing 9:1				
	Wallenberg mine	Gammelgruva	Theoretical	Measured				
				Control	WLD	W*	WCM*	WSRB*
pH	5.52	2.40	3.40	3.08	3.05	3.71	4.22	4.37
SO <sub>4</sub>	2940	6600	3306	1002	936	888	857	896
Ca	500	382	488	194	—	211†	220†	202†
Mg	350	212	336	56.1	—	58.8†	59.8†	55.1†
Al	1.38	263	27.5	28.3	26.1	21.9	18.8	17.7
Fe	139	1160	241	1.89	—	29.0†	26.3†	28.0†
Cu	1.45	99.2	11.2	10.7	9.88	8.84	7.63	4.52
Zn	33.5	89.2	39.1	11.7	10.8	9.80	9.41	8.62
Mn	13.6	11.7	13.4	1.90	1.75	1.78	1.89	1.62

\* = Average of two parallel cylinders.

† = Measured at day 19.



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## Nutrient Level Details

Table 3. Initial and final nutrient concentrations in the water phase of the cylinders

Cylinder	TOC (mg l <sup>-1</sup> )		NH <sub>4</sub> <sup>+</sup> (mg l <sup>-1</sup> )		PO <sub>4</sub> <sup>3-</sup> (mg l <sup>-1</sup> )	
	Day 0	Day 203	Day 0	Day 203	Day 0	Day 203
W 1	1160	1000	6.7	6.4	10.6	4.1
W 2	1140	740	6.7	4.0	10.8	5.3
W LD	43	2.7	0.2	0.2	0.5	<0.1
WCM 1	1240	853	11.4	8.6	8.3	10.0
WCM 2	1160	782	9.6	5.6	8.8	4.8
WSRB 1	1060	217	8.7	2.0	9.6	1.3
WSRB 2	1040	749	8.2	8.0	9.4	1.5
Control	4.5	4.6	<0.1	<0.1	<0.1	<0.1



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## Results

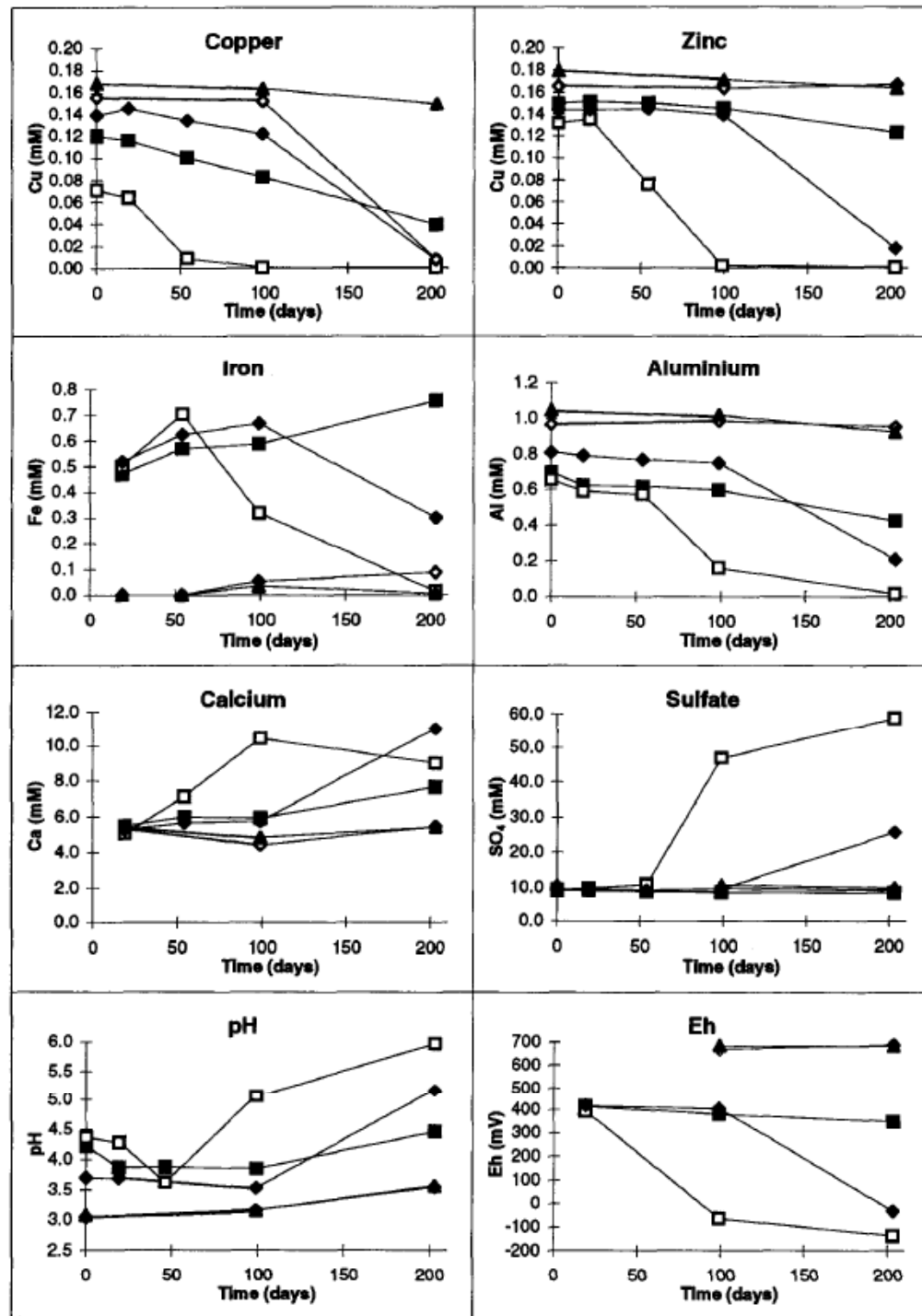


Fig. 2. Temporal variations of pH,  $E_h$ , metal and sulfate concentrations in the water phase of W1 and W2 (◆—◆), WLD (◇—◇), WCM 1 and WCM 2 (■—■), WSRB 1 and WSRB 2 (□—□) and the control cylinder (▲—▲) during the treatment experiment. Values from parallel cylinders are averaged. Average pH was calculated from average  $H^+$ -concentrations.



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## Conclusions

Dairy whey stimulated bacterial sulfate-reduction when added to acid mine water in a bench scale treatment experiment. pH increased and heavy metals were removed from the water phase after on-set of the sulfate-reduction process. The results indicate that it might be feasible to use SRB for treatment of acid mine water *in situ* in waterfilled mines and open pits.

Inoculation of the experimental cylinders with SRB was not necessary to initiate sulfate-reduction, but shortened the lag phase significantly. Most of the bacterial activity took place in the crushed stone layer at the bottom of the cylinders, where growth conditions were found to be more favourable than in the free water phase.

*In situ* treatment by SRB is a possible low cost, low maintenance concept for acid mine water treatment. Sludge handling costs can be minimized or eliminated, since the mine is used as a sedimentation basin. The amount of organic compounds added to a mine water system should be balanced with the metal content and acidity to ensure proper metal removal and avoid a harmful load of excessive organic material and nutrients in the effluent. The *in situ* treatment concept may be particularly useful in small mine water systems where the sulfate-reduction process can be properly governed.