

A Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage



Prepared by

**J. Skousen, A. Rose, G. Geidel, J. Foreman, R. Evans, W. Hellier,
and Members of the
Avoidance and Remediation Working Group
of the
ACID DRAINAGE TECHNOLOGY INITIATIVE (ADTI)**



*Published by the National Mine Land Reclamation Center
at West Virginia University.*

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Published by

The National Mine Land Reclamation Center
located at West Virginia University in
Morgantown, West Virginia

June 1, 1998

ADTI is a government/industry joint venture dedicated to the development and use
of best science applications to the problem of acid mine drainage.

*Funding for the preparation and publication of this document was provided by the U.S. Office of Surface
Mining and the National Mining Association.*

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Acknowledgments

The concept for the Acid Drainage Technology Initiative (ADTI) was developed in the Spring of 1995 by Hammond Eve of USDI, Office of Surface Mining, David Finkenbinder of the National Mining Association, and Paul Ziemkiewicz of the National Mine Land Reclamation Center at West Virginia University. Shortly after the elementary idea was developed, it was enhanced and moved forward through the efforts of Greg Conrad of the Interstate Mining Compact Commission; Roger Hornberger of Pennsylvania Department of Environmental Protection; Rocky Parsons and Charles Miller of West Virginia Division of Environmental Protection; Dan Sweeney of the U.S. Environmental Protection Agency; Kim Burke of Anker Energy; Vance P. Wiram of Cyprus/Amax Coal, Inc.; Bruce Leavitt of Consolidation Coal, Inc.; and Robert Kleinmann of the U.S. Department of Energy.

The outreach for the volunteer technical experts resulted in 51 who would work in two working groups. This handbook is the product of working group two. Section leaders are Gwendelyn Geidel for Alkaline Addition Technologies; John Foreman for Engineered Structural Techniques; Tom Jageman (until January, 1997) and Robert Evans for Active Treatment; and George Watzlaf (until January, 1997) and Arthur Rose for Passive Systems. An initial compilation of technologies was completed by Inhi Hong, Mining Engineer, Office of Surface Mining. Charles Miller, Ben Faulkner, and Marcia Nelson handled most of the management aspects of the first working group meeting. The handbook then developed into a product of the entire working group, comprised as follows:

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ADTI is supported by:

- the U.S. Department of Interior, Office of Surface Mining
- the U.S. Department of Interior, Bureau of Land Management
- the U.S. Environmental Protection Agency
- the National Mining Association
- the Interstate Mining Compact Commission
- the National Mine Land Reclamation Center
- the Eastern Mine Drainage Federal Consortium (15 Federal Agencies).

Overall management is by the Operations Committee, comprised of Gene Kreuger, who represents Federal government; Roger Hornberger, who represents the Interstate Mining Compact Commission; Kim Burke, representing the National Mining Association; Robert Kleinmann, who serves as Chair of Working Group I: Prediction; Charles Miller, Chair of Working Group II: Avoidance and Remediation; and Paul Ziemkiewicz, Director of the National Mine Land Reclamation Center and Secretariat of the Operations Committee.

INTRODUCTION

An array of techniques have been developed during the last several decades to abate or control pollution by acid mine drainage (AMD) from coal and metal mines. Although most of these techniques are successful in eliminating or decreasing the deleterious effects of AMD in some situations, they are unsuccessful in others. Due to the inherent variability between mines and environmental conditions, no one abatement or treatment technique is effective on all sites, and selection of the best method on each site is difficult given the array of methods available. The techniques also vary in the type and size of problem they are capable of handling. Their individual costs, effectiveness, and maintenance are also important considerations. Therefore, accurate information is needed to understand the limitations of the various methods and their response to various site variables. Continued research is imperative for field testing of existing technologies, as well as continued development of new technologies. At present, there is no authoritative guide or manual to assist in evaluating the best technique for a given situation.

In order to continue to mine coal and other minerals without harming the environment, the best science and techniques must be identified and implemented in order to minimize the production of AMD. To accomplish this goal, the Acid Mine Drainage Technology Initiative (ADTI) was organized to promote communication among scientists and engineers dealing with AMD, and to develop a consensus on the identification and optimum usage of each method. The intent is to provide information on selection of appropriate techniques for specific problems that will ultimately lead to a higher level of success in avoidance of AMD and remediation of existing sources, at a savings in cost and staff time, and with greater assurance that a planned technique will accomplish its objective. This effort will result in enhancement of mine drainage quality, improvement in stream cleanup and its cost effectiveness, and development of a mechanism for technology transfer.

ADTI is a coalition of State and Federal agencies, industry and private organizations, academia, and consulting firms. It is a technology-based initiative, not regulatory or political. ADTI is divided into two groups: prediction and avoidance/remediation. About 30 individuals constitute Group 2 (as listed in the acknowledgments), which focused on avoidance and remediation techniques.

The group decided at its initial meeting on April 8-9, 1996 to produce a technology handbook that would describe the many techniques and a set of case studies from which conclusions could be drawn on the applicability and limitations of each technique. The handbook will address all types of mine drainage control and treatment methods, including generalized design and performance criteria, as well as historical case studies. Ultimately, the handbook should enable the user to select the best, technologically proven, most economical method suited to a particular situation. The handbook should provide design details associated with failure to avoid repeating inadequate and inappropriate methods. It should also aid in determining research needs and cost effectiveness for various options.

This Phase I document summarizes the technologies and provides some relevant case studies collected by the various members. Further development of technologies, their description, and increased numbers of case studies will be included in a future document. The work to date has been largely volunteer in nature; support for time and travel has been met by individuals or their organizations without a specific budget for the ADTI work. Although considerable progress has been made, as indicated by this Phase I document, the lack of funding has limited progress, and the results must be considered preliminary.

The initial focus has been on AMD from coal mining, mainly in the eastern U.S., because of the easier logistics in assembling a large group of experts in meetings, and because of the additional complications created by metal mine pollution. Although much of the discussion in this manual also applies to metal mine drainage, future work will contain more emphasis on drainage from metal mines.

The handbook will be updated periodically to add new information from case studies and research, and as improved insights are gained on the optimum applicability of the various techniques.

1.0 ACID MINE DRAINAGE

1.1 Formation

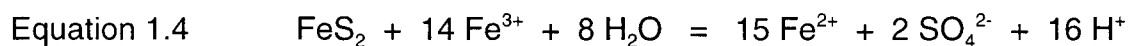
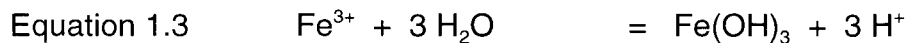
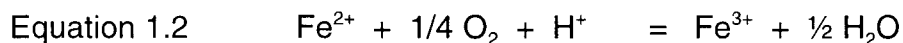
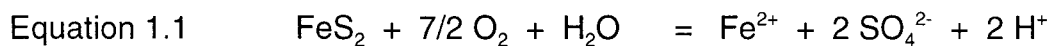
Acid mine drainage (AMD) or acid rock drainage, collectively called acid drainage (AD), is formed when certain sulfide minerals in rocks are exposed to oxidizing conditions. Much of the AD worldwide is commonly thought to be associated with coal mining, but AD can occur under natural conditions or where sulfides in geologic materials are encountered in metal mining, highway construction, and other deep excavations. Iron sulfides common in coal regions are predominately pyrite and marcasite (FeS_2), but other metals may be combined with sulfide in the form of chalcopyrite (CuFeS_2), covellite (CuS), and arsenopyrite (FeAsS) (Table 1.1). Pyrite commonly occurs with other metal sulfides, potentially causing AD.

Table 1.1. Some important metal sulfides which occur in mining regions. The predominant acid producers are pyrite and marcasite.

FeS_2 -	pyrite	MoS_2 -	molybdenite
FeS_2 -	marcasite	NiS -	millerite
Fe_xS_x -	pyrrhotite	PbS -	galena
Cu_2S -	chalcocite	ZnS -	sphalerite
CuS -	covellite	FeAsS -	arsenopyrite
CuFeS_2 -	chalcopyrite		

Upon exposure to oxidizing conditions and in the absence of alkaline materials, some sulfide minerals are oxidized in the presence of water and oxygen to form highly acidic, sulfate-rich drainage. Acidity levels, and metal composition and concentration depend on the type and amount of sulfide mineral and the presence or absence of alkaline materials. In the coal fields when sulfides are present, the oxidation of Fe disulfides and

subsequent conversion to acid occur through several reactions. The following four chemical equations are accepted to explain the processes (Stumm and Morgan 1996).



In equation 1.1, Fe sulfide is oxidized, thereby releasing ferrous iron (Fe^{2+} , the reduced form of iron), sulfate (SO_4^{2-}), and acid. Ferrous iron in equation 1.2 can be oxidized to form ferric iron (Fe^{3+}). Ferric iron can then either be hydrolyzed and form ferric hydroxide, Fe(OH)_3 , and H^+ acidity (equation 1.3), or it can directly attack pyrite and act as a catalyst in generating much greater amounts of ferrous iron, sulfate, and acidity (equation 1.4).

If any of the processes represented by the equations were slowed or altogether stopped, the generation of AMD would also slow or cease. Removal of air and/or water from the system, two of the three principal reactants, would stop pyrite from being oxidized. Almost complete absence of oxygen occurs in nature when pyrite is found beneath the water table where oxidizing conditions are limited. Under these conditions, the pyrite remains almost completely unreacted. When pyrite is enclosed within massive rock, only minimal amounts of pyrite are oxidized through natural weathering, thereby generating only small amounts of acid, and this acid is sometimes naturally diluted or neutralized by surrounding alkaline rocks. However, when large volumes of pyritic material are fractured and exposed to oxidizing conditions, which can occur in mining or other major land disturbances, the pyrite reacts, and water dissolves and moves the reaction products (Fe and other metals, sulfate, and acid) into ground and surface water sources.

Under many conditions, equation 1.2 is the rate-limiting step in pyrite oxidation because the conversion of ferrous iron to ferric iron is slow at pH values below 5 under abiotic conditions (Singer and Stumm 1968, 1970). However, Fe-oxidizing bacteria, principally Thiobacillus, greatly accelerate this reaction, so the activities of bacteria are crucial for generation of most AMD (Leathen et al. 1953, Waksman 1922), and much work in bactericides has been conducted. In contrast, availability of oxygen may be the rate-limiting step in spoil of low porosity and permeability such as that composed of soft shale, so that oxidation is limited to the upper few meters of spoil. In porous and permeable spoil composed of coarse sandstone, air convection driven by the heat generated by pyrite oxidation may provide high amounts of oxygen deep into the spoil (Guo et al. 1994, Guo and Cravotta 1996).

1.2 Forms of Sulfur in Rock

Sulfur in coal and rocks associated with coal mines can occur as organic sulfur, sulfate sulfur, and pyritic sulfur. Some sulfur in coal appears to have been introduced after the peat had been converted to coal, as is evidenced by pyrite coatings on vertical fracture surfaces, called cleat, in the seam. Much of the pyrite present in rocks and overburdens of coal mines occurs as very small crystalline grains intimately mixed in sandstones and shales (Temple and Koehler 1954). The origin of sulfur in large concretions, nodules, lenses, bands, and fillings in porous layers of coal is less well understood (U.S. Geological Survey 1968).

Organic sulfur is believed to be complexed and combined with organic constituents of coal and organically bound within the coal. This form of sulfur is only found in appreciable quantities in coal beds and in other carbonaceous rocks. Generally, the organic sulfur component is not chemically reactive and has little or no effect on acid-producing potential.

Sulfate sulfur is usually only found in minor quantities in fresh coal and other undisturbed pyrite-containing rocks, and is commonly the result of weathering and recent oxidation of sulfide sulfur. Some sulfate minerals like jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) can dissolve and form acid solutions in near surface environments.

Pyritic or sulfide sulfur is the dominant form of sulfur in the majority of coal and associated rocks. It is the sulfur form of greatest concern. Of all the sulfide minerals that may be present, Fe disulfides predominate and are the major acid producers. Accordingly, the maximum potential acidity (MPA) of a fresh overburden sample correlates closely with the pyritic sulfur content. Studies have shown that variations in total sulfur contents of overburden samples reflect similar variations in pyritic sulfur content. Several types of pyritic sulfur are known based on physical appearance, and they are classed into six groups: 1) primary massive, 2) plant replacement pyrite, 3) primary euhedral pyrite, 4) secondary cleat (joint) coats, 5) mossy pitted pyrite, and 6) framboidal pyrite. Caruccio et al. (1988) provide an extensive review of the different forms, morphologies, and reactivity of pyritic materials.

The equations for pyrite oxidation show that a material containing 1% sulfur, all as pyrite, would yield upon complete reaction an amount of sulfuric acid that requires 31.25 Mg of CaCO_3 to neutralize 1000 Mg (or tons/1000 tons) of the material (Sobek et al. 1978). When sulfur in the rock is exclusively pyrite, the total sulfur content of the rock accurately quantifies the acid-producing potential, if it were all to react. When organic or sulfate sulfur are present in significant amounts in partially weathered rocks, total sulfur measurements overestimate the amount of acid that will be formed upon oxidation. Therefore, correction for sulfates and organic sulfur naturally present in some overburdens or resulting from partial weathering of pyritic materials may be necessary to increase accuracy in predicting the acid-producing potential of materials containing mixed sulfur species.

The rate of pyrite oxidation depends on numerous variables such as:

- reactive surface area of pyrite (Singer and Stumm 1968),
- form of pyritic sulfur (Caruccio et al. 1988),
- oxygen concentrations (Smith and Shumate 1970),
- solution pH (Smith and Shumate 1970),
- catalytic agents (Caruccio et al. 1988),
- flushing frequencies (Caruccio et al. 1988),
- the presence of Thiobacillus bacteria (U.S. Environmental Protection Agency 1971).

The possibility of identifying and quantifying the effects of these and other controlling factors with all the various rock types in a field setting is unlikely. A variety of approaches to evaluating the rate are discussed in the following pages.

1.3 Alkalinity in Rocks

The natural base content of overburden materials (alkali and alkaline earth cations, commonly present as carbonates or exchangeable cations on clays) is important in evaluating the future neutralization potential (NP) of the materials. The amount of alkaline material in unweathered overburden may be sufficient to equal or overwhelm the acid-producing potential of the material. Of the many types of alkaline compounds present in rocks, carbonates (specifically calcite and dolomite) are the primary alkaline compounds which occur in sufficient quantities to be considered as effective deterrents to AMD generation.

In overburden containing both alkaline and pyritic material, the alkaline material may be sufficient to reduce oxidation from occurring or to neutralize the acid formed from pyrite. Higher alkalinities also help control bacteria and restrict solubility of ferric iron, which are both known to accelerate acid generation. Although a number of factors must be considered, a balance of the acid-producing potential and neutralizing capacity of an overburden sample will indicate whether acidity or alkalinity is expected in the material upon complete weathering (Caruccio and Geidel 1980).

1.4 Acid Mine Drainage

AMD is an acidic, iron and sulfate water that forms under natural conditions when geologic strata containing pyrite are exposed to the atmosphere or oxidizing environments. AMD can form from coal mining, both in surface and in underground mines. Alkaline mine drainage is water that has a pH of 6.0 or above, contains alkalinity, but may still have dissolved metals that can create acid by reactions 1.2 and 1.3. The drainage quality (acid or alkaline) emanating from underground mines or backfills of surface mines is dependent on the acid (sulfide) and alkaline (carbonate material) minerals contained in the disturbed geologic material. 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 net alkaline water.

Mine drainage can be categorized into several basic types (Skousen and Ziemkiewicz 1996): Type 1 mine drainage has little or no alkalinity (pH <4.5) and contains high concentrations of Fe, Al, Mn, and other metals, acidity, and oxygen. This type of water is called AMD. AMD may also refer to water that has a pH <6.0, and contains net acidity (acidity is greater than alkalinity).

Type 2 mine drainage has high total dissolved solids containing high ferrous iron and Mn, no or low oxygen content, and pH >6.0. Upon oxidation, the pH of this water drops dramatically and becomes Type 1 AMD.

Type 3 mine drainage has moderate to high total dissolved solids, low to moderate ferrous iron and Mn, no or low oxygen content, pH >6.0, and alkalinity greater than acidity (commonly called alkaline mine drainage). Upon oxidation, the acid generated from metal hydrolysis and precipitation reactions are neutralized by alkalinity already present in the water.

Type 4 mine drainage is neutralized AMD with pH >6.0 and high total suspended particulates. Settling of metal hydroxides in the water has not yet occurred. With residence time in a pond, the particulates will settle out and form Type 5 water.

Type 5 water is neutralized AMD, with pH >6.0 and high total dissolved solids. After most metal hydroxides have precipitated in a settling pond, the main cations left in high concentrations in the water are usually dissolved Ca and Mg. Soluble oxy-anions like bicarbonate and sulfate also remain in solution. If alkalinity or oxygen is lacking in the neutralization process, the water will not reach Type 5.

Another type of mine drainage occurs from mines with minor sulfides and low to moderate amounts of carbonate. The water typically is near neutral pH, the specific conductance is low (<100 uS/mm) and acidity and alkalinity are nearly balanced. These are classified as inert or neutral waters.

Mixing among these various types of waters creates transitional types of water, so adequate sampling and analysis of the pH, oxygen status, and metal concentrations is important to determine the type of mine drainage and the intensity of its acidic character.

1.5 Discharge Limits

Coal mine operators are required to meet environmental land reclamation performance standards established by federal (the Surface Mining Control and Reclamation Act, SMCRA) and state regulatory programs. 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 the CWA. Allowable pollutant discharge levels are usually determined by the U.S. Environmental Protection Agency's (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. NPDES permits on surface mines usually require monitoring of pH, total suspended solids (TSS), Fe and Mn concentrations. Other parameters may be required by the regulatory authority to address specific concerns in a particular mining situation.

1.6 Acidity and Alkalinity Measurements

Acidity and alkalinity can be measured in various units such as equivalents/L, milliequivalents/L, mg/L as CaCO_3 , and mg/L as HCO_3^- (Eaton et al. 1995). In this document, mg/L as CaCO_3 will be used as the unit for acidity and alkalinity. Acidity is a measure of the amount of base needed to neutralize a volume of water. For AMD, the acidity should be measured by a "hot acidity" procedure that oxidizes Fe^{2+} and Mn^{2+} so that their acid character is correctly measured. Acidity in AMD is comprised of mineral acidity (Fe, Al, Mn, and other metals depending on the specific metal sulfide exposed during disturbance) and hydrogen ion acidity. Other metals in AMD vary widely, but AMD is characterized by low pH, high sulfate and Fe. As contaminated streams flow into larger uncontaminated streams or lakes, dilution occurs. Also, natural chemical and biological reactions cause some neutralization of acidity and precipitation of metals. In studies of uncontaminated natural water, the term acid water commonly refers to water with low pH. For example, waters contaminated from "acid rain" usually have low pH (from 3.5 to 4.5), but have very little mineral acidity.

Drainage from metal mines (acid rock drainage) may contain significant amounts of Zn, Cu, Ni, Pb, etc. However, when dealing with AMD from coal mines in the eastern U.S., the pH, Fe, Al, and Mn usually account for the majority of the acidity (Hedin et al. 1991). Acidity can also be estimated for acid rock drainage from metal mines by incorporating additional metals into the equation, and by knowing their concentrations, their molecular weights, and valences.

As an example, acidity of coal mine drainage can be estimated by using metal concentrations in the following manner:

$$\text{Estimated Acidity} = 50 (2 \text{ Fe}^{2+}/56 + 3 \text{ Fe}^{3+}/56 + 3 \text{ Al}^{3+}/27 + 2 \text{ Mn}^{2+}/55 + 1000(10^{-\text{pH}}))$$

where estimated acidity is expressed as mg/L CaCO₃ equivalent, all metal concentrations are in mg/L, and 50 transforms milliequivalents (meq) of acidity into mg/L CaCO₃ equivalent. For AMD with a pH <4.5 (no alkalinity present), this equation can be used to estimate the actual titrated, laboratory measured acidity of the water.

For example, a water sample was measured to have an acidity value of 410 mg/L as CaCO₃, pH of 3.1, ferrous iron (Fe²⁺) content of 14 mg/L, ferric iron (Fe³⁺) of 33 mg/L, Al of 47 mg/L, and Mn of 9 mg/L. Substituting the ion concentrations into the equation above, the milliequivalents (meq) of each ion are: hydrogen ion is 0.8, ferrous iron is 0.5, ferric iron is 1.77, Al is 5.22, and Mn is 0.33. These ions total 8.62 meq. Multiplying by 50 gives 431 mg/L of acidity as CaCO₃. This calculated value is close to the laboratory measured value of 410 mg/L as CaCO₃.

Additional metals such as Pb, Cu, Zn and Ni may furnish acidity, but the amount depends on their concentration, the specific solid that is precipitated, and the anion composition of the solution. For example, the precipitation of PbSO₄ from a sulfate rich AMD generates no acidity; precipitation of PbCO₃ produces 1 H⁺ per Pb²⁺, and PbO precipitation would generate 2 H⁺. Precipitation of ZnO in principle produces 2 H⁺ but is not complete at pH 8.3, which is where the acidity titration is usually measured. Unless these metals are present in high concentrations (tens of mg/L), they are probably not significant in estimating acidity.

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2.0 Alkaline Addition and Overburden/Refuse Reclamation

During mining or other rock disturbing activities, strata of varying chemical compositions are disturbed and the ultimate quality of the drainage is a blend of all drainage chemistries produced by each disturbed rock type. Various techniques are available to evaluate the acid and alkaline potentials of overburden material and these techniques are fully discussed by the Prediction Committee report of ADTI (In preparation, 1998; see also Skousen et al. 1987, Sobek et al. 1978). This section of the handbook discusses the *in situ* or at-source control technologies and reclamation techniques which have been developed and evaluated for disturbances predicted to have a mine drainage quality concerns. These technologies, while used to either 1) prevent or retard the oxidation of pyrite and production of acid or 2) neutralize the acid produced within the backfill, are often used in conjunction with each other. Attempts have been made to provide case studies which have utilized only one technology, however, in Section 2.9 the synergistic effects of various reclamation techniques are discussed.

Once overburden materials have been identified and classified based on overburden analyses, the overburden (including toxic material) handling and placement plan for the particular site must be carefully followed. The plan often has a number of elements which may include, depending on the nature of the overburden: selective handling of the acid-producing materials (section 2.6); the addition of alkaline materials which serve to either neutralize the acid generated or retard the oxidation of pyrite (section 2.2); encapsulation of the acid-producing material, a technique which has been used both during and post reclamation (section 2.4); removal of toxic material by reining, reprocessing or daylighting deep mines (sections 2.5 and 2.8); and inhibition of pyrite oxidation by bactericides (section 2.1), through the incorporation of sewage sludge (section 2.3) or by inundation of the acid-producing materials (section 3.1).

In the Appalachian Coal Region of the U.S., recommended reclamation procedures have included segregating and placing acid-producing materials above the water table on top of a 1- to 2-m layer of nontoxic material on the pavement, and then treating, compacting and covering the materials with a clay cap or other type of sealant material to

reduce surface water infiltration into this material (Skousen et al.1987). Except when alkaline infiltration techniques (such as surface applications, trenches or alkaline funnels) are part of the plan, diverting surface water above the site to decrease the amount of water entering the mine has also been highly recommended.

An alternative approach to controlling the release of acid products from pyritic material is to rapidly and permanently inundate the acid-producing material, thereby preventing pyrite oxidation. Inundation is only suggested where a water table may be permanently reestablished to cover acid-producing materials (such as below drainage deep or surface mines), or where the materials such as tailings, can be placed in a lake (section 3.1). Inundation has not been commonly used as an alternative for surface-mined lands or above-drainage underground mines in the mountainous Appalachian region.

Limestone or other alkaline materials may occur in the overburden or, if calcareous material is deficient in the section, limestone may be imported and incorporated into the overburden handling and placement plan. This plan may include blending alkaline overburden or imported limestone to neutralize acid-producing materials in the overburden or to neutralize any residual acid in topsoil materials to aid vegetation establishment. Alkaline materials may also be used to create zones of alkaline rich waters to infiltrate through controlled seepage areas and increase the alkalinity of the backfill. Upgradient of mined areas, surface and ground water with low mineral acidity can be treated with limestone (section 4.2.1) or other alkaline material in either the water course or watershed to improve water quality.

Acid mine drainage control technologies are measures that can be undertaken where AMD formation has already taken place or is anticipated. At-source control methods treat the acid-producing rock directly and stop or retard the production of acid, whereas treatment methods add chemicals directly to acidified water leaving the rock mass (section 4.0) or direct the acid water through various passive systems for treatment (section 5.0). Coal companies mining in acid prone areas of the eastern U.S. must treat AMD and face the prospect of long term to indefinite water treatment and its attendant liabilities. It is

obvious that cost-effective methods which prevent the formation of AMD at its source would be preferable. Some control methods are most suitable for abandoned mines and others are only practical on active operations. Other methods can be used in either setting.

Some of the techniques described below have been very successful. Others have been only partially successful and have demonstrated less than 100% control of acid produced on-site. This may be due to several site specific factors including: mining technique, rock type and chemistry, ground water flow rates, etc. While a technique that controls 80% of a site's acid production and reduces long-term operation and maintenance costs may not relieve a mine operator of liability, the method may be suitable for active sites which meet certain criteria, abandoned mine reclamation programs, or watershed restoration projects. Removing a significant portion of the acid or metal load in a watershed by partially-effective control strategies may improve the health of a stream to a point of re-introducing some fish species or re-establishing some designated uses of the stream. Alternatively, the method may be combined with another partial control scheme to achieve effluent limits. Since partial control methods are often the least costly, their use in combination with other techniques is often financially attractive. For example, a partial control method such as regrading/topsoiling can be combined with alkaline amendment to reduce the amount of alkalinity required to offset potential acid production.

2.1 Bactericides

Anionic surfactants are used to control bacteria that catalyze the conversion of Fe^{2+} to Fe^{3+} , which thereby control pyritic oxidation (Equation 1.2, section 1.1) (Kleinmann et al. 1981). They are used primarily in situations where immediate control of AMD formation is important and work best on fresh, unoxidized sulfides. Bactericides are often liquid amendments, which can be applied to refuse conveyor belts or sprayed by trucks on cells of acid-producing materials in the backfill. Bactericides have also been used successfully at metal mines (Parisi et al. 1994).

Surfactants, by themselves, are not seen as a permanent solution to AMD. Eventually the compounds either leach out of the rock mass or are decomposed. However, slow-release formulations are commercially available and have been successfully used at regraded sites (Splittorf and Rastogi 1995). Bactericides appear to

work best when used in combination with other control methods and can be useful in preventing acid conditions in pyritic rock piles which remain open for several years until the site is reclaimed.

Case Studies:

One example of surfactant application was done in 1988 on a 4.5 ha refuse site in Pennsylvania. Surfactant was applied via a hydroseeder at rates of 225 kg/ha initially, then successive amounts were added as fresh refuse was deposited. Effluent from the pile showed a 79% decrease in acidity and an 82% decrease in Fe. Cost savings at the AMD plant were \$300,000 per year (Rastogi 1994).

In another example, a 14 ha (35 acre) coal refuse pile in West Virginia was regraded, then controlled release surfactant pellets (Promac) were applied to the surface, followed by topsoiling, liming, and revegetation between 1986 and 1988 at a cost of \$124,180. Compared with the 0.5 ha untreated control portion of the project, the discharge from the 14 treated ha improved from pH 2.9 to 6.2, acidities decreased from 1680 to 1 mg/L as CaCO₃, and Fe and Mn concentrations were reduced to 2 and 0.8 mg/L from 300 and 25 mg/L, respectively.

Bactericides were not as effective when applied to the overburden surface of a pre-1970 mined site in Ohio. No topsoil was applied at the site, but reclamation efforts had established some surface vegetation. Controlled release surfactant pellets were applied by hydroseeder in 1982 to a predominantly sandstone overburden containing pyrite nodules. Seeps discharging from the site initially had acidities between 1000 to 3000 mg/L as CaCO₃; however, there was only minor improvement (Geidel, personal communication).

2.2 Alkaline Addition

Recent studies have indicated that certain types of alkaline amendments can successfully control AMD from pyritic spoil and refuse (Brady et al. 1990, Burnett et al. 1995, Perry and Brady 1995, Rich and Hutchinson 1990, Rose et al. 1995, Wiram and Naumann 1995). The use of alkaline additions can be divided into several categories, including: 1) blended with potentially acid-producing material to either neutralize the acid or to retard and, in some cases, prevent the oxidation of pyrite; 2) incorporated as

stratified layers at specific intervals within the backfill or spoil; 3) applied as trenches or funnels to create alkaline groundwater conduits through the reclaimed mine; 4) applied on or near the surface to enhance plant growth and create an alkaline wetting front that will migrate downward through the overburden, and 5) applied as a chemical cap to create a hardpan (either on the surface or the floor of the mine).. Because a number of alkaline materials can be used or applied by various methods, the discussions which follow will identify the material used (e.g. limestone) and then provide case studies evaluating the use and effectiveness of the material under different application methodologies.

When alkaline material is blended or incorporated in stratified layers, especially in coal mines, the schemes usually rely on Acid Base Accounting (ABA) to estimate the required amount of alkalinity for neutralization of pyritic materials. The rationale behind this reliance is based on a total neutralizing capacity of the section compared with the total acid production capacity. While this does not take kinetics of release into account, it recognizes that if all of the pyrite were to oxidize, then there would be sufficient alkaline material to neutralize the acid. Therefore, accurate, representative overburden analyses before mining are crucial in developing mining plans and alkaline addition programs in acid-producing areas. When acid problems are identified, it is best to generate cost-effective control strategies during premining planning. Errors in predicting postmining water quality from premining overburden analyses include unrepresentative sampling of overburdens and inaccurate analyses (Rymer et al. 1991, Wiram and Naumann 1995) and non-homogeneous placement of spoils. For example, Schueck (1990) reported AMD generation from a surface mine in Pennsylvania resulted largely from buried refuse and pit cleanings within an otherwise neutral to alkaline spoil matrix as identified by ABA. If insufficient alkalinity is available in the spoil, then external sources of alkalinity may be imported (Skousen and Larew 1994, Wiram and Naumann 1995).

2.2.1 Limestone

Limestone is often the least expensive and most readily available source of alkalinity. It has an NP of between 75 and 100% and is safe and easy to handle. On the other hand, it has no cementing properties and cannot be used as a barrier. Field and laboratory studies have indicated that there are threshold levels of Neutralization Potential

(NP), above which acid conditions in coal mines do not develop when the mines are properly reclaimed. Bradham and Caruccio (1997) found that within the northeastern U.S. coal fields, at 3.7% NP no acid would be produced at a 95% confidence level. diPretoro and Rauch (1988) found sites with >3% NP as CaCO₃ equivalent in overburden produced alkaline drainages, while acid drainage resulted at ≤1% NP. Brady and Hornberger (1989) suggest threshold values of NP ≥3% and S <0.5% as guidelines for delineating alkaline-producing strata. Brady et al. (1994) showed that 3% net NP in an overburden caused alkaline drainage while <1% net NP produced acid drainage from 38 mines in Pennsylvania. They concluded that mining practices (such as selective handling and concurrent reclamation) enhanced that effect of alkaline addition on reducing acid production. Further refinements (Perry and Brady 1995) gave a value of 21 Mg/1000 Mg net NP (2.1%) to produce alkaline drainage at 40 sites in Pennsylvania.

Brady and Hornberger (1990) conclude that NP from ABA shows the strongest relationship with actual postmining water quality. This relationship is only qualitative (e.g. acid vs. non-acid) and NP must significantly exceed maximum potential acidity (MPA) in order to produce alkaline water. If NP and MPA are similar, AMD will most likely result (see ADTI Prediction Committee report on Prediction of Mine Drainage 1998).

2.2.1.1 Blending and Stratified Layers

Spoils are composed of a mixture of acid-forming, alkaline-generating and inert rocks, while materials like refuse are dominated by acid-producing rocks with no NP. In spite of significant alkalinity in overburdens, AMD may originate from localized sites within the backfill. Due to the pseudo-karst hydrology of many surface mines (Caruccio et al. 1984, Hawkins and Aljoe 1992), infiltrating water is influenced only by acid and alkaline rocks directly in its path. If water flows primarily through permeable acid rocks, AMD can result and the water may discharge to the nearest stream while the alkaline material in the pile remains unreacted. Unless contacted directly by acid water, most of the spoil limestone will remain in solid form. Thus the presence of alkaline material in the backfill does not ensure that it will neutralize acidity. For efficient neutralization, the acid-forming and alkaline material must be thoroughly mixed. Where insufficient alkalinity is present, it is necessary to add alkaline material to the rock mass. If one relied on random spoil

dumping, an overwhelming supply of alkaline material would be needed. If there were a consensus on the subject, it would appear that material mixtures with an NP/MPA ratio above 2 and a net NP above 30 Mg/1000 Mg (3.0% net NP) generate alkaline water. Even at high NP/MPA ratios, acidity may be produced if the acid-producing materials are incorrectly placed so that they intercept the groundwater, or insufficient alkaline material is added only to the surface (Lusari and Erickson 1985). Thorough mixing during materials handling can reduce the required NP/MPA ratio.

Addition of alkaline material to refuse is a relatively simple process. Since the refuse leaves the preparation plant on a belt conveyor or in a slurry line, the alkalinity can be metered directly into the refuse stream and thoroughly mixed.

Adding alkalinity to spoil requires more care during mining and reclamation. The high volume of spoil necessitates applying alkalinity only to those rock masses that are identified as potentially acid-producing. Surface coal mining operations can remove the identified rock (often the coal roof rock, partings and pavement) and place the acid-producing materials in cells in the backfill for treatment with alkaline amendments (Skousen and Larew 1994). Since acid-producing rock types are often a small percentage of the total spoil, such a procedure results in efficient use of the alkaline material. Additional compaction is desirable during placement of cells. Often the final pit floor contains considerable pyrite, much of it within 30 cm of the coal. Two approaches can be taken: 1) remove the pyritic material and place it in cells for alkaline amendment or 2) seal the pit floor with self-cementing material such as FBC ash.

Case Studies:

In Tennessee, a surface coal mine, using both cast blasting and dragline equipment for overburden handling, incorporated limestone on the pit floor, in spoil during cast blasting, on the dragline bench, and at the topsoil/backfill interface (Wiram and Naumann 1995). The amount of limestone added was calculated based on net NP and also taking into account the presence of siderite. While the handling plan also included surface alkaline recharge structures, the ground water in the vicinity of the blended limestone showed high alkalinities (400 to 500 mg/L as CaCO_3), a 10 fold decrease in Fe concentrations, and a 2 to 3 times decrease in Mn concentrations.

A surface coal mine in Pennsylvania improved the water quality from an old deep mine by partially re-mining the deep mine and by adding 1350 Mg/ha (600 tons/ac) limestone. Of the 1350 Mg, 225 Mg (100 tons) were added to the pit floor, 225 Mg/ha were applied at the top of the regraded backfill prior to the replacement of topsoil, and 900 Mg/ha were dispersed throughout the mine spoil. The 900 Mg/ha were mixed by a simple yet innovative and practical technique. Drill holes, charged with explosive for overburden blasting, were "stemmed" with imported waste limestone rather than drill cuttings. Because the waste limestone is a mixture of sizes (from 200 mesh to 0.8 cm), it provided a dense explosive cover. The alkaline material was mixed effectively by the blasting and was further mixed by the dragline's random spoiling process. The mine water discharge improved from an acidity of 120 mg/L as CaCO_3 to 19 mg/L net alkalinity and Fe was significantly reduced (Smith and Dodge 1995).

2.2.1.2 Alkaline Recharge Structures

Alkaline recharge structures are surface structures designed to collect and divert infiltrating water through porous alkaline zones thereby inducing alkaline water into the reclaimed area. In many instances, recharge zones can be determined from surface depressions and the construction of structures, whether trenches, funnels or pits, will provide an avenue for alkalinity. Infiltrating alkaline waters provide an alkaline front that migrates through the backfill, neutralizing acidity and raising pH. This alkalinity can displace bacteria and cause the acid-producing reaction to be slowed or completely stopped.

Case Studies:

Fifteen alkaline recharge trenches, averaging 3 m wide, 1 m deep and varying in length from 23 to 220 m, were installed on a previously mined WV surface coal mine (Caruccio et al. 1984). Concurrent with the emergence of halogen tracers, the seep quality improved from 600 mg/L acidity as CaCO_3 to around 100 mg/L, and the metal and sulfate concentrations decreased. Acidities remained at about 100 mg/L as CaCO_3 for a number of years. In 1994, zones of ground water recharge were identified and eight alkaline funnels (recharge structures which were approximately 3 m deep and 1 m in diameter)

were installed. The spoil was excavated and the "funnel" filled with coarse limestone. The quality of the seeps improved by about 50% (Carrucio and Geidel 1995).

Alkaline structures have also been incorporated into active mine plans (Wiram and Naumann 1995). In a Tennessee surface coal mine, recharge structures, approximately 45 m long by 15 m wide by 4 m deep, were placed over chimney drains installed in the backfill and filled with 2.5 m of limestone. Monitoring of wells showed a significant increase in alkalinity levels and a decrease in Fe and Mn concentrations.

2.2.1.3 Surface Application

While limestone or lime is routinely added to the soil to enhance reclamation and vegetation growth, it has also been used as a surface amendment to improve ground water quality (Caruccio and Geidel 1996). The concept of surface application is that rainwater in contact with limestone will generate alkalinity and the alkalinity will create a wetting front which moves through the spoil. This technique has had limited success and, unless the seeps or discharges were initially low in acidity (<100 mg/L acidity as CaCO₃), the limestone only minimally improved seep quality.

Case Studies:

A 12 year old, partially reclaimed, pre-SMCRA surface mine in Ohio was amended with a surface application of limestone in five of seven areas (two areas were controls). Limestone was applied at rates varying from 90 to 160 Mg/ha (40 to 70 tons/ac) over the 60 ha site and 25 seeps were monitored for six years. Concurrent with tracer appearance, the low acidity (50 to 70 mg/L as CaCO₃) seeps became alkaline, however, the highly acid seeps (500 to 3000 mg/L as CaCO₃) showed only minimal response to the limestone. While the seep acidity decreased by about one third over the six years, the rate of decrease in the treated compared to the control seeps was only slightly improved (Geidel and Caruccio 1982).

2.2.2 Calcium and Magnesium Oxides

Because of limestone's limited solubility, it can only raise the pH of a system to approximately 8.3. Under certain situations, primarily when Mn levels must be decreased, higher pH levels are required. Examples of such materials that can increase water pH above 8.3 include: calcium-magnesium oxide (Magnalime), CaO and Ca(OH)₂.

Case Studies:

Since 1994, a surface coal mine in WV has been using Magnalime (a highly alkaline material containing approximately 30% CaO and 20% MgO, a waste by-product marketed by Ashland Chemical) to precipitate metals on the pit floor, thereby creating a seal. Applying approximately 112 Mg/ha (50 tons/ac) to the pit floor, the oxide forms a layer similar to cement thereby sealing the pit floor and providing alkalinity to the water accumulated there. While the primary objective was to reduce the level of available Mn, the acidity also decreased and the site was reclaimed with good vegetation (Faulkner, personal communication).

Alkaline recharge trenches have also been constructed with CaO and Ca(OH)₂ on top of an 8 ha coal refuse disposal site, which produced AMD seepage (Nawrot et al. 1994). After installing the alkaline recharge pools, acidity reductions of 25 to 90% were realized with concomitant 70 to 90% reductions in Fe and sulfate in seepage water. The following conclusions and recommendations were made: 1) use highly soluble alkaline materials (e.g., CaO, Ca(OH)₂ waste products); 2) maximize water volumes through trenches by directing surface water flow into the pool; 3) use multiple alkaline recharge pools to increase chances of influencing groundwater flows; 4) construct infiltration paths into the backfill to improve alkaline diffusion and flushing; and 5) allow sufficient time (possibly 3 to 5 annual cycles) for the effect to become apparent.

2.2.3 Coal Combustion By-Products

Fluidized Bed Combustion (FBC) ash is produced at power generating plants that burn high sulfur coal or refuse in an FBC system. Sulfur dioxide emissions are controlled by injecting limestone into the combustion bed. At combustion temperatures, the limestone calcines leaving calcium oxide. About one-half of the CaO reacts with sulfur dioxide to form gypsum and the rest remains unreacted. Therefore, FBC ashes generally have NP's of between 20 to 40% and they tend to harden into a cement after wetting (Skousen et al. 1997a). Other power generation ashes, like flue gas desulfurization (FGD) products and scrubber sludges, may also have a significant NP which make them suitable alkaline amendment materials (Stehouwer et al. 1995).

Case Studies:

Hamric (1993) used FBC ash as material to seal the pit floor thus preventing groundwater from contacting acid-producing shales immediately below the coal in northern West Virginia. The ash was also placed on top of the regraded area to reduce infiltration and to lime the soil. Results of the application showed slight reductions in acidity of AMD coming from the mine site where ash was applied.

Researchers from American Electric Power and Ohio State University used FGD material to amend coal refuse in field and laboratory studies at the Rehobeth site. The FGD was determined to have a neutralizing potential of 15% CaCO₃ equivalency and a permeability of 1 x 10⁻⁶ cm/sec. The FGD material produced a larger yield of vegetation than refuse amended with agricultural lime at equivalent amounts. Water quality from the field experiments met drinking water standards, while untreated (control) runoff had high acidity and metal concentrations. Additionally, FGD material test plots had reduced infiltration rates, were highly stable, and resisted erosion (Mafi 1995).

2.2.4 Kiln Dust and Steel Slags

Kiln dust, produced by lime and cement kilns, contains 15 to 30% CaO with the remaining 70 to 85% of the material being hydrated lime and limestone. Kiln dust absorbs moisture and also hardens upon wetting. It is widely used as a stabilization and barrier material.

Steel making slags are locally available in large quantities at low cost and, when fresh, have NP's from 45 to 90%. Studies indicate that columns of steel slag maintain constant hydraulic conductivity over time and produce highly (>1,000 mg/L as CaCO₃) alkaline leachate (Ziemkiewicz and Skousen 1998). Steel slag can be used as an alkaline amendment as well as a medium for alkaline recharge trenches. Slags are produced by a number of processes so care is needed to ensure that candidate slags will not leach metal ions such as Cr, Mn, Ni, or Pb.

Other alkaline materials may have higher NPs than limestone, but the source of the material should be checked and a complete analysis done to evaluate NP and metal content before use. Quicklime, kiln dust and hydrated lime all react more rapidly than limestone, though it is not clear whether this is an advantage in AMD prevention. These

substances also have the potential to create pH values above 11, though such values are rarely reached in field applications.

Case Studies:

Rich and Hutchison (1990 and 1994) reported a successful operation where 2% lime kiln dust is added to refuse at a preparation plant in West Virginia. Not only did the kiln dust prevent acid formation, it improved the strength of the refuse pile by absorbing moisture from the filter cake, allowing easy access for large haulage trucks. Currently at least eight preparation plants in the eastern U.S. are using this technique.

Lime kiln dust has also been added to the overburden of a coal mine having alkaline deficiencies of up to 2450 Mg CaCO₃/ha (1090 tons CaCO₃/ac). The dust was applied to the pit floor at about 224 Mg/ha (100 tons/ac), also around special-handled cells, and also on fractured overburden after blasting. After grading, the dust was applied to the backfill surface, back-dragged by bulldozers to afford some mixing, and then topsoiled. Because the lime kiln dust could be back-hauled in coal trucks, about \$0.81/Mg (\$0.90/ton) of coal were estimated to be added to the normal mining costs. Compared to an acid discharge from an adjacent mine in the same coal bed, the water quality from this amended site is alkaline with low metal concentrations (Rose et al. 1995).

2.2.5 Phosphate Rock

Phosphate rock has been used in some studies to control AMD. It may react with Fe released during pyrite oxidation to form insoluble coatings (Evangelou 1995), but phosphate usually costs much more than other calcium based amendments and is required in about the same amounts (Ziemkiewicz and Meek 1994).

Case Studies:

Small field plots have been tested but no large scale case studies are available at this time.

2.2.6 AMD Sludge

Addition of alkaline sludges or flocs, generated from the neutralization of AMD, to the surfaces of backfills or to acid-producing materials during mining and backfilling may provide several benefits. First, flocs from all neutralization processes contain excess alkalinity and this alkalinity may be used to neutralize acid-producing materials or acidic

water in the backfill. Lime-treated flocs often contain up to 50% unreacted lime, which may be used to further neutralize acidity. Second, disposal of the metal flocs from AMD treatment ponds is an expensive and long term problem and disposal in nearby surface mine soils or within spoil materials during mining can provide a cost effective alternative to other disposal options.

Case Studies:

Coleman et al. (1997) studied the application of lime-treated AMD floc to the surface of spoils and to acid-producing materials. In a column test, the floc did not accelerate or reduce the generation of acidity by acid-producing materials. Further, metal hydroxides contained in the floc did not dissolve in the presence of acid-generating material under these conditions. The floc did not develop low permeability properties, thus it could not be used as a capping material over acid-producing materials.

This technology was applied in the field at a coal refuse disposal area in West Virginia where dry AMD treatment sludge was used as a substitute for soil cover. The sludge was concentrated by pumping it to steel dumpsters lined with filter fabric, thereby allowing the water to filter into a sediment pool. This concentrated sludge was hauled to drying cells and then moved to the refuse pile for spreading and seeding. The sludge generated by AMD neutralization with calcium oxide was well suited for establishing and supporting vegetation. Vegetation on this soil substitute surpassed growth on native soils. Water quality was positively influenced by the improved vegetation and metals were stabilized. Underground disposal of this material into abandoned deep mines on this property was initiated in 1997 and careful monitoring of all deep mine openings related to these underground works is being conducted (Faulkner, personal communication).

2.2.7 Organic Wastes

Organic wastes as alkaline additions are discussed in detail in Section 5.7 (Bioremediation). While most bioremediation of AMD has been noted to occur in passive treatments such as anaerobic wetlands, organic wastes (such as sawdust and sewage sludge) have been incorporated into spoils to aid in the *in-situ* treatment of water by the use of indigenous microorganisms (Rose et al. 1996).

2.2.8 Others

Over the years other types of alkaline amendments have been tried by various mine operators and researchers to control AMD. These have included, among others: sodium carbonate, as briquettes, in recharge areas of spoil and in the base of alkaline trenches (Caruccio et al. 1984), $\text{Ca}(\text{OH})_2$ in alkaline trenches (Nawrot et al. 1994) and sodium hydroxide (NaOH) liquid poured into backfills via well bores. Most of these techniques have been used in conjunction with other amendments or reclamation efforts and no definitive information is available regarding their sole use.

2.3 Sewage Sludge

There is evidence from laboratory studies that the oxidation of pyrite can be inhibited by organic waste materials such as manures and sewage sludge (Backes et al. 1987). The inhibition process may be a combination of several mechanisms. First, Thiobacillus bacteria, which can catalyze iron oxidation in Equation 1.2 (section 1.1), may convert from a chemolithotrophic bacteria to a heterotroph in the presence of readily decomposable organic matter (Lundgren 1971). A second mechanism of inhibition may allow the sludge to complex Fe and eliminate it from oxidizing more pyrite, or adsorb/complex Al and other metal ions, thereby reducing hydrolysis and pH decreases. Sludge may also coat pyrite surfaces minimizing reaction surfaces. Decomposition of sludge consumes oxygen, thereby decreasing its availability for pyrite oxidation.

Case Study:

In 1977, digested and dewatered municipal biosolids were applied to an abandoned surface mine at the rate of 184 Mg/ha (85 tons/ac) on a 0.4 ha plot in Pennsylvania. Data were collected for a 5-year period and the site was re-evaluated after 12 years. The results showed that vegetation could be established and that the groundwater quality improved (Sopper and Seaker 1990). The State of Pennsylvania has used this technology to revegetate over 2,000 ha (5,000 ac) of mine land (Sopper 1993).

2.4 Encapsulation

This process encircles or covers acid-producing material with an impermeable material to limit its exposure to air and water. The material can be a synthetic liner or it may be a clayey material or other compacted material, which results in a layer with a low

hydraulic conductivity (Meek 1994, Geidel and Caruccio 1984). The material surrounding the acid-producing material may also be composed of alkaline material. Encapsulation can occur during the mining process where acid-producing materials are placed “high and dry” off the pit floor and away from the highwall (Skousen et al. 1987). After placement and compaction (and treatment with alkaline material if required), the acid-producing material is then covered with local clayey material or topsoil and this material is also compacted on top of the acid-producing material. Backfilling then continues over the layers of acid and cover material until the final grade is achieved.

Encapsulation has also been attempted after reclamation. If AMD is coming from a site, geophysical techniques are used to map the location of “hotspots” in a backfill by the use of conductivity or resistivity measurements. Wells are drilled into the hotspots in the backfill, encountering the acid material and cased. A grout mix is then pumped down the wells to encapsulate or permeate through the acid-producing material.

Case Studies:

At two West Virginia mines where synthetic materials (PVC liners) were used and one mine where compacted clay was used to encapsulate acid-producing material (Caruccio 1983, Geidel and Caruccio 1984, Meek 1994), both methods were only partially successful. This probably was due to incomplete coverage of the acid-producing material with the barrier material.

The plastic liner technology was applied at a surface coal mine in Alton, WV (Caruccio 1983). Approximately 18 ha (45 ac) of a combined refuse disposal and overburden site were covered with a 20 mil continuously-seamed PVC liner. The liner was placed over the surface of the backfill material and covered with 0.5 m (18 in) of soil. Due to the steep slopes on the periphery of the backfill, approximately 3 ha (or about 20% of the site) were not covered. The seeps and groundwater fluctuations from a larger, unlined portion of the mine were compared to seeps and groundwater levels from the PVC-lined area. The ground water wells in the lined area reflected a diminution in groundwater recharge. During the year following the installation, the seeps emanating from the PVC-lined area showed a 63% reduction in acid loads while there was no reduction in the seeps from the unlined portion .

In a series of studies and demonstrations, several organizations determined the location of acid-producing material in several backfills, drilled and cased wells, and pumped grout down the wells into the acid-producing material in the backfill (Ackman and Cohen 1994, Jones et al. 1997, Schueck et al. 1994). The use of coal combustion by-products, which may set up like concrete, have largely been used as the grouting and encapsulation material. Grouts of fly ash, lime and cement, when injected underground, decreased permeability and porosity, diverting water away from the pyritic material. Both mechanisms, alkaline additions and water diversion, are expected to reduce the amount of acid produced. Uninjected grout wells have been observed to discharge grout that was being injected 45 m away. The pH of water from ungrouted wells rose from 3 to 11. The amount of grout injected into the backfill was minimal (<4% of total volume) when considering the amount of void space in the subsurface of a reclaimed surface mine. Slight, but significant improvements in water quality have been observed. More notable changes may have occurred had the amount of grout injected been larger.

2.5 Removal of Toxic Material (Remining and Reprocessing)

Remining is returning to abandoned surface or underground mines for further coal removal. Where AMD occurs, remining reduces acid loads by: 1) decreasing infiltration rates, 2) covering acid-producing materials, and 3) removing the remaining coal which is the source of most of the pyrite. Remining has been combined successfully with alkaline addition and special handling to change water quality from acid to alkaline at specific sites.

Case Studies:

Hawkins (1994) studied 57 discharges from 24 remined sites in Pennsylvania, and found contaminant loadings (e.g. flows and metal concentrations) were either reduced or unchanged after remining and reclamation. Short term loads were sometimes increased during the first six months after remining and reclamation. Reduction in loads resulted from decreased flow rather than large changes in concentrations. An evaluation of ten remining sites in Pennsylvania and West Virginia showed eight of the sites to produce a net profit from coal sales (Skousen et al. 1997b). All the sites were reclaimed to current standards, thereby eliminating highwalls, covering refuse, and revegetating the entire areas. All sites also had improved water quality and some completely eliminated AMD

leaving the site. Faulkner and Skousen (1995) found significant reductions in acid loads after land reclamation, and the acid load reductions were due both to reductions in water flow from the site and reductions in acid concentration in the water.

Skousen and Larew (1994) described the surface re-mining of an underground mine in Preston County, West Virginia. Alkaline overburden from an adjacent mine was imported at a rate of 15,000 Mg/ha (6,700 tons/ac) to the re-mining job at a cost of \$0.55/Mg (\$0.50/ton) of coal removed. An average of about 18,000 Mg/ha (8,000 tons/ac) of coal was removed, making the cost of hauling the alkaline material to the site around \$9,900/ha (\$4,000/ac). Water quality from the deep mine prior to re-mining averaged pH 3.7 and 75 mg/L acidity as CaCO₃, while after re-mining and reclamation, pH was above 7.0 with no acidity. Based on average pre-mining water flows and analyses of the deep mine discharge on the site, the chemical cost for treating AMD on this site would have been around \$200,000 over a 20-year period. The alkaline addition had a one-time cost of \$45,000.

2.6 Selective Handling

Selective handling or “special” handling is used in surface coal mining operations to dispose of potentially acid-producing materials in backfills. In the eastern U.S. coalfields, identification of potentially acid-producing materials in the overburden is necessary to selectively handle this material for placement in specific areas of the backfill. As toxic material is encountered, the primary strategy is to segregate and place this material as quickly as possible off the pit floor and away from the highwall to limit its exposure to air and water (Skousen et al. 1987). Compaction of the material upon placement is helpful and sometimes treating the acid material with alkaline amendments will help neutralize the acid-producing potential.

Selective handling may also create a postmining hydrologic regime that minimizes the contact between acid-forming rock and groundwater or it may isolate potential acid-producing rocks from the rest of the backfill by the use of barriers (Geidel and Caruccio 1984). The coal pit floor is often rich in pyrite, therefore, isolating it from groundwater may be necessary. Isolation methods can include building highwall drains to move incoming groundwater away from the pit floor or placing impermeable barriers on the pit floor.

Proper identification, handling, blending or treatment, and placement of the acid-producing materials in the backfill are key issues to controlling AMD (Skousen et al. 1987).

Case Studies:

Perry et al. (1997) found that special handling techniques did not always have an effect on reducing AMD from acid-producing materials. They found that speed and continuity of mining operations affected post mining water quality more than the specific mining techniques used. Sites where mining ceased, and then resumed, generally produced poorer quality drainage than sites where mining proceeded rapidly to completion. Extended exposure of unreclaimed spoil to infiltration and circulation of water and oxygen apparently encouraged substantially greater pyrite oxidation and AMD generation.

2.7 Reclamation (regrading and revegetation)

Backfilling and revegetation together are one method of reducing acid loads from current mining operations or abandoned mine sites. Covering pyritic refuse or other acid-producing materials on a site with good soil material and establishing vegetation has a major impact on reducing acid concentrations in water and often decreases the flow of water from these sites by encouraging infiltration into soil and evapotranspiration by plants. If the majority of the water from an abandoned site is coming from underground mines, then surface treatments may have limited effects on reducing acid loads.

Regrading and revegetation have the potential to reduce acid loads and improve water quality to the point of meeting effluent limits. Backfilling and revegetation remains the primary approach to reducing water quality problems at surface mines (Skousen et al. 1995). If the pavement is visible and toxic materials present, appropriate material handling to keep toxic material "high and dry" in the backfill is desirable. Liming the pit with alkaline materials or lime products will also reduce the acid produced on-site. Encouraging controlled, rapid runoff and discouraging recharge into zones of pyritic backfill materials will help reduce the total acid load from the site. Results demonstrate that backfilling generally reduces total acid load either by reducing the flow or by reducing acidity concentrations in the water, or both.

Case Studies:

Water flow was reduced on 12 out of the 16 sites in West Virginia where reclamation was accomplished on bond-forfeited and unreclaimed areas (Faulkner and Skousen 1995). On those sites where flow was not reduced, water quality changed from acid to alkaline. In only two out of 16 cases was the acidity increased in the water, but flows were reduced dramatically causing a 45% decrease in total acid load. Vegetation establishment greatly reduced the occurrence and amount of runoff compared to a barren tailings area in Montana (Spotts et al. 1997). Runoff water from the vegetated area had a higher pH (6.2 vs 4.0), and metal loadings of As, Cu, and Zn were also more than four orders of magnitude lower than the unvegetated area.

2.8 Daylighting Deep Mines

See section 2.5 Removal of Toxic Material (Remining and Reprocessing)

2.9 Synergistic Effects

Many of the techniques and methods described above are often used in combination and as a result produce synergistic effects. Mining operators recognize that if the materials have the potential to produce AMD, a number of techniques can be incorporated into their material handling plans to minimize or eliminate the production of AMD. These often include selective handling of the overburden, alkaline additions and reclamation/revegetation. While each of these technologies may be effective by itself, that is not always the case, as demonstrated in some of the preceding case studies. The combined use of several methods, however, has allowed the key aspects of each technique to interact with other techniques. For example, selective handling of acidic material and segregating it out of the water table, in conjunction with blending alkaline material and constructing alkaline recharge zones have been successful (Wiram and Naumann 1995).

2.10 New Techniques

While a number of new techniques may be attempted each year, this section will be devoted to those new techniques that have data which are of sufficient duration to adequately evaluate the technology, preferably three years of data, but shorter time spans may be sufficient depending on the technology and its application.

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3.0 Engineered Structural Techniques

3.1 Water Management

Diverting surface water from the spoil above the site to decrease the amount of water entering the mined area is highly recommended in acid-producing areas. Channeling surface waters or mine waters to control volume, direction and contact time can be used to minimize the effects of acid mine drainage on receiving streams. The diversion of water from mining areas and from acid-producing materials is an abatement technique used in both surface and underground mines. Surface diversion of runoff involves the construction of drainage ditches to move surface water quickly off the site before infiltration or to limit its movement into the backfill. The diversion is accomplished either by ditching on the uphill side of surface mines or by providing new channels or impervious channels for existing surface streams to convey water across the disturbed area.

Alternatively, pyritic material can be placed where it will be rapidly and permanently inundated, thereby minimizing oxidation of acid-forming materials. Inundation is only suggested where a water table may be re-established to cover acid-producing materials (such as below drainage deep mines) and has not been recommended for surface mined lands or above drainage deep mines in the mountainous Appalachian U.S. region. Complete inundation has been used successfully in other areas where acid-producing materials are submerged in lakes or other permanent impoundments. Other methods of water management involve alkaline loading of water upgradient of mined areas where alkaline water will buffer the effects of subsequent acid water and alkaline loading of the backfill with structured alkaline recharge systems.

3.1.1 Inundation (Saturation)

3.1.1.1 Surface Mine Spoil

The physical saturation of spoil by constructing impoundments within an isolated area of a surface mine has been used to minimize or eliminate AMD. Inundation of acid-producing materials may be a less expensive reclamation technique on some areas than traditional reclamation by backfilling and planting, although the latter are required by law.

Improvements in the quality of impounded waters flowing from acid areas have not always resulted. While pH has not always shown such marked improvement, there has been some reduction in total acid and Fe. Even in the less satisfactory cases, the drainage has had a less deleterious effect on downstream water quality than that from unreclaimed areas. The creation of an impoundment in the final cut of a surface mine not only lowers the cost of reclamation, but also has several other advantages. It forms recreation areas, aids in recharging the water table in the local area, and can eliminate or greatly reduce the amount of pollution from acid mine drainage and silt. By carefully designing the impoundment size and depth so the body of water formed will cover all acid-producing and carbonaceous materials, and also completely flood any intercepted deep mine workings or auger mining holes, the pyrite oxidation process will be stopped and thus the formation of acid will cease. Field studies have confirmed this action, and have also shown that the resulting impoundment quickly flushes the oxidized acid salts from the contacted area and produces a body of water of near neutral to alkaline quality.

Case Studies:

Perry et al. (1997) found that acid-producing materials placed in a seasonal water table produced acid drainage in the eastern coal fields of the U.S. Intended placement above the water table was not accomplished. Perry provided field validation for previous laboratory studies (Leach 1990) which found that fluctuating water tables or partial flooding produced worse drainage than that predicted for either “dry” or submerged placement.

3.1.1.2 Underground Mines

Inundation of an underground mine can be an effective method of decreasing AMD by depriving pyrite of oxygen. In addition, if overlying rocks contain carbonate minerals, flooding can provide additional alkalinity by increasing the volume of alkaline strata in contact with mine water and increasing the residence time so that chemical equilibrium is more closely approached. On the other hand, if the mine walls contain readily soluble oxidation products of the sulfides, then the water quality draining from the mine can get worse.

A wet mine seal is a wall across a draining mine entrance that allows flow of water through the seal but prevents air from entering the mine. A dry mine seal is a wall across a mine entrance where water does not drain from the entrance. To the extent that the seal raises the water level in the mine and inundates the workings, the production of AMD can be inhibited. Although complete blockage of adits at the down-dip side of underground mines has been attempted in order to prevent drainage and raise the water level in the mine, this procedure has commonly led to breakout of the water, sometimes explosively, either at the seal or at nearby locations. The placement and construction of mine seals, therefore, must be carefully planned and executed.

Case Studies:

Case study summary is not available at this time.

3.1.1.3 Coal Refuse

The disposal and placement of acid-producing coal refuse in a saturated condition to limit its exposure to air and water has been used for decades with mixed results. Many coal slurry impoundments have been constructed for disposal of pyritic materials near coal preparation plants. In most cases, oxidation and generation of acid products are stored in the slurry impoundment and are released as water drains from the impoundment. Many coal refuse disposal sites must treat the drainage with chemicals before discharge.

Case Studies:

Case study summary is not available at this time.

3.1.1.4 Reactive Tailings

Disposal of sulfide tailings under a water cover, such as a lake or fjord, has been used extensively as another way to prevent acid generation by excluding oxygen to sulfides. Wet covers also include flooding of above ground tailings ponds. Deposition of sulfide tailings under water has been used at various mines in Canada and Norway.

Case Studies:

Case Studies are reported in the Metals Mining Handbook.

3.1.2 Dewatering

Removing water, one of the principal reactants in pyrite oxidation, should theoretically stop the production of AMD. With no water to move reaction products from the surfaces of pyrite, no contamination of waters should occur. While this can be done in a laboratory setting, the total and complete removal of water in nature is nearly impossible and therefore the complete control of AMD, even in dry situations or climates, does not occur. However, reducing the amount of water contacting pyritic material and containing water that is in contact with acid-producing materials may reduce the impacts of AMD to off site water bodies and streams.

Case Studies:

Norton (1987) designed and constructed a series of peripheral deep wells to dewater abandoned deep mines adjacent to the Crouch Mining - Dahlquandy surface mine (UK) to allow the water to be discharged without treatment. This mine is one of the largest open cast mines in the UK. Pit water quality from nearby surface mines was sufficiently degraded by oxidation of coal fines on the pit floor that chemical treatment was required. The quality of water pumped from the wells was alkaline and metal concentrations were low enough that the water could be discharged to receiving streams without treatment. Another benefit was the working conditions in this pit were greatly improved with respect to water management.

3.1.3 Drains

Draining water away from pyritic materials as rapidly as possible may keep water from reacting and forming acid products. Various types of drains may be used to convey water out of the backfill or away from acid-producing materials, or coarse materials placed around tightly-packed pyritic materials may take water away from these acid-producing materials.

3.1.3.1 Porous Envelope

A porous envelope effect may occur in groundwater systems when mine tailings of low permeability are placed within high-permeability soils and overburden within or on a

backfill. If the permeability contrast between the tailings and the surrounding material is large, groundwater will flow around the tailings mass rather than through it, and metal leaching will be minimized.

Case Studies:

Case studies are reported in the *Metals Mining Handbook*.

3.1.3.2 Chimney, Highwall, French, Blanket Drains

Drains can be installed in various places to move water from one area to another. Chimney drains collect water from a backfill or valley fill and convey the water through a long, high, column of hard, coarse sandstone. Highwall drains collect water from the highwall along permeable channels of sandstone or limestone. French drains are small, distinct constructed channels in disturbed rock, usually along the pavement, where water is directed to flow out of the fill. Blanket drains are constructed by forming a coarse, permeable rock covering along the entire fill bottom to allow drainage water to move out of the fill through the base. All of these methods are reliable methods for moving water from spoil, refuse, and fills.

Case Studies:

Geidel and Caruccio (1984) used a blanket drain in a hydrologically isolated surface mine to evaluate its effectiveness in reducing AMD. Even though the pavement had been treated with lime, the water flowing through the drain and across the pavement provided a favorable environment for AMD formation.

3.2 Impervious Soil Cover or Membrane

Dry barriers are constructed from natural or man-made materials that retard the movement of water and oxygen into areas containing acid-producing rock. Barriers can achieve substantial reductions in water flow through piles, but generally do not control AMD completely.

Plastic liners are rarely used in mining because covering the large volumes of waste with a liner is usually too expensive. However, this method may be appropriate in settings where isolation of small pods of acid-producing material is possible.

Case Studies:

At the Upshur Mining Complex in West Virginia, Meek (1994) reported covering a 20-ha spoil pile with a 39-mil PVC liner. This treatment reduced acid loads by 70%.

A cover system was developed for a coal refuse disposal area in Illinois (Gentile et al. 1997). The system comprised a graded and compacted refuse layer, overlain by a compacted clay liner, and a protective soil cover. Infiltration was reduced by about 18% initially compared to an unreclaimed refuse surface. Over time it is predicted that the cover should reduce infiltration by 84%.

3.3 Underground Mine Sealing

Throughout most of the Appalachian coal fields, abandoned underground mines are considered to be the principal source of AMD pollution. This perception is based on the sheer number of abandoned underground mines, the number of very large acreage abandoned mines, and the fact that most older mines were developed updip to promote gravity drainage. The AMD problems associated with older underground mines can be increased by inadequate barrier pillars between mines, inadequate outcrop barriers, and hydraulic interconnection of adjacent mine complexes and/or connection of superimposed mines.

While AMD problems associated with some of these older mine complexes can be addressed by reining of the abandoned mine complex, this option is not economically viable for a majority of abandoned mine complexes in the Appalachian coal fields. Mine sealing can, in many instances, be an effective and economically viable means of eliminating or minimizing the AMD pollution associated with abandoned underground mines.

Regulators were faced with the numerous gravity drainage deep mines that contributed to an ever increasing AMD pollution problem. They responded by requiring that deep mines be sealed at closure to ensure public health and safety. For example, the Commonwealth of Pennsylvania passed the "Bituminous Coal Mine Act" in 1961, which mandated that all permanently abandoned mines be plugged, sealed or filled.

In 1977, Office of Surface Mining (OSM) regulations on deep mine surface facilities and entry closure became law. In 1978, the Mine Safety and Health Administration (MSHA)

adopted regulations which further defined the procedures and conditions for sealing an abandoned underground mine. Currently, nearly every federal and state agency that regulates deep mining has adopted some regulations mandating mining down-dip and mine sealing at closure to minimize AMD effects and to ensure the health and safety of the public. Conversely, throughout much of the rest of the world, the practice of mining up-dip to facilitate gravity drainage continues unabated.

Deep mine sealing is defined as closure of mine entries, drifts, slopes, shafts, boreholes, barriers, outcrops, subsidence holes, fractures and other openings into underground mine complexes. Deep mine seals are constructed to achieve one or more functional design goals including: 1) eliminate potential access to the abandoned mine works following closure, 2) minimize AMD production by limiting infiltration of air and water into the deep mine, 3) minimize AMD production by maximizing inundation of the mine works, 4) minimize AMD exfiltration through periphery barriers to surface water systems, and 5) develop staged internal mine pools to regulate maximum hydraulic head and pressure. The primary factor affecting the selection, design and construction of underground mine seals is the anticipated hydraulic pressure that the seal will have to withstand when sealing is completed.

3.3.1 Surface Access Dry Seals

Surface access seals are installed in entries (drifts, slopes, shafts and subsidence areas) where little or no hydrostatic pressure will be exerted on the seals. The primary functions of the seals are to eliminate potential access to the abandoned mine works following closure and to decrease AMD production by limiting infiltration of air and water into the deep mine. Typically, these seals are installed in entries positioned in the structurally upgradient areas of the mine where the majority of the mine works lie "below" the mine seal site. These seal areas are often backfilled from the front side of the seal to the ground surface and then the seal backfill areas are stabilized, amended, resoiled and revegetated. These seals have good long term effectiveness due to the lack of hydraulic head (pressure) on the seals (Figures 3.1 and 3.2).

Surface access seals have been used extensively throughout the world. The lack of hydraulic head allows these seals to be both simple in construction and low cost.

Surface access seals are typically constructed using concrete block or masonry, although more recent surface seals have been constructed using compacted clay and concrete-flyash mixtures.

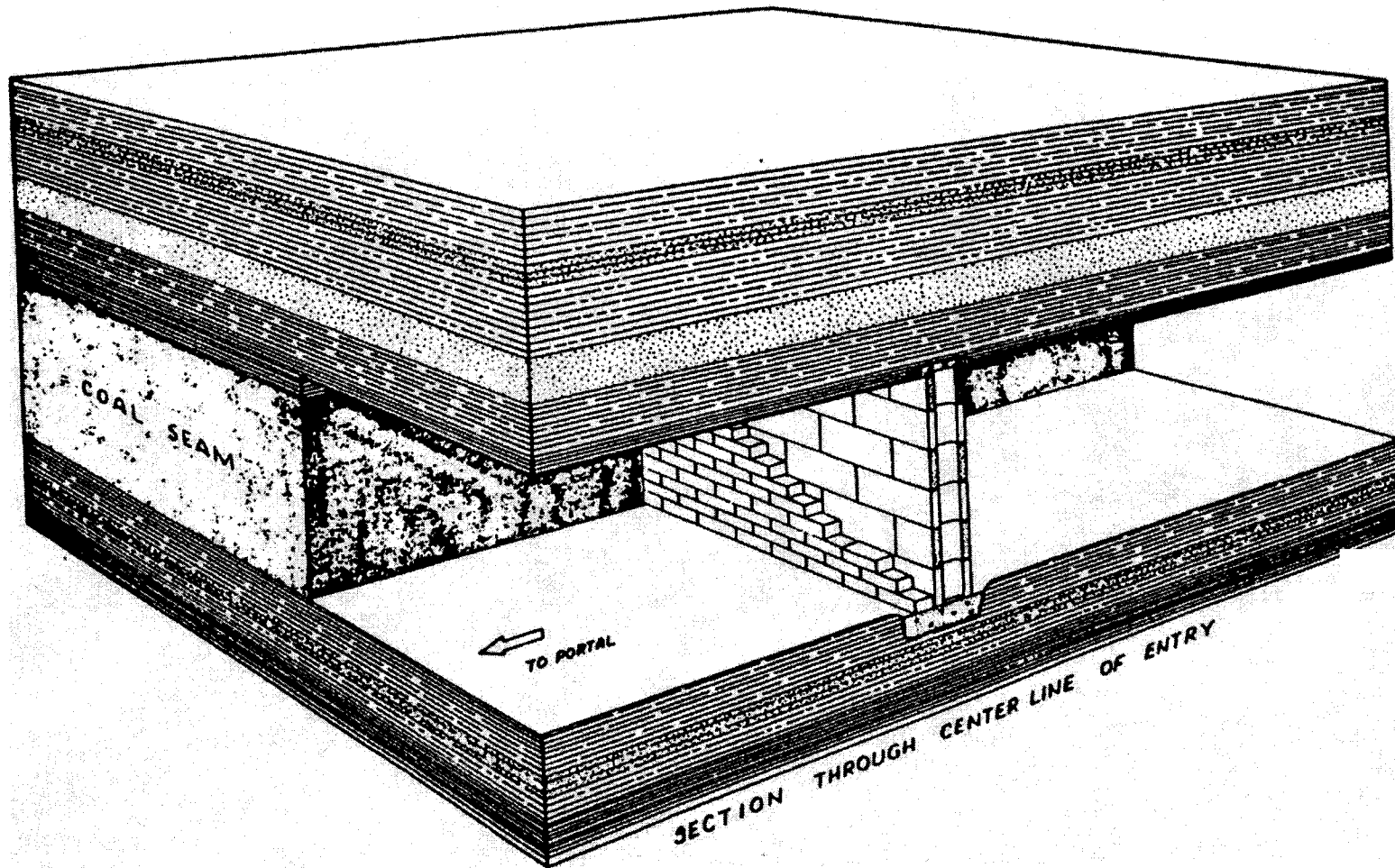
3.3.2 Air Trap Seals

Air trap seals are installed in mine entries where mine discharges flow from the mine. Conventional mine sealing using air-trap seal methods began in the 1920's and was used extensively in the 1930's in the U.S. in conjunction with the Works Project Administration (WPA) mine sealing efforts. The primary functions of these seal types are to eliminate potential access to the abandoned mine works following closure and to minimize AMD production by limiting infiltration of air and water into the deep mine.

The initial appeal of the air-trap sealing system was that this was a simple, low-cost sealing approach, which still allowed water to discharge without affecting the mine seal integrity. Construction was almost always using concrete blocks (Figures 3.3 and 3.4). In a typical air-trap sealing program, surface access seals were first constructed in the upgradient mine entries (which were sometimes backfilled), and then the air-trap seals were constructed in the downgradient mine entries where water historically discharged from the mine.

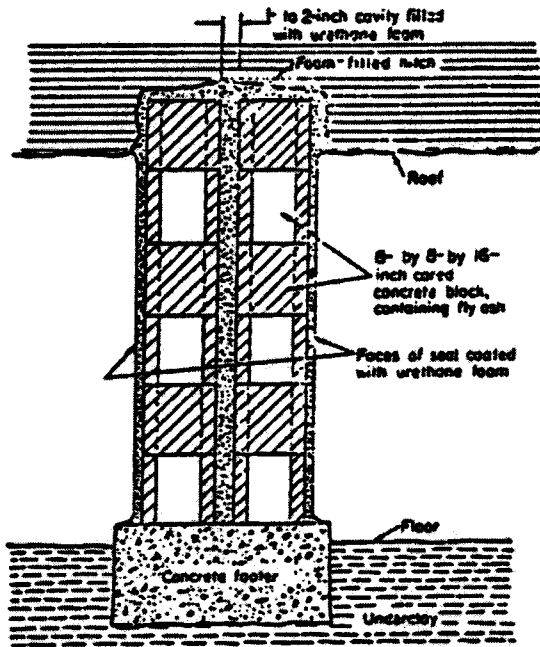
Unfortunately, the long term effectiveness of this sealing method was generally poor. Failures of these seals usually occurred when rock, wood, debris and sediment clogged the air-trap. This restricted outflow from the mine causing increases in volume and head of the impounded water in the mine. The subsequent increase in pressure caused many of these seals to collapse.

A study done by the US Bureau of Mines (Borek et al. 1991) showed that 14 mine seals installed in 1967 were all intact and only a few small leaks from weir walls were noted. Acidity and metal concentrations decreased over time, but this decrease may be due to a natural decrease or to the seals. Based on measurements taken after sealing and several times since then, pH values slightly increased over time.

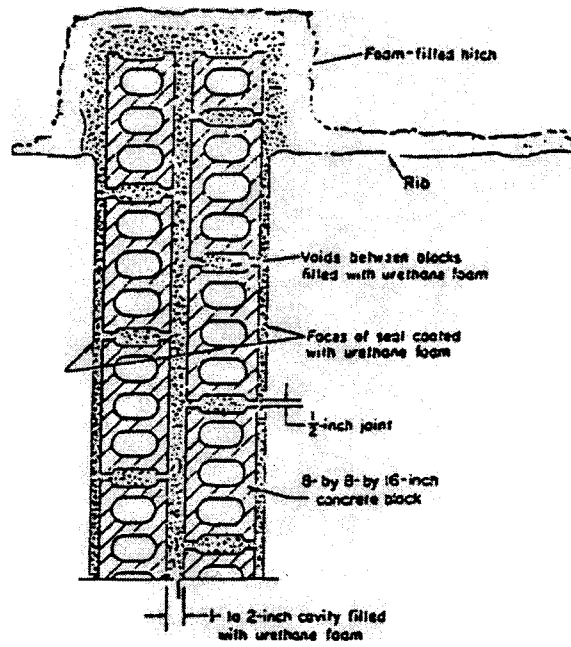


Typical Masonry Seal
Air Seal - Ventilation Stopping

Figure 3.1

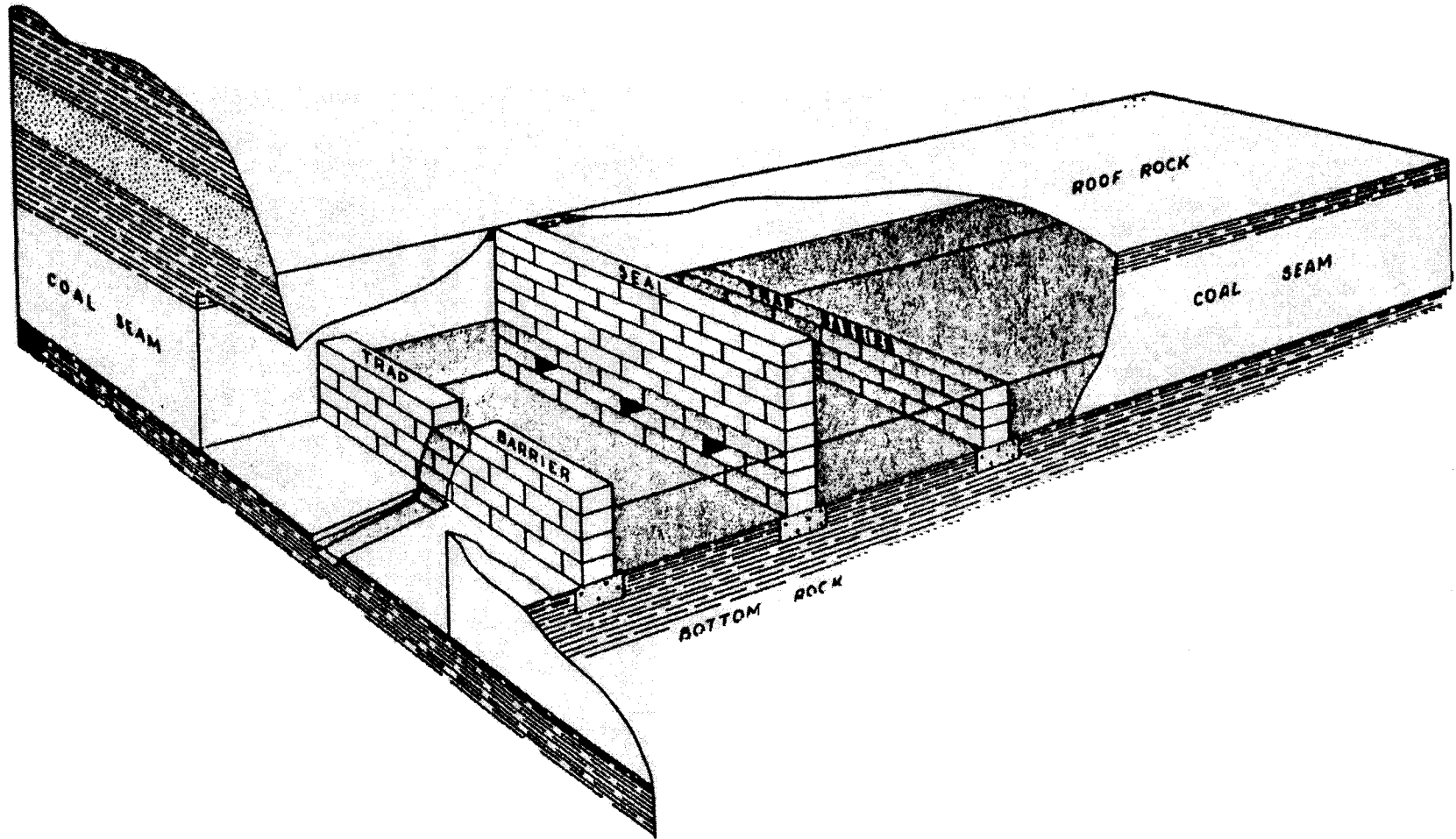


Cross-Sectional View of Masonry Seal Showing Method of Construction, Hitching Into Roof, and Concrete Footer.



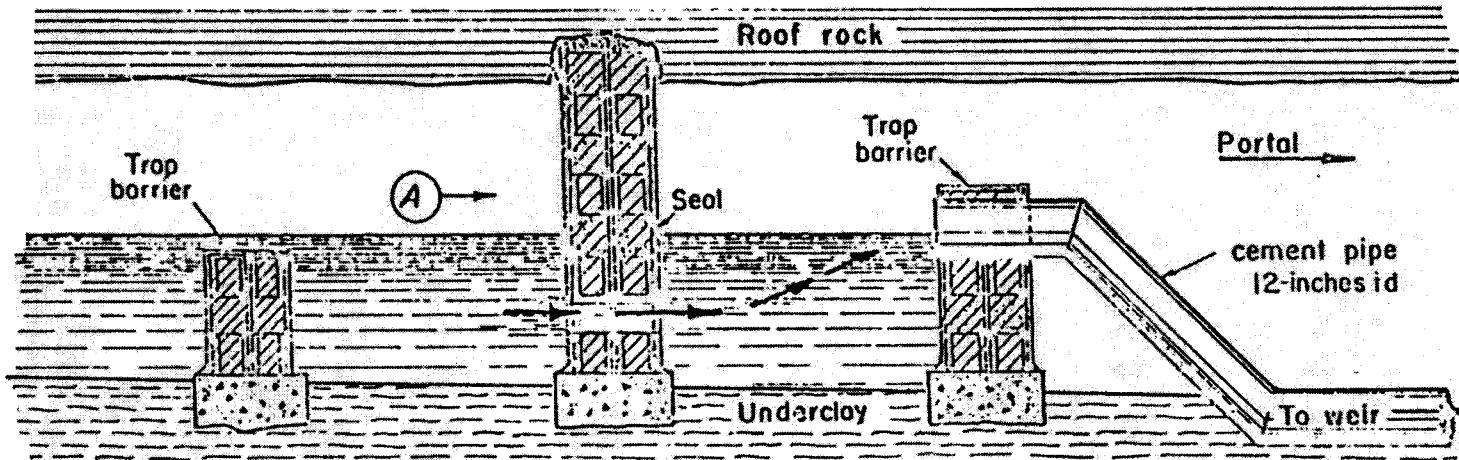
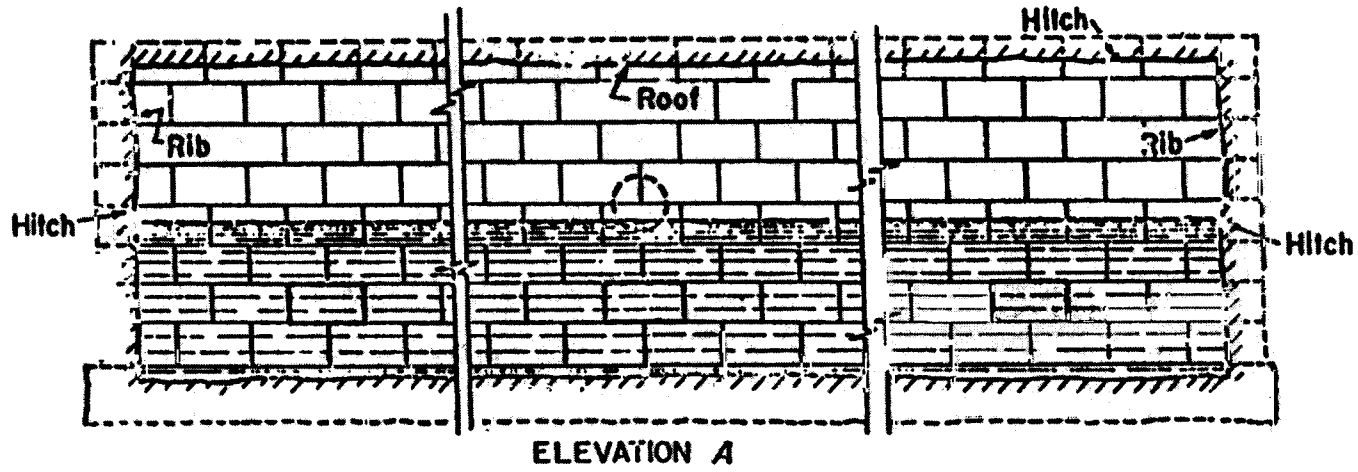
Top View of Masonry Seal Showing Method of Construction and Hitching Into Rib.

Figure 3.2



Conventional Type Air Seal with Discharge

Figure 3.3



General Arrangement of a Wet Seal With Air Trap.

Figure 3.4

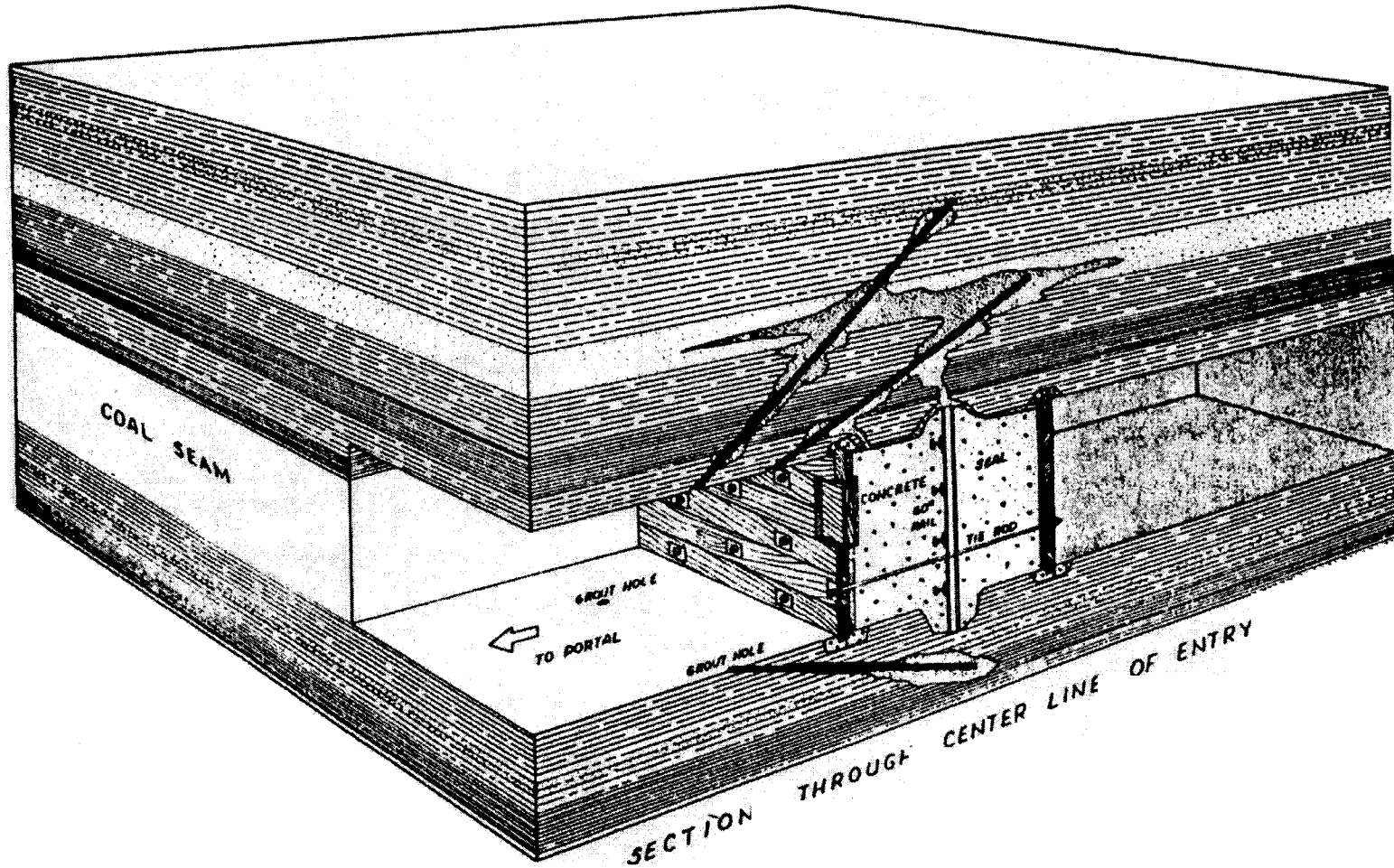
3.3.3 Hydraulic Mine Seals

Currently, most underground mine seals being constructed are hydraulic mine seals although surface access seals are still used in "no water, no head" situations for economic reasons. The numerous, long term failures of the air-trap seal systems coupled with the inability of this design to withstand significant hydraulic pressures has caused these seals to become obsolete. Hydraulic mine seals are installed in entries (drifts, slopes, shafts and adjacent strata) where significant hydrostatic pressure will be exerted on the seals. The primary functions of the seals are to eliminate potential access to the abandoned mine works following closure, to minimize AMD production by limiting infiltration of air and water into the deep mine, and to minimize AMD production by limiting exfiltration of water and maximize inundation (Figures 3.5 and 3.6). Further, hydraulic mine seals have been constructed to repair/replace breached areas of coal barrier pillars and to provide "constructed internal barriers" in sections of the mine complex to minimize AMD exfiltration through coal barrier pillars to adjacent flow systems and develop staged internal mine pools to regulate maximum hydraulic head and pressure. The primary goal in the design and installation of hydraulic mine seals is to construct a mine seal system that serves as a structural bulkhead and acts as a water tight dam capable of withstanding the maximum hydrostatic head that may develop as a result of the flooding of the mine complex. A secondary consideration in the design and siting of hydraulic mine seals is the hydrologic performance of the seal. The adjacent stratum has natural joints, bedding planes and subsidence cracks (from mining) that may serve to transmit significant water around the mine seal area. Thus, while the structural design will specify a minimum required thickness necessary to safely impound the water at design heads and pressures, the potential for water to migrate around the mine seal area through adjacent strata must be compensated for in the design.

Typically, three common and successful approaches are used separately or in combination to minimize the potential migration of impounded water around the mine seal area. These are:

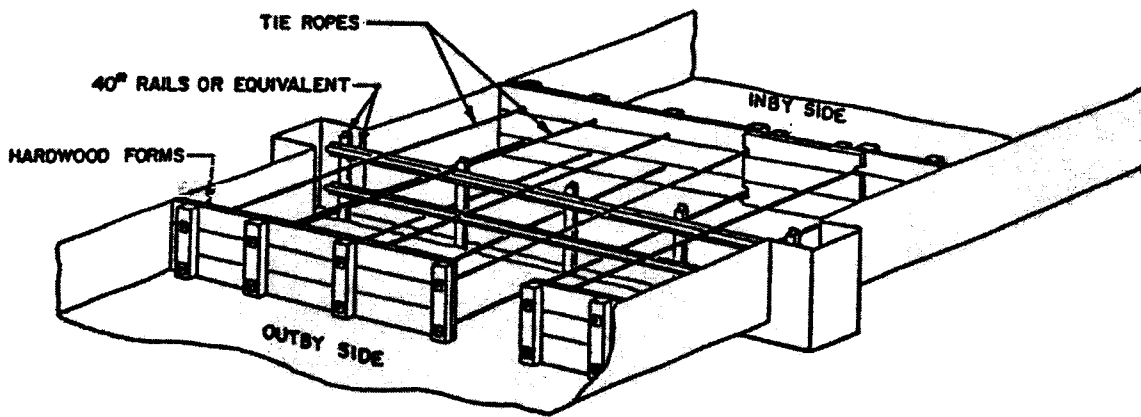
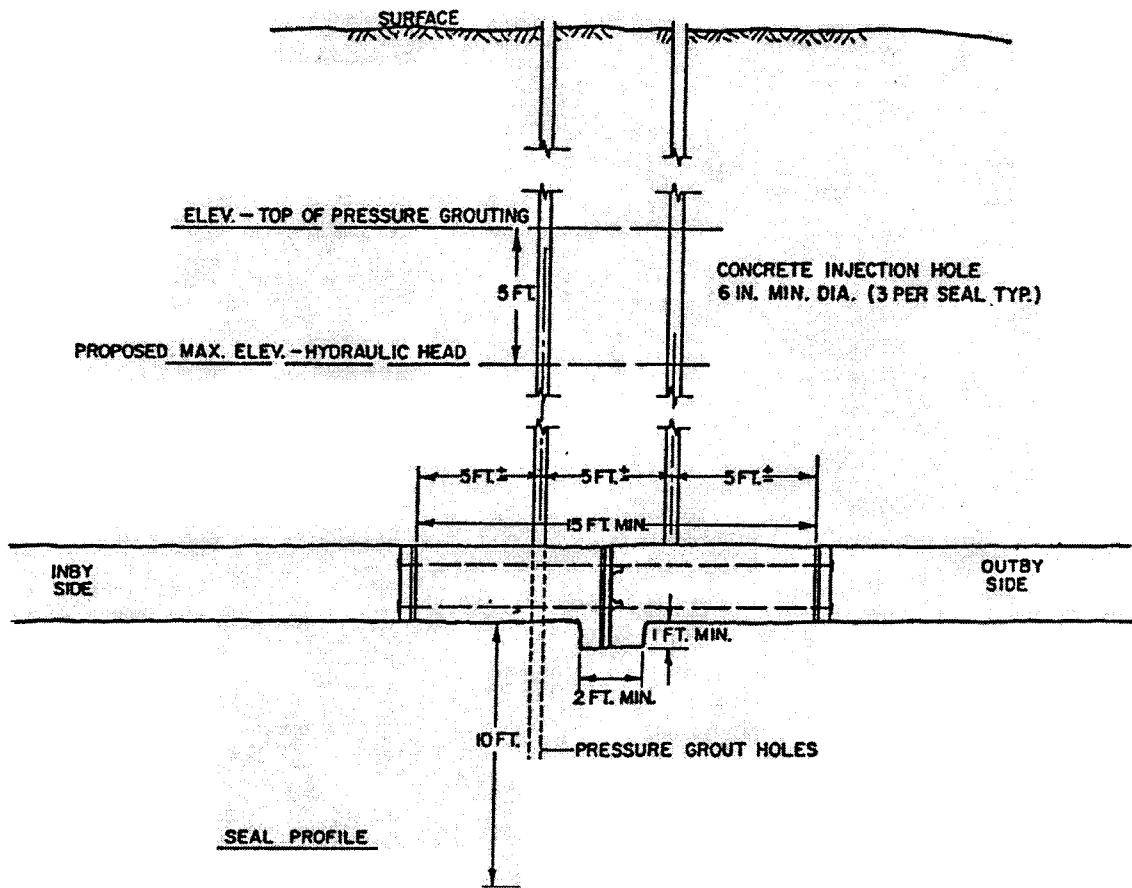
1. Pressure grouting of the adjacent strata - this process injects grout into the natural and mining related cracks in adjacent strata thus minimizing migration of water past the seals.
2. Increase mine seal thickness - this increases "flowpath distance" that migrating water must travel to bypass the seals and greatly increases the safety factor for the structural design.
3. Install secondary mine seals - provides redundant mine seals to limit potential migration around seals. This approach is mostly limited to very high head sites due to the high costs.

Another fundamental design consideration in the siting of mine seals is the accessibility of the mine entries where the seals are to be constructed. In most abandoned mines and in areas of active mines where conditions are unreasonable or unsafe, mine seals can be remotely placed through drill holes (Figures 3.7 to 3.10).



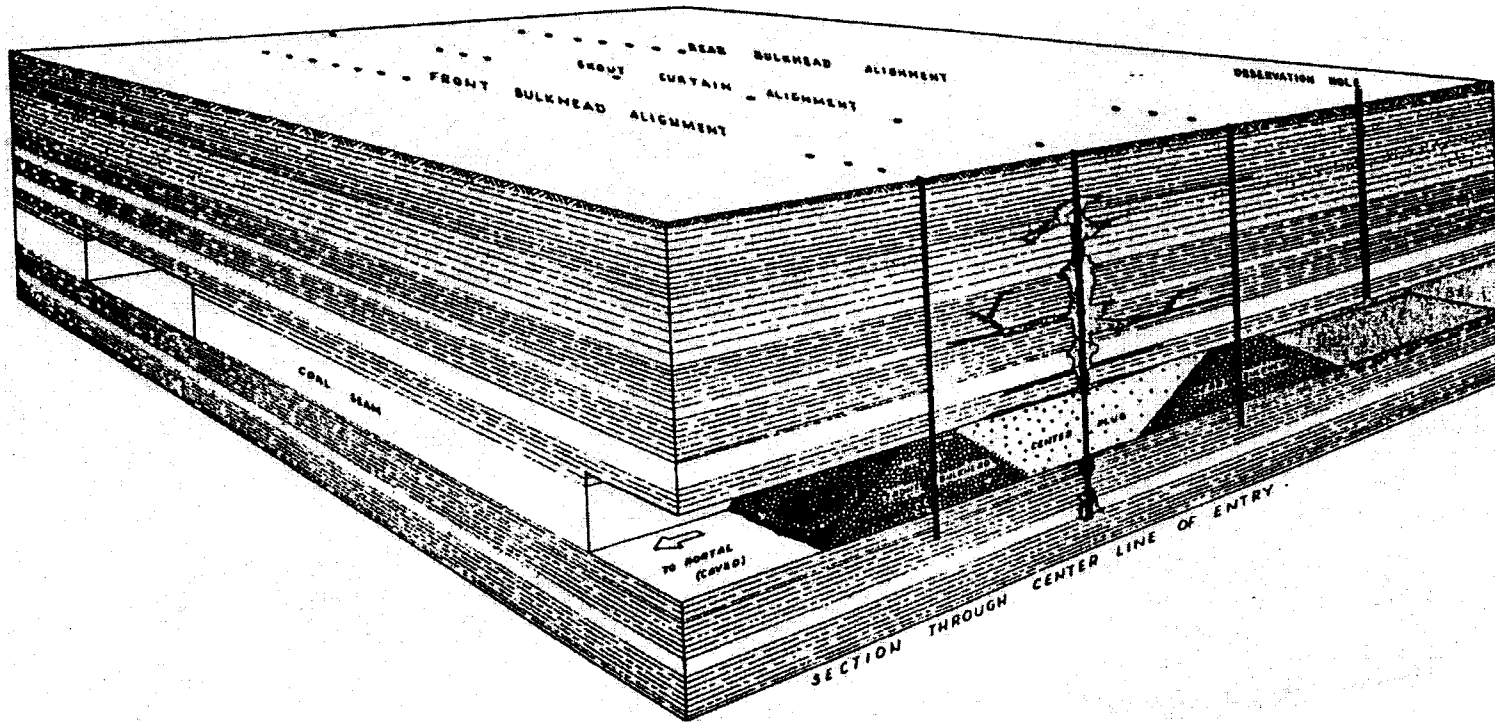
Deep Mine Hydraulic Seal -
Underground Barrier Dam

Figure 3.5



MINE SEAL FORM DETAILS PRIOR TO INSERTION OF CONCRETE

Figure 3.6



Deep Mine Hydraulic Seal By Remote Installation

Figure 3.7

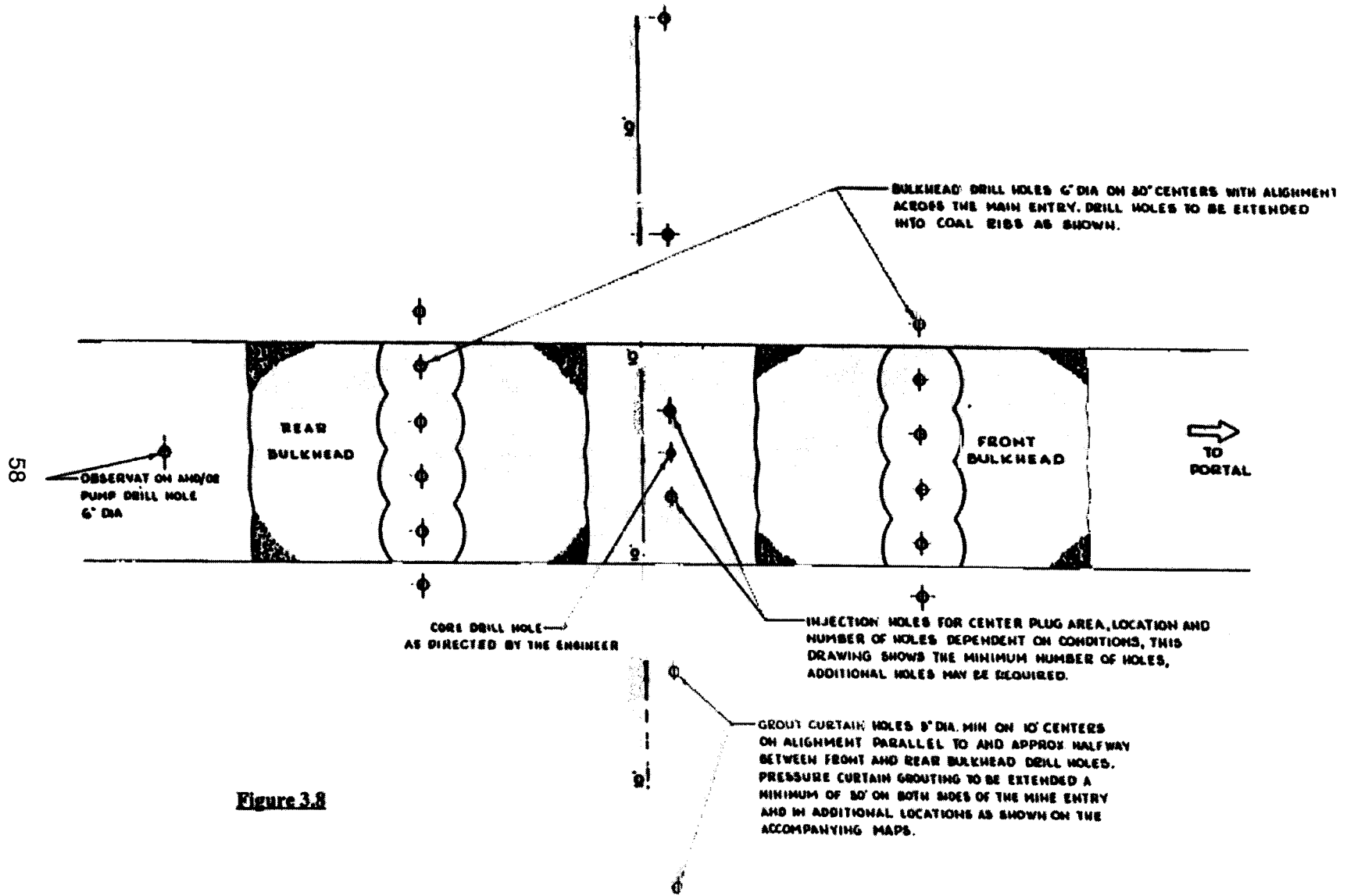
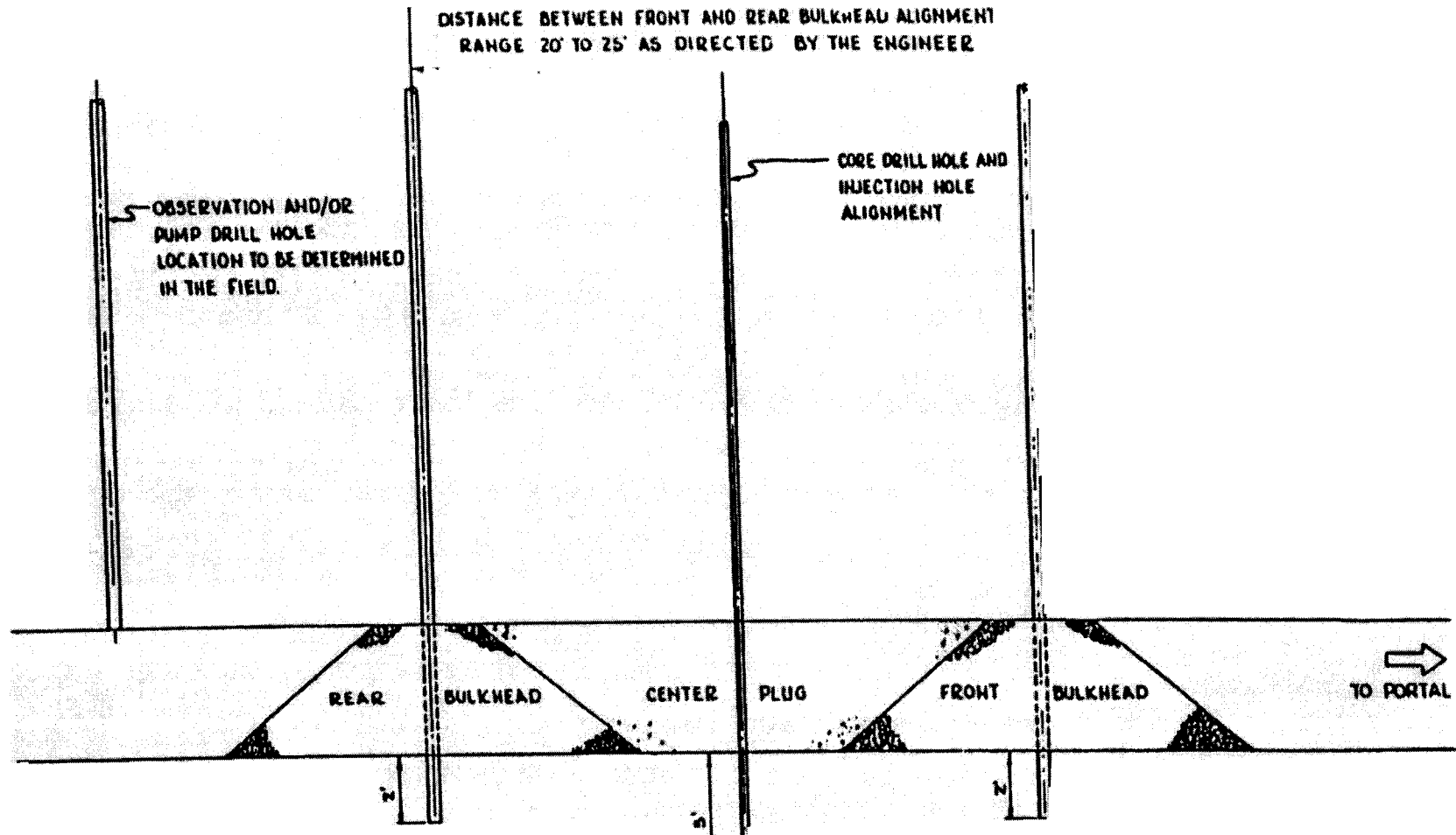


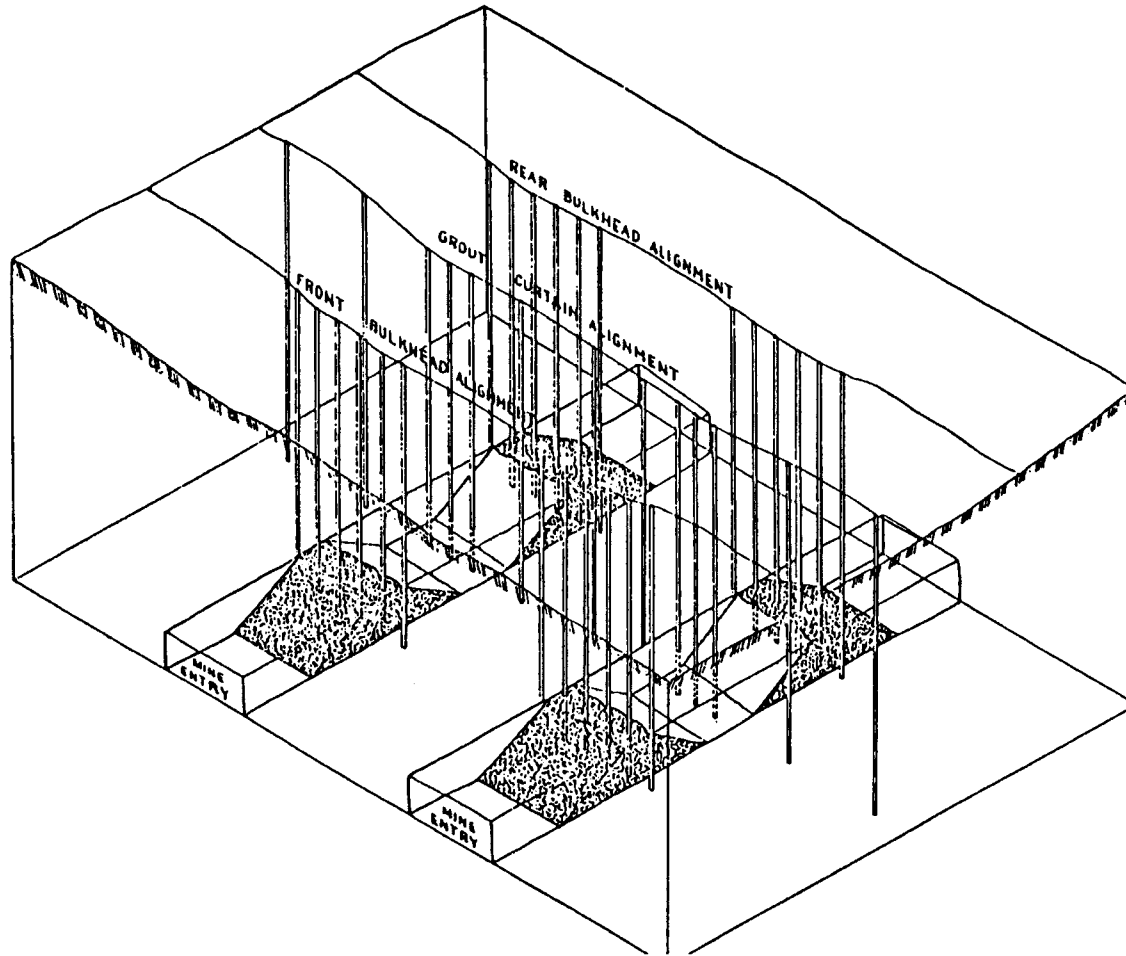
Figure 3.8

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Construction Drawing of Deep Mine Seal

Figure 3.9



Isometric Drawing of Deep Mine Seals
No Scale

Figure 3.10

3.3.3.1 Hydraulic Mine Seals - Drift Areas

Mine drifts are horizontal entries allowing the deep mine to be accessed from the surface. Typically, the selection of mine seal design is based on the anticipated maximum pressure and the choice of construction materials used for the seals is an economic decision. Generally, drift seals at active mine sites are constructed in surface accessible areas and thus these mine seals are rarely constructed using remote placement construction methods unless severe subsidence is occurring or believed to be possible. Conversely, drift seals at abandoned mine sites are typically unsafe and often constructed using remote methods.

Case Studies:

Foreman (1964) designed and constructed the first known remotely placed, double bulkhead mine seal at an abandoned deep mine with a pollutional discharge situated in Blair County, PA. The seal eliminated the pollutional discharge and proved that mine seals could be effectively placed using remote methods. Foreman, Bullers and Hong (1969) constructed 69 remotely placed, deep mine seals at Moraine State Park (Butler County, PA). These seals were constructed to abate AMD discharges emanating from 22 abandoned mine complexes which drained to Lake Arthur. Maksimovic and Maynard (1982) performed a follow-up assessment of the mine sealing and concluded that total mean discharge, alkalinity, and Fe increased while total mean acid loads decreased. Overall, they found mine sealing improved the water quality of Lake Arthur.

Foreman, Ward and Bullers (1970) constructed 32 remotely placed, deep mine seals at the Argentine/Whiskerville project area (Butler County, PA). These seals were constructed to abate AMD discharges emanating from several abandoned mine complexes draining to Slippery Rock Creek. Followup hydrogeologic and geochemical assessment of the mine sealing by state engineers concluded that the mine seals were functioning and the mine achieved about 6 m of inundation before reaching equilibrium without any AMD discharge to Slippery Rock Creek..

Foreman, Hong and Foreman (1979) designed and constructed a large clay dike and 35 hydraulic drift seals at Lake Hope State Park in Zaleski National Forest (Vinton County, OH). These seals were constructed to abate severe AMD discharges emanating from six

abandoned deep mine complexes draining to Lake Hope. Nichols et al. (1983) performed a followup assessment of the mine sealing and reported an increase in pH of nearly 2 units and corresponding decreases in conductance (25%), sulfates (40%) and total Fe (84%). Subsequently, Lake Hope has improved to the point where a viable bass fishery has been reestablished.

Beck and Foreman (1985) constructed and evaluated six concrete seals installed at the Oneida Mining Co. - Dilltown facility (Indiana County, PA) designed to prevent a post-mining AMD discharge from the mine after closure and inundation. A later assessment of the mine seals concluded that the seals were effective with no discharge found and no impact to underlying groundwater systems.

3.3.3.2 Hydraulic Mine Seals - Slopes

Mine slopes are angular entries allowing the deep mine to be accessed from the surface. Typically, the selection of mine seal design is based on the anticipated maximum pressure, and the choice of construction materials used for the seals is an economic decision. Generally, slope seals at active mine sites are constructed in surface accessible areas. Thus these mine seals are rarely constructed using remote placement construction methods unless severe subsidence is occurring or believed to be possible. Conversely, slope seals at abandoned mine sites are typically unsafe and often constructed using remote methods.

Case Studies:

Foreman and Foreman (1985) designed and constructed two concrete slope seals installed at the Island Creek Coal Co. - Bird #2 and Bird #3 deep mines (Cambria and Somerset Counties, PA) to prevent or minimize post-mining AMD discharges from the slope following closure and inundation. No post-construction discharge has been identified from the slope.

Foreman and Foreman (1992) designed and constructed a concrete slope seal, which was installed at the PA Mines Corp. - Rushton deep mine (Centre Co. & Clearfield Co., PA), to prevent or minimize post-mining AMD discharge from the slope following closure and inundation. No post-construction discharge has been identified from the slope.

3.3.3.3 Hydraulic Mine Seals - Shafts

Mine shafts are vertical entries allowing the deep mine to be accessed from the surface. Typically, the selection of mine seal design is based on the anticipated maximum pressure, and the choice of construction materials used for the seals is an economic decision. Generally, shaft seals at active mine sites are constructed in surface accessible areas and thus these mine seals are rarely constructed using remote placement construction methods unless severe deterioration is occurring or believed to be possible. Conversely, shaft seals at abandoned mine sites are typically unsafe and often constructed using remote methods.

Case Studies:

Beck and Foreman (1985) constructed and evaluated a concrete shaft seal installed at the Oneida Mining Co. - Dilltown facility (Indiana County, PA), which was designed to prevent a post-mining AMD discharge from the mine after closure and inundation. The assessment of the shaft seals concluded that the seal was effective with no discharge found and no impact to underlying groundwater systems.

Foreman, Beck and Foreman (1984) constructed and evaluated a concrete shaft seal installed at the PA Mines Corp. - Lady Jane Collieries deep mine. The shaft seal was effective with no discharge found and no impact to underlying groundwater systems.

Foreman and Foreman (1985) designed and constructed seven concrete shaft seals installed at the Island Creek Coal Co. - Bird #2 and Bird #3 deep mines (Cambria and Somerset Counties, PA) following closure. No post-construction discharge has been identified from the shaft.

Foreman and Foreman (1992) designed and constructed a concrete shaft seal installed at the PA Mines Corp. - Rushton deep mine (Centre and Clearfield Counties, PA) following closure. No post-construction discharge has been identified from the shaft.

3.3.3.4 Hydraulic Mine Seals - Coal Barrier Pillars

Coal barrier pillars are intact blocks of coal left unmined to provide hydraulic barriers for water management as well as to assist in ventilation and roof support. Occasionally, coal barrier pillars are breached during active operations and need to be repaired to return them to original condition. Coal barrier pillars can be classified as peripheral barriers (intact coal

at the edge of the deep mine works) or internal barriers (intact coal located in the interior of the mine works). Generally, both peripheral and internal coal barrier pillars at active mine sites are accessible and thus hydraulic barrier seals installed at these mine seals are rarely constructed using remote placement methods unless the area is flooded or is abandoned. Typically, peripheral barriers at abandoned mine sites are accessible if the barriers are situated above regional drainage levels. Conversely, both peripheral barriers below regional drainage and internal barriers at abandoned mine sites are typically unventilated and often flooded making them unsafe. These are often constructed using remote methods.

Peripheral coal barrier pillars are often limiting factors in the design of mine seals for abandoned mines, particularly along downgradient outcrop areas of mines situated above regional drainage levels. Further, internal coal barrier pillars are often limiting factors to achieving maximum inundation in upgradient mines where significant recharge potential exists for water movement through the barrier to adjacent, downgradient mine works.

Case Studies:

Foreman, Hong and Foreman (1979) constructed a large clay dike and 35 hydraulic drift seals at Lake Hope State Park in Zaleski National Forest (Vinton County, OH). This mine sealing project was undertaken to abate severe AMD discharges emanating from six abandoned deep mine complexes which drained to Lake Hope. The clay dike was constructed to continuously replace the inadequate downgradient outcrop barrier along the edge of the mine. The functional repair of the barrier allowed the mine complex to achieve full inundation when coupled with the construction of the mine seals. Nichols et al. (1983) found an increase in pH of nearly 2 points and corresponding decreases in conductance (25%), sulfates (40%) and total Fe (84%). Subsequently, Lake Hope has improved and a viable bass fishery has been reestablished in the Lake.

Foreman and Foreman (1985) constructed a concrete mine seal in the breached barrier of the active Island Creek Coal Co. - Providence #1 deep mine (Webster County, KY) to reestablish the functional aspect of the barrier and return the mine to active production. The miners at the Providence deep mine had inadvertently mined through the barrier into the adjacent, abandoned Hall-Luton #9 deep mine which was fully flooded at that time. The resultant inflow flooded over 60% of the Providence mine causing full evacuation of the

workforce and complete destruction of most of the ventilation stoppings in the mine. Because of the presence of an overlying, flooded mine complex, the cost of placing remote seals was deemed excessive and it was decided to renovate the immediate section and construct the mine seal at the face. The MSHA approved mine sealing was totally successful and allowed the mine to be reopened and returned to full productivity.

Foreman, Moore and Foreman (1982) designed and constructed a remotely placed, deep mine seal in an entry which breached the peripheral barrier of the Guarnieri deep mine complex for the Adobe Coal Mining Company (Lawrence County, PA) to restore the function of the barrier and eliminate drainage of the deep mine reservoir into the active surface mine pit adjacent to the mine. Following construction, the drainage was abated and Adobe was able to surface mine without further inflows from the adjacent deep mine reservoir.

Foreman, Hong and Ward (1977) designed and constructed a slurry trench to abate the discharge from an abandoned deep mine (Mercer County, PA). The slurry trench was developed along the peripheral outcrop barrier of the mine and was excavated from the surface using large backhoes. The trench was then backfilled with a soil-bentonite stabilized slurry which provided a hydraulic barrier to prevent lateral discharge from the abandoned deep mine. The slurry-trench seal was effective since there was no discharge following construction and the deep mine became fully inundated.

Foreman and Glenn (1980) designed and constructed a slurry trench to abate the discharge from an abandoned deep mine (Clarion County, PA). The slurry trench was developed along the peripheral outcrop barrier of the mine and was excavated from the surface using large backhoes. The trench was then backfilled with a stabilized soil-cement slurry which, when set-up, provided a relatively impervious barrier to prevent lateral discharge from the abandoned deep mine. The slurry-trench seal was effective since there was no discharge following construction and the deep mine became fully inundated.

3.3.4 Flowing Artesian Wells

Flowing artesian wells are wells that overflow onto the ground surface and then flow overland to surface drainage features such as streams, rivers or lakes. Historically, some flowing artesian wells were developed to supply water without pumping. Flowing artesian wells occur when the ground surface elevation of the well is lower than the equivalent

elevation (pressure head) of the flow system into which the well was developed. The pressure head in the flow system attempts to reach equilibrium with atmospheric pressure and becomes the driving force that causes water level to rise in the well and overflow from the well.

Flowing artesian wells and their flow system are developed into confined areas, typically by overlying strata which have very low hydraulic conductivity. The drilling operation punctures this confining stratum and allows the water to rise. The scope of AMD problems associated with flowing artesian wells range from minor pollutional effects such as slightly elevated metals concentrations associated with natural flow systems to major pollutional discharges which are directly connected to significant sources of AMD such as abandoned deep mine pools. In fact, many major pollutional discharges from flowing artesian wells are linked to improperly sealed deep well drilling associated with oil and gas development.

Sealing abandoned and newly drilled flowing artesian wells can be an effective and economically viable means of eliminating or minimizing AMD pollution associated with flowing artesian wells. The technical approach to design and construction of seals for flowing artesian wells is dictated by the pressure and hydraulic conductivity of the flow system in which the well was developed. For purposes of discussion, four general flowing artesian well seal types will be discussed.

Seal type 1: Low pressure head, low hydraulic conductivity

Seal type 2: Low pressure head, high hydraulic conductivity

Seal type 3: High pressure head, low hydraulic conductivity

Seal type 4: High pressure head, high hydraulic conductivity

Flowing wells with high pressure heads generally must be sealed using either concrete or a cement grout mixture, since a bentonite seal is unable to withstand the pressure and will ultimately fail. The use of an expanding grout admixture is essential to provide a controlled swell to the concrete or grout to assure that the mixture fully fills the seal area and does not develop shrinkage cracks. An additional consideration is whether the flowing wells are uncased or cased. For cased wells, further consideration must be given to the condition of the casing and whether the annular space between the casing and the adjacent strata have been properly sealed when the casing was installed.

Flowing wells in high hydraulic conductivity flow systems must be temporarily dewatered to stop overflow during seal construction. Placement of concrete or grout in water is acceptable, however placement in **flowing water** will result in erosion of the seal material. Again, the use of an expanding grout admixture is essential for successful sealing of these flowing wells.

A final consideration is on sites where temporary dewatering to facilitate sealing is unachievable due to terrain (flat topography areas). For these sites, the installation of casing may be required and a two-part seal may be necessary with dewatering initially occurring in the cased part of the well.

3.3.4.1 Flowing Well Seals - Low pressure head, low hydraulic conductivity wells

Flowing well seal design considerations are relatively straightforward for this type of well since the combination of low pressure and low hydraulic conductivity generally translates to very low flow rate wells with slow rates of pressure increase against the seal over time. The very low flow rate and slow pressure increases usually allow the well to be effectively sealed by direct injection methods where either concrete, grout or bentonite is "tremmied" directly into the well, beginning at the bottom of the well and continuing to the surface. This is the only flowing well condition where bentonite-only seals may be effective.

Case studies:

Foreman (1993) designed and constructed a seal to abate a flowing well condition which had occurred at a recently constructed industrial water supply well which was developed into a low pressure flow system having low hydraulic conductivity. The well was sited next to a manufacturing facility in Clearfield County, PA. Both the measured pressure head and the flow rates were very low and adjacent well sites that were just slightly topographically higher did not exhibit flowing artesian conditions. Unfortunately, the adjacent wells were not "accessible" and we were unable to use these wells to locally dewater the flow system at the flowing well site. However, the characteristics of the flow system were such that a decision was made to proceed with the seal construction without the benefit of temporary dewatering and abatement of flow. Since the well was recently drilled and had

not been cased, there was no need to ream the well. Casing was set to a level where sufficient depth was available to construct a seal with a grout basket installed at the casing base (although a packer could have been used).

Sealing of the flowing artesian well was accomplished by initial placement of bentonite pellets into the annular space between the well and the casing. After the initial swelling of the bentonite temporarily abated the flow, a high strength concrete mixture was poured into the remaining annular space until the annular space was filled to the ground surface. No reoccurrence of the flowing condition was observed at the well site.

3.3.4.2 Flowing Well Seals - Low pressure head, high hydraulic conductivity wells

Flowing wells developed in regional synclinal flow systems with low pressure and high hydraulic conductivity may have highly variable flow rates due to regional connectivity. The well must be purged of casing by reaming or using churn drills unless it has been found that the annular space between the casing and strata was fully and properly grouted. Sealing considerations for these types of wells requires positive measures to temporarily abate the flowing condition at the well surface. Typically this is accomplished by "local" dewatering the flow system near the flowing well by pumping from adjacent wells. Once the flowing condition has been temporarily abated, sealing work can begin. The well can now be sealed by tremmie placement of either a high strength concrete or a high penetration grout mixture, depending on the characteristics of the well and aquifer. Addition of an expanding grout admixture is essential to provide a controlled swell to the concrete or grout assuring full sealing and to prevent development of shrinkage cracks. The high hydraulic conductivity condition often translates to high volume pumping efforts to locally dewater the seal area and also requires continuous dewatering during sealing. The low pressure condition allows the "local" dewatering to be terminated within 7 days following seal placement. This time period is necessary to assure concrete/grout set-up.

Case Studies:

Foreman (1996) designed and constructed several seals to abate flowing well conditions which had occurred at several recently constructed monitoring wells developed in the lowwall area adjacent to a reclaimed surface mine in Centre County, PA. The reclaimed surface mine was developed below regional drainage levels and the mining had

breached a regional confining member. During operations, the company had to pump and treat excessive volumes of water to maintain a condition where mining was feasible. Following completion of mining, backfilling and revegetation, a final cut impoundment was developed as a wetland. The regional flow system underlying the mine site prior to mining was no longer being pumped and immediately began to rebound. This flow system recharged the spoil and eventually began to discharge along the lowwall as the regional flow system continually attempted to establish pressure equilibrium with the atmosphere.

Discharge rates from this reclaimed mine site varied from very low flows (6 L/min) to very high flows (>1000 L/min) based on the recharge into the regional system. The high flow rates were not due to high pressures, but were due to the high hydraulic conductivity of the flow system where regional inflows could move very rapidly to this discharge area. As part of a passive treatment construction program, the discharge from the regional flow system was temporarily abated by pumping and treating the final cut wetland and regionally dewatering the flow system. This also stopped flows from the monitoring wells.

Sealing of the flowing artesian well was accomplished by tremmie placement of concrete down the drill hole until the hole was filled to the surface. The concrete was a high strength mixture that had an expanding grout admixture added to assure complete sealing. The dewatering continued during the construction of the passive treatment systems and no reoccurrence of the flowing condition was observed at any of the monitoring wells.

3.3.4.3 Flowing Well Seals - High pressure head, low hydraulic conductivity wells

Flowing wells developed in regional synclinal flow systems with high pressure and low hydraulic conductivity typically have low flow volume with flow sustained year-round. The well must be purged of casing by reaming or using churn drills unless it has been found that the annular space between the casing and strata was fully and properly grouted. Sealing considerations for these types of wells requires positive measures to temporarily abate the flowing condition at the well surface. Typically this is accomplished by "local" dewatering the flow system near the flowing well by pumping from adjacent wells. Once the flowing condition has been temporarily abated, sealing work can begin. The well can now be sealed by tremmie placement of either a high strength concrete or a high penetration grout mixture, depending on the characteristics of the well and aquifer. Addition of an expanding grout

admixture is essential to provide a controlled swell to the concrete or grout to assure full sealing and to prevent development of shrinkage cracks. The low hydraulic conductivity translates to small pumping efforts to dewater the seal area. The high pressure condition requires that "local" dewatering be continued up to 28 days following seal placement. This time is necessary to assure full concrete/grout strength.

Case Studies:

Beck and Foreman (1985) designed and constructed a seal in a flowing artesian well at the Oneida Mining Co. - Dilltown facility in Indiana County, PA. This flowing artesian well was inadvertently developed as part of an on-going hydrogeologic investigation at the site. The well was initially drilled to a depth of approximately 17 m to provide monitoring capabilities for the adjacent surface facility area, specifically the rotary dump loading site. The drilling at the well site penetrated approximately 10 m of intact claystone and shales and the drilling continued for an additional 7 m until reaching a large, regional sandstone member which was believed to be the immediately underlying aquifer.

After drilling was completed, the well began to flow steadily and the discharge had both acidity and sufficient metals concentrations to warrant abatement, otherwise the company would have been required to treat the discharge from the well to meet effluent standards. Since the well was recently drilled and not cased, there was no need to ream the well. The flow system from which the well received recharge was dewatered using an existing, nearby water well which was sited topographically upgradient and had no history of flowing artesian conditions. This temporarily abated the discharge at the flowing well. Sealing of the flowing artesian well was accomplished by tremmie placement of concrete down the drill hole until the hole was filled to the surface. The concrete was a 4000 psi mixture that had an expanding grout admixture added to assure complete sealing.

Following the placement of the concrete seal in the flowing well, the dewatering continued for about one month to minimize pressure on the concrete seal and to assure that the concrete seal had fully cured and reached ultimate design strength. The dewatering was terminated after one month and the sealed well was monitored for several years. No reoccurrence of the flowing condition was observed.

3.3.4.4 Flowing Well Seals - High pressure head, high hydraulic conductivity wells

Flowing wells developed in regional synclinal flow systems with high pressure and high hydraulic conductivity typically have very high flow rates with flow sustained year-round. The well must be purged of casing by reaming or using churn drills unless it has been found that the annular space between the casing and strata was fully and properly grouted. Sealing considerations for these types of wells requires substantial positive measures to temporarily abate the flowing condition at the well surface. Typically this is accomplished by "local" dewatering the flow system near the flowing well by pumping from adjacent wells. Once the flowing condition has been temporarily abated, sealing work can begin.

The well can now be sealed by tremmie placement of either a high strength concrete or a high penetration grout mixture, depending on the characteristics of the well and aquifer. Addition of an expanding grout admixture is essential to provide a controlled swell to the concrete or grout to assure full sealing and to prevent development of shrinkage cracks. The high hydraulic conductivity and high pressure translates to a very high volume, continuous pumping effort to locally dewater the seal area and maintain the drawdown. The high pressure condition requires that "local" dewatering be continued up to 28 days following seal placement. This time is necessary to assure full concrete/grout strength.

Case Studies:

Foreman, Moore and Foreman (1984) designed and constructed a flowing well seal at a flowing artesian well known as "Big Bertha" located in Butler and Venango Counties, PA. This well had been identified as a major polluttional source in Slippery Rock Creek. Hydrogeologic studies of the abandoned gas well performed during the design stage determined that flows from the well varied annually from approximately 75 L/min (20 gpm) to nearly 680 L/min (180 gpm). The chemistry of the well was strongly polluttional and representative of AMD and not saline water which would be typically anticipated from an abandoned gas well. The hydrogeologic study also identified five separate flow systems that recharged this well. Discrete interval chemical samples and dye studies jointly conducted with the USGS determined that the upper two flow systems were strongly polluttional and had

highly variable inflow rates to the well, while the lower three flow systems contributed approximately 65 L/min (17 gpm) of steady state inflow to the well and these were not polluttional.

The flow systems were strongly confined at the flowing artesian well. Geologic correlation of the strata associated with the upper two flow systems indicated that the probable source of the AMD in the flow systems was originating from a nearby abandoned mine and was traveling both topographically and structurally downgradient towards the well. A decision was made to "partially seal" the flowing well such that inflow from the upper two polluttional flow systems would be abated while the lower three flow systems would be allowed to recharge the well, thus creating a steady-state, non-polluttional flowing artesian well which would discharge alkaline water into Slippery Rock Creek at 65 L/min (17 gpm). The well was first purged and reamed. New casing was set to a stratigraphic level below the base of the upper flow systems and the annular space was then sealed using an expanding grout. Placement was facilitated by "downhole pump" dewatering techniques.

3.3.5 Grout Curtains / Walls

Grouts can be used to separate acid-producing rock and groundwater. Injection of grout barriers may significantly reduce the volume of groundwater moving through spoil and thereby greatly reduce the amount of AMD coming from a site.

Case Studies:

Gabr et al. (1994) characterized the groundwater flow of an acid-producing reclaimed site where a 1.5-m thick wall was installed by pumping a mixture of class F fly ash and portland cement grout into vertical boreholes near the highwall. After two years, the grout wall reduced groundwater inflow from the highwall to the spoil by 80%, resulting in one of two seeps completely drying up and substantially reducing the flow of the other seep.

Foreman, Ward and Schettig (1973) designed and constructed a grout curtain along Interstate 80 (Clarion County, PA) to abate significant seepage through an inadequate coal barrier pillar and overlying strata which was causing slippage of the road cut highwall and AMD pollution to a tributary draining to the Clarion River. The grout curtain was developed by drilling grout injection holes along the top of the road cut and then grouting was done continuously along the length of the cut from the base to the ground surface. Following

completion of the grouting, no further discharges or slippage was observed. Foreman, Hong and Ward (1977) designed and constructed a slurry trench to abate the discharge from an abandoned deep mine (Mercer County, PA). The slurry trench was developed along the peripheral outcrop barrier of the mine and was excavated from the surface using large backhoes. The trench was then backfilled with a soil-bentonite stabilized slurry which provided a hydraulic barrier to prevent lateral discharge from the abandoned deep mine. The slurry-trench seal was effective since there was no discharge following construction and the deep mine became fully inundated.

Foreman and Glenn (1980) designed and constructed a slurry trench to abate the discharge from an abandoned deep mine (Clarion County, PA). The slurry trench was developed along the peripheral outcrop barrier of the mine and was excavated from the surface using large backhoes. The trench was then backfilled with a stabilized soil-cement slurry which, when set-up, provided a relatively impervious barrier to prevent lateral discharge from the abandoned deep mine. The slurry-trench seal was effective since there was no discharge following construction and the deep mine became fully inundated.

3.3.6 Underground Disposal

The disposal of AMD related mine wastes in underground mines has historically included the disposal of mine gob, mine treatment sludge and flyash. The mine gob is typically disposed when excessive partings in the coal seam and excess roof/floor rock are removed during deep mining operations. This material often has potential to cause AMD and is typically placed in cross-cuts where access is not needed.

Mine treatment sludge is typically placed in isolated mine reservoir areas where the precipitate rich sludge will not create future treatment problems if the metals are redissolved in the mine water since the reservoir is isolated from the mine pumps.

The disposal of fly ash holds significant promise since this material may prove to be doubly-beneficial in instances where backstowing to prevent subsidence effects can be accomplished with a material that may also produce some alkalinity to the water.

Case Studies:

Mine gob disposal is a common practice in underground mines throughout the world. The return of alkaline mine treatment sludge to isolated mine reservoirs was done throughout

the 1980's by several underground mine operators with good success. No long term studies are known for fly ash disposal into deep mine works.

3.3.7 Injection

The placement of acid-producing materials, AMD or their altered product into the subsurface through a vertical drilled hole has been an effective method of disposal in some situations. The practice of drilling a well down to porous rock strata and then injecting fluids into the underground formation is a technique that has only recently become popular for dispersing pollutants to a confined subsurface area. The most favorable geologic depths present in the Appalachian region dictate a depth range of 1,000 to 2,000 m. This technique is significantly limited by factors that would either allow the injected waste to escape from the containing strata and polluting ground waters or cause other secondary effects. The actual space available for deep well disposal is limited, since the space used by injected material must be made by displacing other materials (ground water) and increasing rock pressures. Increases in deep geologic pressures can, and have, caused ground movement. Possible long term chemical reactions between the strata and the injected waste pose another constraint. While areas of oil and gas deposits have favorable strata for injection, all of the abandoned wells have to be located and plugged. Another limitation is that this technique does not destroy the pollutant, but transfers it from a place of immediate concern to a place where its presence is not anticipated at the time to be of concern. The difficulty in obtaining adequate sub-surface geologic information and the lack of knowledge of how the geology would react to injected wastes are the most important reasons for not being able to adequately anticipate short and long term effects. This technique is regulated by the Federal Safe Drinking Water Act and it appears that the general use of this technique in areas with suitable geology is not warranted at this time.

Case Studies:

There had been six active deep wells handling acid waste in Appalachia. The advent of disposal wells in Appalachia is relatively new and such information as has been obtained is not publicized. Determination of the capacity (rate) of a well requires drilling the well and running a pressure test to determine the capacity curve. It is reasonable to place an upper limit of approximately 4 million L/day (1 Mgal/day) on individual well capacity for any

reasonable injection pressure. Thus deep well disposal does not appear to be a reasonable control technique for unconcentrated acid mine drainage. Concentration techniques such as reverse osmosis, evaporation, or ion exchange, however, can use it successfully.

3.3.8 Inert Gas Blanket

This involves the placement and retention within an underground mine of an inert gas (a gas that is not reactive in the AMD forming process). Such gases include carbon dioxide, nitrogen, and methane. Inert gas blanketing of abandoned deep mines has great promise, since it prevents the oxidation of acid material and thus does not produce residues for disposal such as from neutralization. This process can be used based on the dependability and security of mine seals. If the mine can be sealed completely, little additional makeup gas will be necessary after the initial injection. If the mine is only partially sealed, considerable amounts of gas will be necessary to keep the underground mine atmosphere filled with inert gas. As soon as oxygen is readmitted, acid is produced.

Case Studies:

Case study summaries are not available at this time.

3.3.9 Regulated Pumping

Regulated pumping is the discharge of AMD at volumes, rates, times and locations so that the contaminating effects will be minimized. Pumping is applied largely to active mines to regulate mine water depths. Most pumping of drainage is accomplished over a short period of time each day in order to avoid pumping during periods of peak use. There is an attempt by regulatory agencies to require pumping continuously to avoid slugs of waste being discharged to streams.

Case Studies:

Case study summaries are not available at this time.

3.3.10 Stream Flow Regulation

Stream flow regulation is the containment and release of stream waters at volumes, rates, times and locations so that the contaminating effect will be minimized. Controlled releases of stored water at periods of high concentrations of mine drainage in streams would disperse the pollutants to predetermined concentration levels. The types of reservoirs that would be considered effective for mine drainage control would be similar to those designed

for low stream flow augmentation. This is an area control technique particularly applicable where there are a great many small sources of contamination in a watershed. Much additional detailed information needs to be determined on the acid yield, the weighted acidity, by day or by week for contaminated streams or watersheds, as well as the weighted alkalinities of the uncontaminated streams in order to apply this flow control technique. Once the required reservoir has been determined by equating alkalinity to the actual acidity, the costs can be estimated.

Case Studies:

Case study summaries are not available at this time.

3.3.11 Dispersion and Containment

If acid mine drainage pollutants can be reduced to tolerable concentrations or manageable volumes, then dispersion and containment techniques offer an option for the effective control of mine drainage pollution under some conditions.

Case Studies:

Case study summaries are not available at this time.

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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 O₂ 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 Fe²⁺ 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

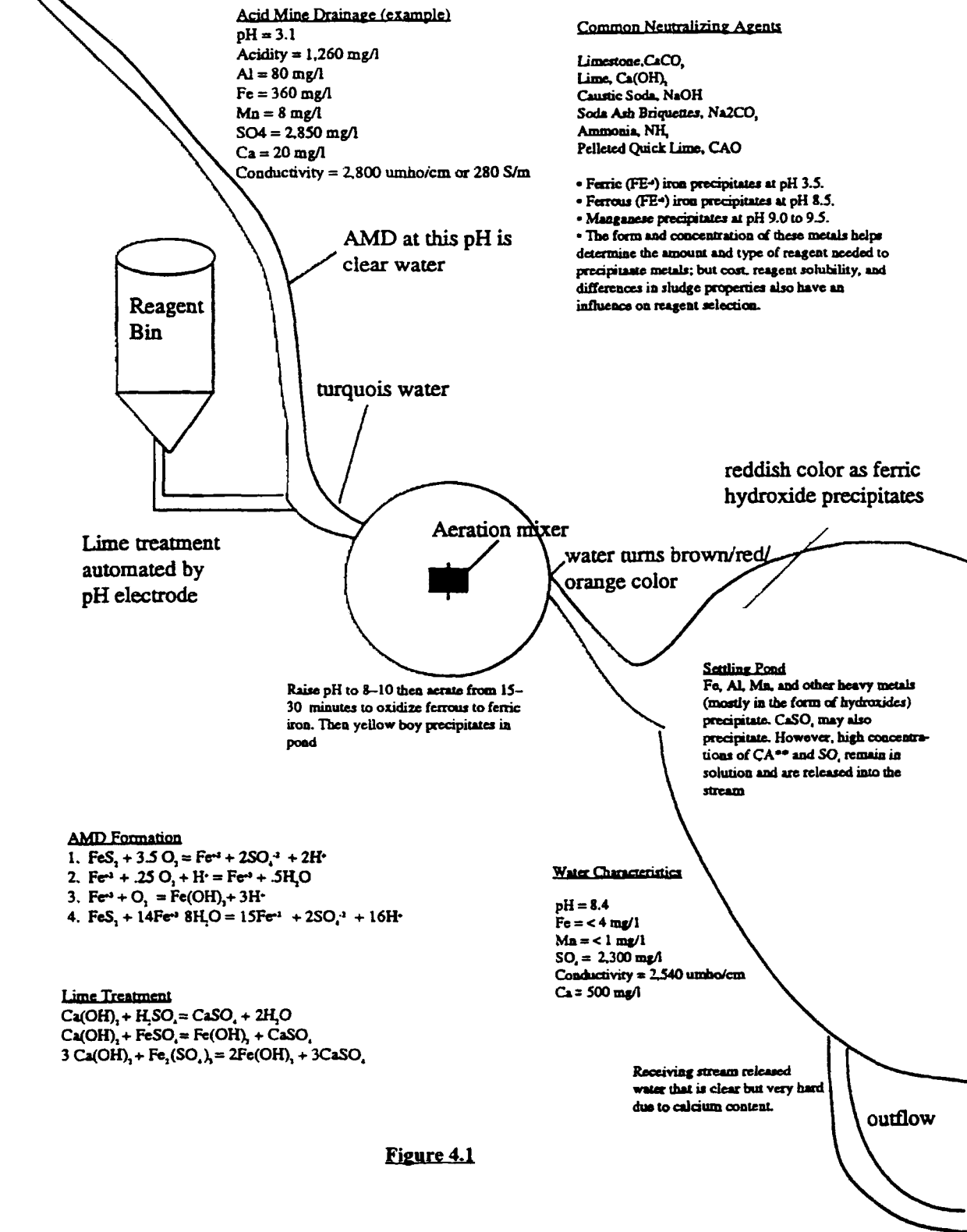


Figure 4.1

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 ₂ CO 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 ₂ CO 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 ₄ OH	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 ₂ O 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 $\text{pH} \geq 8.5$. 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 $\text{pH} \geq 3.5$. 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 $\text{pH} \geq 5.0$ 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, $\text{Ca}(\text{OH})_2$, 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 $\text{Ca}(\text{OH})_2$. 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 $\text{Ca}(\text{OH})_2$, 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 $\text{Ca}(\text{OH})_2$ 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 CaCO₃) 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, Na₂CO₃, 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 (NH₃), 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 CaCO₃. 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.

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5.0 Passive Systems Technologies

Active chemical treatment of AMD to remove metals and acidity is often expensive and a long term liability. Recently, a variety of passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated mine waters. The primary passive technologies include constructed wetlands, anoxic limestone drains (ALD), vertical flow systems such as successive alkalinity producing systems (SAPS), limestone ponds, and open limestone channels (OLC) (Figure 5.1).

Natural wetlands are characterized by water-saturated soils or sediments with supporting vegetation adapted to reducing conditions in their rhizosphere. Constructed wetlands are man-made ecosystems that mimic their natural counterparts. Often they consist of shallow excavations filled with flooded gravel, soil, and organic matter to support wetland plants, such as *Typha*, *Juncus*, and *Scirpus* sp. Treatment depends on dynamic biogeochemical interactions as contaminated water travels through the constructed wetland. Aerobic wetlands promote oxidation and hydrolysis in the surface water of the wetland. In anaerobic wetlands, the metabolic products of sulfate-reducing bacteria, usually accompanied by limestone, are major reactants in raising pH and precipitating metals as sulfides, hydroxides and/or carbonates. The bacteria use organic substrates and sulfate as nutrients; plants are not required but may be present. ALDs are abiotic systems consisting of buried limestone cells that passively generate bicarbonate alkalinity as anoxic water flows through. Vertical Flow Systems such as SAPS combine treatment concepts from both wetlands and ALDs. Oxygenated water is pre-treated by organic matter removing O_2 and reducing Fe^{3+} to Fe^{2+} , and then the anoxic water flows through limestone at the base of the system. Limestone ponds are ponds built over the upwelling of a seep, which are filled with limestone for treatment. OLCs are surface channels or ditches filled with limestone. Armoring of the limestone with Fe hydroxides reduces limestone dissolution, so longer channels and more limestone is required for water treatment.

At their present stage of development, passive systems can be implemented as a single permanent solution for many types of AMD a much lower cost than active treatment. Alternatively, passive systems can furnish partial treatment that greatly improves the quality

of receiving streams, or greatly decreases the costs of active treatment. Relative to active chemical treatment, passive systems generally require longer retention times and greater space, but markedly decrease long-term costs. Many passive systems have realized successful short term implementation in the field and have substantially reduced or eliminated water

treatment costs at many mine sites (Faulkner and Skousen 1994). Current research seeks to understand the dynamically complex chemical and biological mechanisms that occur within passive systems and that are responsible for successful AMD treatment (Watzlaf and Hyman 1995).

Selection and design of an appropriate passive system is based on water chemistry, flow rate and local topography and site characteristics (Hyman and Watzlaf 1995), and refinements in design are ongoing. Figure 5.2 (adapted from Hedin et al. 1994a) summarizes current thinking on the appropriate type of passive system for various conditions and Table 5.1 summarizes characteristics, design considerations and sizing factors. In general aerobic wetlands can treat net alkaline water, ALDs can treat water of low Al, Fe^{3+} and dissolved O_2 (DO), and SAPS, anaerobic wetlands and OLCs can treat net acidic water with higher Al, Fe^{3+} , and DO, as well as net alkaline water. As scientists and practitioners improve treatment predictability and longevity of passive systems, they will be better able to treat the more difficult waters of high acidity and high Al content.

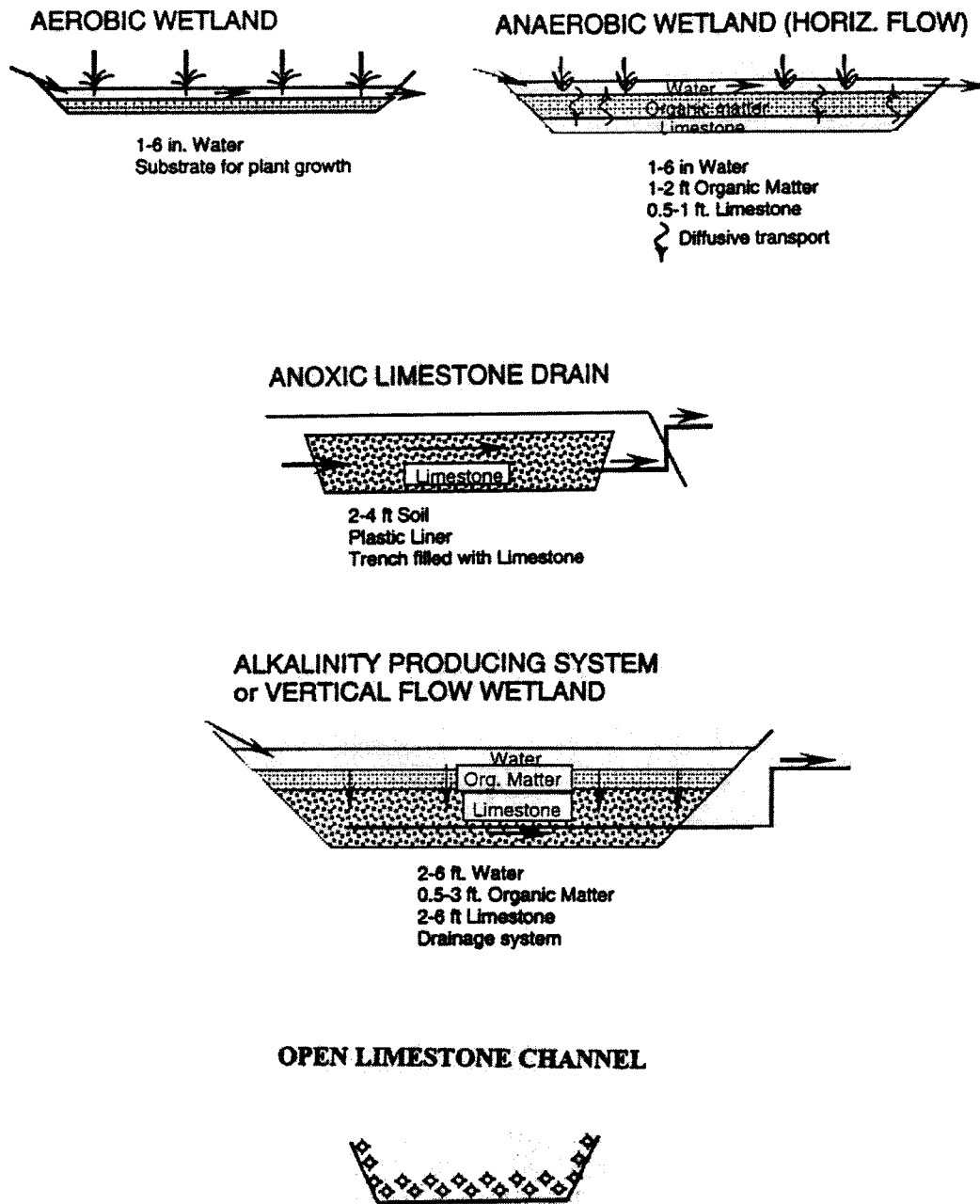
These technologies have potential application in the treatment of AMD from both coal and hard-rock mining. Drainage from hard-rock mining areas contains elevated concentrations of various heavy metals (copper, lead, zinc, cadmium, etc.) which contribute to overall acidity and can greatly increase the toxicity of the water, but the general nature of AMD from coal and hard-rock areas is similar (e.g., acidity, high Fe and SO_4), as are most of the problems in treatment. The processes that occur in passive systems to reduce acidity and remove metals from coal mine drainage are essentially the same as for metal mine drainage. Although concentrations of heavy metals in coal mine drainage are generally low, Hyman and Watzlaf (1996) found that at about 10% of over 100 coal mine drainage sites, zinc was >5 mg/L, nickel >2 mg/L, cobalt >1 mg/l and copper >0.5 mg/L. In addition, the mine drainage at a few sites contained beryllium and chromium (both >0.1 mg/L), and

cadmium and lead (both >0.05 mg/L), as well as detectable antimony, arsenic and barium. Discussions and case studies in this section will focus on coal mine drainage, but many aspects can also apply to metal mine drainage.

A major problem in treatment of AMD is removal of iron and, at many sites, manganese and aluminum. To simplify wording in the remainder of the section, the term "metals" will be used for these three constituents, even though the elements concerned occur as dissolved cations in the AMD and are not in the metallic state.

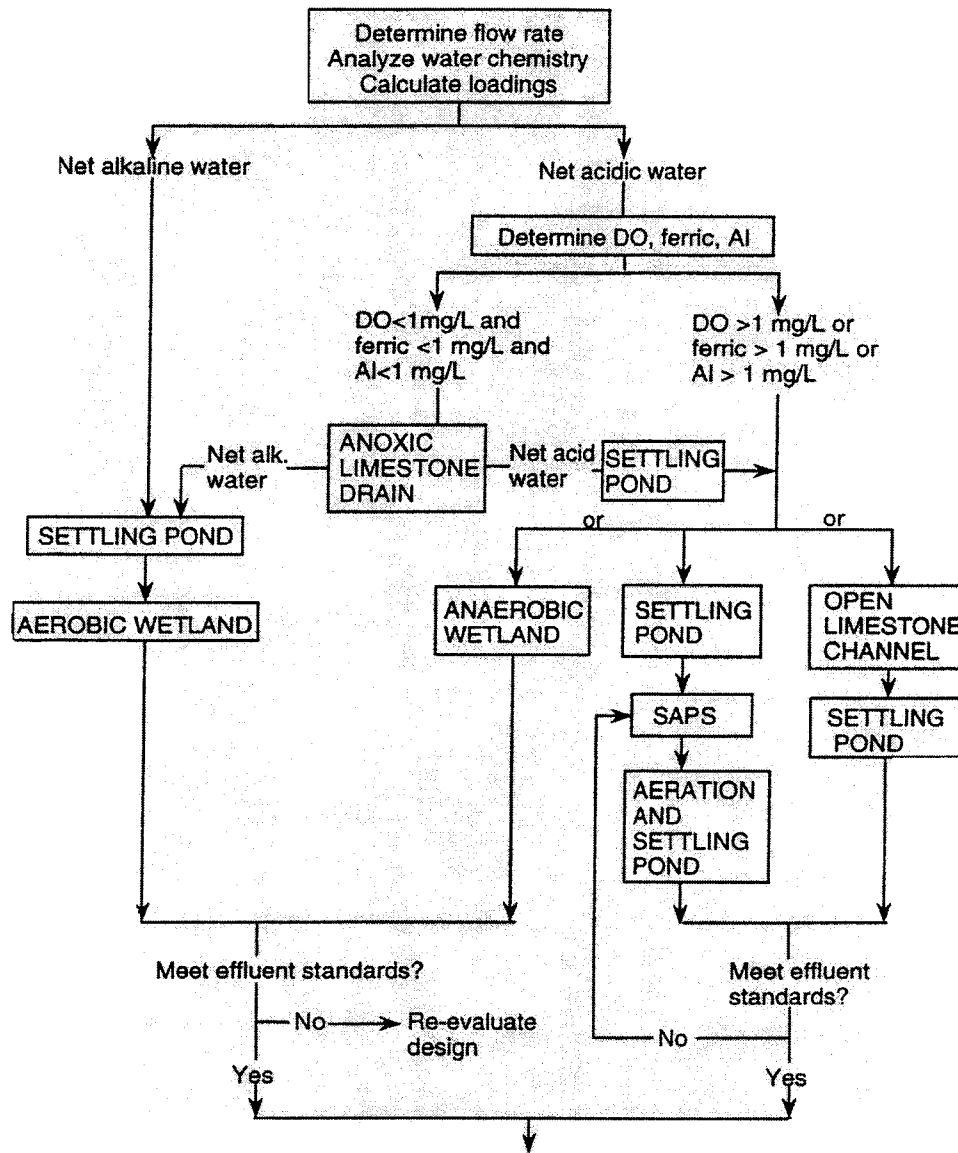
5.1 Natural Wetlands

Huntsman et al. (1978) and Wieder and Lang (1982) first noted amelioration of AMD following passage through naturally occurring *Sphagnum* bogs in Ohio and West Virginia. Studies by Brooks et al. (1985), Samuel et al. (1988), and Sencindiver and Bhumbla (1988) documented similar phenomena in *Typha* wetlands. Although evidence suggests that some wetland plants show long term adaptation to low pH and high metal concentrations, AMD eventually degrades the quality of natural wetlands, which is contrary to federal laws designed for wetland protection and enhancement. Such regulations do not govern use of artificially constructed wetlands for water treatment, leading to the suggestion that these engineered systems might provide low cost, low maintenance treatment of AMD (Kleinmann 1991). Over a thousand wetlands have since been constructed to receive AMD from both active mines and abandoned mine lands.



Schematic diagrams of passive treatment systems.

Figure 5.1



Flow sheet for selecting passive treatment system for various conditions. Additional treatment may be required for Mn and heavy metals. See text for further discussion and possible limitations. (Modified from Hedin et al. 1994).

Figure 5.2

Table 5.1 Design of Passive Treatment Systems.

Treatment System	General Requirements	Construction	Design Factors	References
Aerobic wetland	Net alkaline water	Overland flow Cattails planted in substrate	<ul style="list-style-type: none"> • 10-20 g Fe/m²/d • 0.5-1 g Mn/m²/d 	Hedin et al (1994)
Horizontal-flow Anaerobic wetland	Net acidic water, generally low flow rate	Horizontal flow above organic substrate	<ul style="list-style-type: none"> • 3.5 g acidity/m²/d. • Hydraulic conductivity of substrate (generally 10³-10⁴ cm/sec) • Rate of sulfate reduction (~ 300 mmoles/m³/day - see text) • Hydraulic loading 	Hedin et al (1994) Wildeman et al (1993) Eger (1994)
Anoxic Limestone Drain (ALD)	Net acidic water DO, Fe ⁺³ , Al <1.0 mg/L	Horizontal flow through buried limestone	<ul style="list-style-type: none"> • 15 hours contact time • 6 to 15 cm diam. limestone • Lifetime limestone consumption 	Hedin and Watzlaf (1994)
Successive alkalinity producing systems (SAPS)	Net acidic water	vertical flow through an organic layer overlying a limestone bed	<ul style="list-style-type: none"> • 15-30 cm organic matter with adequate permeability • 15 hours contact time in limestone • Lifetime limestone consumption • 6 to 15 cm diam. limestone 	

5.2 Constructed Wetlands

Mechanisms of Fe, Mn and Al retention within wetlands listed in their approximate order of importance include: 1) formation and precipitation of metal hydroxides, 2) microbial sulfate reduction forming metal sulfides, 3) organic complexation reactions, 4) exchange with other cations on negatively-charged sites, and 5) direct uptake by living plants. Other mechanisms include neutralization by carbonates, attachment to substrate materials, adsorption and exchange of metals onto algal mats, and microbial reduction of dissolved Fe^{3+} and Fe hydroxides to furnish energy for their metabolism.

The way in which a wetland is constructed ultimately affects how water treatment occurs. Two construction styles currently predominate: 1) "aerobic" wetlands consisting of *Typha* and other wetland vegetation planted in shallow (<30 cm), relatively impermeable sediments comprised of soil, clay or mine spoil, and 2) "anaerobic" wetlands consisting of *Typha* and other wetland vegetation planted into deep (>30 cm), permeable sediments comprised of soil, peat moss, spent mushroom compost, sawdust, straw/manure, hay bales, or a variety of other organic mixtures, which are often underlain or admixed with limestone. In aerobic wetlands, treatment is dominated by processes in the shallow surface layer. In anaerobic wetlands, treatment involves major interactions within the substrate. A third type, vertical flow "wetlands," is discussed in the later section on Vertical Flow Systems (Section 5.4)

5.2.1 Aerobic wetlands

Aerobic wetlands are generally used to collect water and provide residence time and aeration so metals in the water can precipitate. The water in this case usually has net alkalinity. Iron and Mn precipitate as they oxidize, and the precipitates are retained in the wetland or downstream. Wetland plants encourage more uniform flow and thus more effective wetland area for water contact.

Because of their extensive water surface and slow flow, aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn hydroxides. The extent of metal removal depends on dissolved metal concentrations, exposure to air and the resulting dissolved oxygen content, pH and net alkalinity of the mine water, the presence of active microbial biomass, and retention time of the water in the wetland. The pH and net acidity/alkalinity of the water are particularly

important because pH influences both the solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis. Metal hydrolysis produces H^+ , but alkalinity in the water buffers the pH and allows metal precipitation to continue. Rates of inorganic oxidation decrease a hundred-fold with each unit drop in pH, but microbial oxidation may increase these rates. Following Fe oxidation, abiotic hydrolysis reactions precipitate Fe hydroxides. Therefore, aerobic wetlands are best used with water that contains net alkalinity to neutralize metal acidity. Abiotic Mn oxidation occurs rapidly at $pH > 8$ while microorganisms are thought to catalyze this reaction at $pH > 6$ (Wildeman et al. 1993). Manganese oxidation occurs more slowly than Fe and is sensitive to the presence of Fe^{2+} , which will prevent or reverse Mn oxidation. Consequently in aerobic net alkaline water, Fe and Mn precipitate sequentially, not simultaneously, with the practical result that Mn precipitation occurs (if at all) mainly in the later stages of wetland flow systems, after all Fe is precipitated.

Case Studies:

Brodie and co-workers at the Tennessee Valley Authority (TVA) have reported extensively on their use of aerobic wetlands to treat AMD (Brodie 1993). A typical staged design might include an anoxic limestone drain (ALD, see next section) to passively add alkalinity to the source AMD, a settling basin to hold precipitated Fe flocs, followed by two or three aerobic wetland cells to sequentially remove additional Fe and Mn. Nine TVA wetlands receive moderate quality AMD (pH range of 4.1 to 6.3; total Fe < 70 mg/L; total Mn < 17 mg/L; total Al < 30 mg/L; net alkalinity 35 to 300 mg/L as $CaCO_3$), which require no further post-system treatment of water exiting the wetlands. Four TVA wetlands treat water with high Fe (> 170 mg/L) and no net alkalinity. Two of these systems require NaOH treatment to comply with NPDES effluent limits, while two others use ALDs for further treatment of the effluent. A final TVA wetland system receives low Fe (< 0.7 mg/L) and Mn (5.3 mg/L) and is ineffective in Mn removal. Based on their experience with these systems since 1985, Brodie (1993) suggests that staged aerobic wetland systems can accommodate Fe loads of up to 21 grams/ m^2 /day even in the absence of excess alkalinity. Manganese loads up to 2 grams/ m^2 /day can be accommodated, if alkalinity is present.

Hedin et al. (1994a) also provide factors for sizing of wetlands based on studies of many wetlands. Specifically, for net alkaline waters, the wetlands can be sized using 10 to 20 g/ m^2 /day for Fe and 0.5 to 1 g/ m^2 /day for Mn. Duggan et al. (1992) found in bench-scale

tests that Mn could be removed at rates of about 0.2 g/m²/day using *Cladophora*, an algae, in a limestone-lined basin, even in partly frozen conditions.

Analysis of 73 sites in Pennsylvania suggested that constructed wetlands are the best available technology for many post-mining ground water seeps, particularly those of moderate pH (Hellier et al. 1994). However, those sites with net acidic discharges have a much lower successful treatment efficiency. For example, the Rougeux #1 site has a flow of 5.2 gpm and influent chemistry of 2.9 pH, 445 mg/L acidity as CaCO₃, Fe 45 mg/L, Mn 70 mg/L, and Al 24 mg/L. After flowing through a two-celled aerobic wetland, pH increased to 3.2, acidity was decreased by 43%, Fe by 50%, Mn by 17%, and Al by 83% (Hellier 1997). The wetland cost about \$15/m² to build in 1992 and was severely undersized. Although there is improvement in the water, the wetland effluent did not conform to effluent limits. Two other wetlands constructed on the site show similar results.

5.2.2 Horizontal flow anaerobic wetlands

Horizontal flow anaerobic wetlands encourage interaction of water with organic-rich substrates, which contribute significantly to treatment. The wetland substrate may contain a layer of limestone in the bottom of the wetland or the limestone may be mixed among the organic matter. Wetland plants are transplanted into the organic substrate. These systems are used when the water has net acidity, so alkalinity must be generated in the wetland and introduced to the net acid water in order to accomplish significant precipitation of dissolved metals.

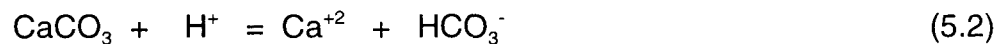
The alkalinity can be generated in an anaerobic wetland system in two ways (Hedin and Nairn 1990). Certain bacteria, Desulfovibrio and Desulfotomaculum, can utilize reactions between organic substrate (CH₂O, a generic symbol for organic carbon) and sulfate as a source of energy for their metabolism. The bacteria require relatively simple organic compounds, so only part of the organic matter is normally usable by them, or they

require action by fermenting or other bacteria to degrade complex compounds. In the bacterial conversion of sulfate to hydrogen sulfide, bicarbonate alkalinity is produced:



The sulfate-reducing bacteria function best in the pH range 6 to 9 (Widdell 1988) and can function down to about pH 5. However, the bacteria can control their microenvironment so that successful sulfate reduction has been reported at influent pH as low as 2.0 to 2.8 (Gusek 1998, Bolis et al. 1991, Tuttle et al. 1969). However, if the rate of acidity input exceeds the neutralization capacity of the system, pH will decrease and sulfate reduction will stop (Eger 1994).

Alkalinity can also be generated as the limestone under the organic material reacts with acidity in the wetland:



The limestone continues to react when kept in an anaerobic environment because ferrous iron is relatively soluble at pH 7 in anoxic water and ferrous hydroxide does not form and coat the limestone. If ferrous iron is oxidized, forming ferric iron, then the ferric iron will precipitate as a coating of ferric hydroxide on the limestone. Bacterial sulfate reduction and limestone dissolution produce water with higher pH and add bicarbonate alkalinity for metal removal.

The surface water in anaerobic wetlands is oxidizing, so oxidation and precipitation of Fe and Mn is promoted in this zone to the extent that alkalinity is available. Organic matter and the resulting bacterial reduction of O_2 and Fe create reducing conditions in the subsurface zone. Sulfate reduction and limestone dissolution in this zone consume acidity, produce alkalinity and cause Fe-sulfide precipitation. Increase of pH may cause Al hydrolysis and precipitation. Some alkalinity is transported to the surficial zone by diffusion and minor flow, promoting hydrolysis and precipitation there. Iron, Al and H^+ are similarly transported into the anaerobic subsurface zone for precipitation and neutralization.

Several treatment mechanisms are enhanced in anaerobic wetlands compared to aerobic wetlands, including formation and precipitation of metal sulfides, metal exchange and complexation reactions, microbially generated alkalinity due to reduction reactions, and continuous formation of carbonate alkalinity due to limestone dissolution under anoxic conditions. Since anaerobic wetlands produce alkalinity, their use can be extended to poor quality, net acidic, low pH, high Fe, and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are likely to be of critical importance to long term AMD treatment. However, Wieder (1992) documents that the mechanism and efficiency of AMD treatment varies seasonally and with wetland age. Like their aerobic counterparts, anaerobic wetlands are most successful when used to treat small AMD flows of moderate water quality.

Hedin et al. (1994a) suggest that anaerobic wetlands to treat net acid waters be sized using a factor of 3.5 g of acidity/m²/day.

Another criterion for sizing is sulfate reduction rate (Eger 1994). In order to maintain a healthy population of sulfate-reducing bacteria, the pH in the bacterial microenvironment must be maintained in the range 5 to 9. In order to sustain this type of environment, the rate at which acidity is applied to the system must be less than the wetland's ability to neutralize this acidity. Sulfate reduction rates, expressed as moles per unit volume of substrate per day, have generally been reported to range from 100 to 300 moles/m²/day (Table 5.1). The total acidity load that can be neutralized by an anaerobic wetland can be computed as shown below.

$$\text{Incoming acidity load (mmoles/day)} = F(M_2 + 1.5M_3 + 0.5 \times 10^{3-\text{pH}})$$

where M₂ is the concentration of divalent metals (Fe²⁺, Mn²⁺) in the input in millimoles/L, M₃ is the concentration of trivalent metals (Fe³⁺, Al³⁺) in millimoles/L, and F is the flow rate in L/day.

For the system to be effective, the input acidity must be less than the daily rate of sulfate reaction:

$$\text{Input acidity (mmoles/day)} < R \times V$$

where R is the rate of sulfate reduction (100-300 mmoles/m³/day) and V is the volume of substrate (m³). This simple balance works when the pH of the input drainage is within the optimum range of the sulfate-reducing bacteria. If the pH is low, the input water must be spread over a larger area to avoid removing all the neutralizing capacity in the top of the

substrate. Since there is essentially no mixing in the substrate and if the acid load per unit area is too high, the pH in the top of the wetland will decrease to the level of the input and sulfate reduction will cease. James Gusek (personal communication, 1998) has found from experience that the areal loading can range from less than 70 to more than 360 L/min/m², depending on pH. These rates are in general agreement with the value of 3.5 g acidity/m²/day proposed by Hedin et al (1994a).

Case Studies:

Sorption onto organic materials (such as peats and soils) initially decreased Fe from 32 mg/L to 5 mg/L (84%), Mn from 15 to 14 mg/L (7%), and total suspended solids from 32 to 12 mg/L (63%), but eventually all sorption sites on substrate materials were exhausted by continual introduction of metals in acid water (Brodie et al. 1988). Kleinmann (1991) suggested adsorption of metals by organic substrates may compensate for limited initial biological activity during the first few months of operation in a new wetland system. A field study, which examined five wetland substrate types over a 25-month period, also demonstrated that organic substrates were saturated after only one to seven months of AMD input at 9 to 17 mg Fe per gram substrate (Wieder 1993). Although some natural inputs of organic matter occur annually at plant senescence, the adsorption capacity of a wetland is limited by saturation of all exchange sites (Wieder 1988). Substantial artificial inputs of organic matter or fertilizer have been used as a successful strategy to temporarily renew this adsorption capacity, following an observed decline in wetland performance (Eger and Melchert 1992, Haffner 1992, Stark et al. 1995).

Insoluble precipitates such as hydroxides, carbonates, and sulfides represent a major sink for metal retention in wetlands. About 50 to 70% of the total Fe removed from AMD by wetlands is found as ferric hydroxides (Henrot and Wieder 1990, Calabrese et al. 1991, Wieder 1992). Ferric hydroxide formation depends both on the availability of dissolved oxygen and on the initial oxidation state of Fe in the AMD. Wieder (1993) reported significant retention of ferric hydroxides in surface sediments of anaerobic wetlands. Up to 30% of the Fe retained in wetlands may be found as ferrous iron and may be combined with sulfides (Calabrese et al. 1991, McIntyre and Edenborn 1990, Wieder 1992). Iron mono and disulfides form as a result of H₂S formation by microbial sulfate reduction in the presence of an oxidizable carbon source. In addition to its metal removal potential, sulfate reduction

consumes acid and raises water pH (Hedin and Nairn 1992, Rabenhorst et al. 1992).

Long term retention of Fe sulfides and Fe hydroxides in a wetland is not well understood. Under continued anoxic conditions and in the absence of soluble Fe^{3+} , pyrite should remain stable. Calabrese et al. (1994) changed the influent of their anaerobic wetland from AMD to freshwater with no concomitant export of Fe^{2+} . The effluent pH was >6 due to continued limestone dissolution.

Some workers have indicated that wetland systems can be seeded with specially designed and selected microorganisms (Davison 1993, Phillips et al. 1994) to introduce or re-establish microbial activity. However, experiments utilizing appropriate controls have not established the efficacy of this approach (Calabrese et al. 1994). Experience with bioremediation of other wastes suggests that selection and enrichment of naturally occurring microbial populations is a superior, more cost-effective approach (Alexander 1993).

In constructed wetlands, higher plants serve several purposes including: substrate consolidation, metal accumulation, adsorption of metal precipitates, stimulation of microbial processes, wildlife habitat, and aesthetics. Wetland plant species vary in their ability to accumulate metals (Fernandes and Henriques 1990). Some reports document elevated tissue concentrations (Spratt and Wieder 1988), while others show little metal accumulation (Folsom et al. 1981). On an annual basis, uptake by *Typha* accounted for less than 1% of the Fe removed by volunteer wetlands treating AMD (Sencindiver and Bhumbra 1988). While wetland vegetation can accumulate heavy metals, this is not a major removal mechanism. However, the accumulation of toxic metals like Cd and Se can be a potential hazard.

Several studies report on the effects of different plant species in wetlands. Early in the development of treating AMD with constructed wetlands, *Sphagnum* was the predominant wetland species. *Sphagnum* has a well documented capacity to accumulate Fe (Gerber et al. 1985, Wenerick et al. 1989). However, Spratt and Wieder (1988) found that saturation of *Sphagnum* moss with Fe could occur within one growing season. Some have indicated that metal retention over the long term is limited in some wetlands because organic matter inputs by wetland plants are limited (Kleinmann 1990). Many of the original constructed wetlands were vegetated with *Sphagnum* but few remained effective. Cattails (*Typha*) have been found to have a greater environmental tolerance than *Sphagnum* moss

(Samuel et al. 1988). One of the reasons is that cattails do not accumulate metals into their tissues through uptake. Algae and a few other wetland species have also received attention due to the observation that enhanced metal removal was associated with algal blooms (Hedin 1989, Kepler 1988, Pesavento and Stark 1986, Phillips et al. 1994). In Colorado, algal mixtures were found to aerobically remove Mn from mine drainage (Duggan et al. 1992), presumably due to elevated pH resulting from algal growth and the extra oxygen generated photosynthetically by the algae. Probably the most important role that wetland plants serve in AMD treatment systems may be their ability to stimulate microbial processes. Kleinmann (1991) explains that plants provide sites for microbial attachment, release oxygen from their roots, and supply organic matter for heterotrophic bacteria.

Long term successful treatment by a staged anaerobic wetland has also been reported for slightly net acidic water (Fe 89 mg/L; net acidity 40 mg/L as CaCO₃) at the Simco constructed wetland near Coshocton, OH (Stark et al. 1994). The wetland, built in 1985, has improved in treatment efficiency over time, not requiring any chemical treatment since 1990. The density of cattail shoots has increased to a current density of 17 shoots/m². Success at the Simco wetland is attributed to the presence of moderate mine water quality (near neutral pH and Fe <100 mg/L), sound wetland design, periodic site maintenance, and high vegetative cover.

Five anaerobic wetland systems in WV receiving 4 to 98 L/min of net acid water (110 to 2400 mg/L acidity as CaCO₃ and Fe from 10 to 376 mg/L) reduced acidity by 3 to 76% and Fe concentrations by 62 to 80% (Faulkner and Skousen 1994). These wetlands were generally much smaller in area than that recommended by early formulas published by the U.S. Bureau of Mines (Hedin 1989) based on iron loads. For example, one of these wetlands, Keister, reduced the acidity of a 17-L/min flow from 252 to 59 mg/L as CaCO₃ (76% reduction) and increased pH from 3.1 to 5.4. Iron was reduced from 23 to 9 mg/L (62%), Mn from 23 to 20 mg/L (11%), and Al from 27 to 13 mg/L (52%). The Pierce wetland used an organic substrate over limestone and treated a 98-L/min flow. Influent pH was 3.3, acidity was 118 mg/L as CaCO₃, Fe of 10 mg/L, Mn of 8 mg/l, and Al of 9 mg/L. Outflow pH was 4.4, acidity was reduced to 57 mg/L as CaCO₃ (52%), Fe decreased to 2 mg/L (80%), Mn was reduced by 11%, and Al by 25%.

A wetland system consisting of six wetland cells (total area of 2500 m²) and a

sedimentation basin each received a small flow (5 L/min) of AMD with pH of 3.0, acidity of 217 mg/L as CaCO₃, Fe of 27 mg/L, Al of 12 mg/L, and Mn of 2 mg/L (Hellier 1996). At this site in Pennsylvania, the effluent after passing through the wetland was raised to pH 5.1, and the water contained a net acidity of 16 mg/L as CaCO₃, with about 46% Fe removal, and 56% Al removal.

A 1022 m² surface flow wetland was constructed in Kentucky to treat 37 L/min of AMD with a pH of 3.3, acidity of 2280 mg/L as CaCO₃, Fe of 962 mg/L, Mn of 11 mg/L, and Al of 14 mg/L (Karathanasis and Barton 1997). After construction in 1989, metal concentrations in the effluent were reduced during the first six months of treatment; however, the system failed thereafter due to insufficient wetland area and metal overloading. In 1995, a two-phase renovation project began incorporating the use of an ALD, and a series of anaerobic drains that promote vertical flow through limestone beds overlain by organic compost (much like a SAPS). Results to date indicate a pH of 6.4, slightly net alkaline water (15 mg/L as CaCO₃), Fe reduction of 96%, Mn removal of 50%, and Al by 100%.

A large anaerobic wetland located at Douglas, WV treated a 1000-L/min flow effectively for one year (Cliff et al. 1996, Skousen 1995). The influent pH was 3.0, with acidity of about 500 mg/L as CaCO₃, Fe of 30 mg/L, and Al of 40 mg/L. An average net alkalinity of 127 mg/L as CaCO₃ was realized in the effluent water. Four years after installation, the original acidity of 500 mg/L as CaCO₃ is being reduced to between 250 to 300 mg/L as CaCO₃. It has remained at this level of treatment for the period 1994-1995.

5.3 Anoxic Limestone Drains

Anoxic limestone drains (ALDs) are buried cells or trenches of limestone into which anoxic water is introduced. The limestone dissolves in the mine water and adds alkalinity. Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe²⁺ does not precipitate as Fe(OH)₂ at pH <8.0. The effluent pH of ALDs is typically between 6 and 7.5. The sole function of an ALD is to convert net acidic mine water to net alkaline water by adding bicarbonate alkalinity. The removal of metals within an ALD is not intended and has the potential to significantly reduce the permeability of the drain resulting in premature failure.

ALDs were first described by the Tennessee Division of Water Pollution Control (TDWPC) (Turner and McCoy 1990). TVA subsequently observed that AMD seeping through a coal refuse dam was being treated passively by limestone contained in an old haul road buried under the dam. Once the water containing excess alkalinity reached aerobic conditions at the ground surface, the metals oxidized and precipitated while the water remained near pH 6 (Brodie et al. 1990). TVA and TDWPC began building ALDs in 1989. Originally, ALDs were used for pre-treatment of water flowing into constructed wetlands. Brodie (1993) reported that ALDs improved the capability of wetlands to meet effluent limitations without chemical treatment.

Longevity of treatment is a concern for ALDs, especially in terms of water flow through the limestone. If appreciable dissolved Fe^{3+} and Al^{3+} are present, clogging of limestone pores with Al and Fe hydroxides has been observed (Faulkner and Skousen 1994, Watzlaf et al. 1994). For waters with high sulfate (>1,500 mg/L), gypsum (CaSO_4) may also precipitate (Nairn et al. 1991). For an accepted design, Fe^{3+} , dissolved oxygen (DO), or Al^{3+} should not be present in the AMD. The presence of any Fe^{3+} , dissolved oxygen (DO), or Al^{3+} in the mine water may significantly decrease the effective life of the ALD. Selection of the appropriate water and conditions is critical for long term alkalinity generation in an ALD. The maximum alkalinity in effluents from 21 ALDs studied by Hedin et al. (1994b) was 469 mg/L as CaCO_3 , with effluent values commonly between 150 and 300 mg/L as CaCO_3 . The level varies with water chemistry, especially CO_2 pressure, and contact time (Watzlaf and Hedin 1993). They suggested that contact times of 15 hr were optimum. In sizing an ALD, the amount of limestone that will dissolve during the design life must also be taken into account. At the end of the design life of the ALD, there should remain enough limestone to provide for the recommended 15 hrs of contact. Based on experiments with limestones of differing purity, Watzlaf and Hedin (1993) showed that limestones with >82% CaCO_3 differed little from purer limestones in their effectiveness in neutralizing acid.

The elevation of the outflow from the ALD should be slightly above the top of the limestone so that the limestone remains water-saturated at all times in order to avoid access of air into the system. A plastic membrane is commonly placed over the limestone to restrict access of air and aerated water. The effluent from the ALD usually flows into a wetland or pond, sized to oxidize and remove the Fe that will precipitate from the water.

Case Studies:

Faulkner and Skousen (1994) reported both successes and failures among 11 ALDs treating mine water in WV. In all cases, water pH was raised after ALD treatment, but three of the sites had pH values <5.0, indicating that the ALDs were not fully functioning or that the acid concentrations and flow velocities were too high for effective treatment. Acidity of water in these drains, varying from 170 to 2200 mg/L as CaCO₃, decreased 50 to 80%, but Fe and Al concentrations in the outflow also decreased. Ferric iron and Al³⁺ precipitated as hydroxides in the drains. With Fe and Al decreases in outflow water, some coating or clogging of limestone is occurring inside the ALD.

At the Howe Bridge and Morrison ALDs, alkalinity in effluents increased by 128 and 248 mg/L, respectively, over influent water, CO₂ pressures were near 0.1 atm and calcite was at about 10% of saturation (Hedin et al. 1994a). For the past eight years, the effluent from the ALD-wetland system at Morrison has always met effluent criteria (pH 6-9, and Fe <3 mg/L). At Howe Bridge, the ALD-wetland system has removed an average of 70% of the Fe over the past seven years.

At the Jennings Environmental Center in Slippery Rock, PA, an ALD was constructed to document the reduction in permeability due to Al hydroxide precipitation within the drain. The system, which received 21 mg/L Al at a flow rate of 92 L/min, began to have permeability problems within three months and plugged with Al hydroxide after about 6 months (Watzlaf et al. 1994).

The ALD at the Elklick I passive treatment system in Garrett County, Maryland has effectively treated 37 L/min of contaminated mine drainage (Watzlaf, 1998). The ALD has imparted an average of 137 mg/L of alkalinity to the mine water. Over the past 3.5 years, the ALD/oxidation pond/wetland system has lowered iron concentrations from 56 mg/L to <1 mg/L and manganese from 4.8 mg/L to <2 mg/L and has converted net acidic water (54 mg/L of net acidity) to net alkaline water (72 mg/L of net alkalinity).

At the Brandy Camp site in PA, an ALD was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the ALD, the effluent had a pH of 6.0, net alkalinity of 10 mg/L as CaCO₃, Fe of 50 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. Most of the Fe and Mn passed through this system and precipitated in subsequent wetlands, while Al was precipitated inside

the drain. Like wetlands, ALDs may be a solution for treating specific types of AMD or for a finite period after which the system must be replenished or replaced.

Limestone has also been placed in 60-cm corrugated pipe and installed underground, and water is introduced into the pipe. Septic tanks have also been filled with limestone and AMD introduced into the tank. These applications have been used on steep slopes in lieu of buried cells or trenches, and on sites that have poor access and small water quality problems (Faulkner and Skousen 1995).

5.4 Vertical Flow Systems

In vertical flow systems, water flows downward, usually from a pond, through organic matter and usually through limestone before flowing out of the system through a drainage system (Figure 5.1). Terminology is varied and includes APS and SAPS (Successive Alkalinity Producing Systems), and vertical flow wetlands. SAPS were described by Kepler and McCleary (1994) and are now being extensively constructed to treat AMD from coal mining.

Compared with horizontal flow anaerobic wetlands, vertical flow systems greatly increase the interaction of water with organic matter and limestone. In addition, passage through an organic layer removes oxygen and Fe^{3+} , which are limitations for ALDs. In situations where DO or Fe^{3+} concentrations are >1 mg/L, they must be removed from the water before introduction into an anoxic limestone bed. In a typical SAPS, acid water is ponded from 1 to 3 m over 0.1 to 0.3 m of an organic compost, which is underlain by 0.5 to 1 m of limestone. Below the limestone is a series of drainage pipes that convey the water into an aerobic pond where metals are precipitated. The hydraulic head drives ponded water through the anaerobic organic compost, where oxygen is consumed and ferric iron is reduced to ferrous iron. Sulfate reduction and Fe sulfide precipitation can also occur in the compost. After aeration and metal precipitation in a pond or wetland, water retaining net acidity can be passed through additional SAPS.

Data are still being gathered on the ability of SAPS to treat high-Al waters. Kepler and McCleary (1997) describe success with periodic flushing of Al precipitates from drainage pipes. One SAPS cited by them treats AMD containing 41 mg/L Al and has been successfully flushed. However, Brodie (personal communication, 1997) described a SAPS receiving >40 mg/L Al at the Augusta Lake site in Indiana being plugged with Al precipitates

after 20 months despite flushing. Successful SAPS have used mushroom compost, while some other types of organic material have problems with plugging. Eger (1995) found that composted municipal waste and several other types of organic material supported reasonable levels of sulfate reduction. Many possible variations in composition and thickness of organic matter, including the addition of limestone, desirability of promoting sulfate reduction, flow rates through organic matter, time schedule for replacement or addition of new organic matter, and precipitation of siderite in the limestone remain to be investigated.

In vertical flow wetlands, the intent is usually to optimize sulfate reduction in the organic layer by causing water to flow through the organic matter. Limestone may be present as an auxiliary reactant to promote optimum pH. At other sites, water in a horizontal-flow wetland is forced downward by baffles or other means so as to increase interaction with the substrate.

Case Studies:

Kepler and McCleary (1994) reported on initial successes for three SAPS in PA. The Howe Bridge SAPS reduced acidity from 320 mg/L to 93 mg/L as CaCO_3 , and removed 2 mg/L ferric iron. The REM SAPS decreased acidity from 173 to 88 mg/L as CaCO_3 , and exported more ferrous iron than entered. The Schnepf Road SAPS decreased acidity from 84 to 5 mg/L as CaCO_3 , but removed all 19 mg/L ferric iron, with only 1 mg/L ferrous iron exiting the SAPS.

Kepler and McCleary (1997) reported the use of SAPs in OH, PA, and WV. In all cases, Al in AMD precipitated in their systems. Their drainage design incorporates a flushing system called the 'Aluminator.' This allows for the precipitated Al to be flushed from the pipes thereby maintaining hydraulic conductivity through the limestone and pipes. One SAPS, Buckeye, received 3 L/min of very acid water (pH of 4.0, acidity of 1989 mg/L as CaCO_3), Fe of 1005 mg/L, and Al of 41 mg/L. Over a two-year period, the effluent had a pH of 5.9, net acidity concentration of about 1000 mg/L, Fe of 866 mg/L, and <1 mg/L Al. A second site, Greendale, treated a 25-L/min flow, and increased the pH from 2.8 to 6.5, changed the water from a net acid water (925 mg/L as CaCO_3) to a net alkaline water (150 mg/L as CaCO_3), Fe from 40 to 35 mg/L, and Al from 140 to <1 mg/L.

At the Brandy Camp site in PA, a SAPS was employed to treat AMD with a pH of 4.3,

acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the SAPS, the effluent had a pH of 7.1, net alkalinity of 115 mg/L as CaCO₃, Fe of 3 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. The system effectively increased alkalinity, but retained most of the Fe and Al inside the system.

At the Jennings Environmental Education Center near Slippery Rock, PA, a modified SAPS was constructed. This system did not have discrete compost and limestone layers. Mushroom compost was mixed with #9 limestone at the site on about a 1:1 weight ratio. The perforated drainage pipes were placed within an inert gravel layer positioned below the limestone/compost layer. Based on laboratory tests, the pH within the unfortified compost layer dropped to less than 4.5 in <3 years of receiving the mine water (Watzlaf 1997). This reduction of pH was due to the high levels of acidity produced during the hydrolysis of about 20 mg/L of Al within the compost layer. These lower pH conditions significantly lowered sulfate reduction rates. Therefore, the field system fortified the compost by admixing limestone to maintain a pH within the compost that would promote sulfate reduction. For the initial eight months of operation, the SAPS has converted the 65 L/min flow of net acid water (averaging over 250 mg/L of net acidity) to net alkaline water (about 200 mg/L of net alkalinity) (Watzlaf, personal communication).

5.5 Limestone Ponds

Limestone ponds are a new passive treatment idea in which a pond is constructed on the upwelling of an AMD seep or underground water discharge point. Limestone is placed in the bottom of the pond and the water flows upward through the limestone (Faulkner and Skousen 1995). Based on the topography of the area and the geometry of the discharge zone, the water can be from 1 to 3 m deep, containing 0.3 to 1 m of limestone immediately overlying the seep. The pond is sized and designed to retain the water for 1 or 2 days for limestone dissolution, and to keep the seep and limestone under water. Like ALDs, this system is recommended for low DO water containing no Fe³⁺ and Al³⁺. However, the advantage of this system is that the operator can observe whether limestone coating is occurring because the system is not buried. If coating occurs, the limestone in the pond can be periodically disturbed with a backhoe either to uncover the limestone from precipitates or to knock or scrape off the precipitates. If the limestone is exhausted by dissolution and acid neutralization, then more limestone can be added to the pond over the seep.

Case Studies:

Three limestone ponds have been installed by Carbon Industries near Charleston, WV, but no information is available on their treatment.

5.6 Open Limestone Channels

Open limestone channels (OLCs) introduce alkalinity to acid water in open channels or ditches lined with limestone (Ziemkiewicz et al. 1994). Acid water is introduced to the channel and the AMD is treated by limestone dissolution. Past assumptions have held that armored limestone (limestone covered or coated with Fe or Al hydroxides) ceased to dissolve, but experiments show that coated limestone continues to dissolve at about 20% the rates of unarmored limestone (Pearson and McDonnell 1975). Recent work has demonstrated that the rate for armored limestone may be even higher (Ziemkiewicz et al. 1997), but continued dissolution probably depends on pH, thickness of coating, and other variables. Field experiments show considerable treatment by OLC's (Ziemkiewicz et al. 1994), but some question remains on the possible effects of dilution by unrecognized inflows at some of these sites (Watzlaf, personal communication). The length of the channel and the channel gradient, which affects turbulence and the buildup of coatings, are design factors that can be varied for optimum performance. Optimum performance is attained on slopes exceeding 20%, where flow velocities keep precipitates in suspension, and clean precipitates from limestone surfaces. In appropriate situations, OLCs are being implemented for long term treatment. Utilizing OLCs with other passive systems can maximize treatment and metal removal.

Among the questions still to be investigated are the behavior of OLCs in waters of different pH and high heavy metal loads (like metal mine drainage), possible interactions of slope with water chemistry, and the possible importance of limestone purity.

Case Studies:

Ziemkiewicz et al. (1997) found armored limestone in a series of laboratory experiments was 50 to 90% as effective as unarmored limestone in neutralizing acid. Seven OLCs in the field reduced acidity in AMD by 4 to 205 mg/L as CaCO₃, at rates of 0.03 to 19 mg/L per meter of channel length. The highest removal rates were with channels on slopes of 45 to 60% and for AMD with acidity of 500 to 2600 mg/L as CaCO₃. For example, the Eichleberger OLC was 49 m long on a slope of 20%, and received about 378 L/min of 510

mg/L acidity as CaCO₃. After flowing down the channel, the acidity was decreased to 325 mg/L as CaCO₃ (36% decrease). The PA Game Commission OLC was only 11 m in length on a 45% slope, and received 484 L/min of 330 mg/L acidity as CaCO₃. The water acidity at the end of the channel was 125 mg/L as CaCO₃ (62% decrease).

Three OLCs were installed in the Casselman River Restoration project (Ziemkiewicz and Brant 1996). One OLC, 400 m long on a 8% slope, received 60 L/min of pH 2.7 water, 1290 mg/L as CaCO₃ acidity, 622 mg/L Fe, 49 mg/L Mn, and 158 mg/L Al. The effluent pH over a two year period was 2.9, acidity was 884 mg/L as CaCO₃ (31% decrease), Fe was 210 mg/L (66% removal), Mn was 42 mg/L (14% decrease), and Al was 103 mg/L (35% decrease).

At the Brandy Camp site in PA, an OLC was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1997). After passage through the OLC, the effluent had a pH of 4.8, net acidity of 50 mg/L as CaCO₃, Fe of 17 mg/L, Mn of 8 mg/L, and Al of 3 mg/L. The OLC removed 72% of the Fe and about 20% of the Mn and Al from the water.

5.7 Bioremediation

Bioremediation of soil and water involves the use of microorganisms to convert contaminants to less harmful species in order to remediate contaminated sites (Alexander 1993). Microorganisms can aid or accelerate metal oxidation reactions and cause metal hydroxide precipitation. Other organisms can promote metal reduction and aid in the formation and precipitation of metal sulfides. Reduction processes can raise pH, generate alkalinity, and remove metals from AMD solutions. In most cases, bioremediation of AMD has occurred in designed systems like anaerobic wetlands where oxidation and reduction reactions are augmented by special organic substrates and limestone. In a few cases, substrates have been incorporated into spoils to aid in in-situ treatment of water by the use of indigenous microorganisms.

Case Studies:

A mixture of organic materials (sawdust and sewage sludge) was emplaced into a mine spoil backfill to stimulate microbial growth and generate an anoxic environment through sulfate reduction (Rose et al. 1996). The results of the organic matter injection process caused no change in water pH, about a 20% decrease in acidity (1500 to 1160 mg/L as

CaCO₃) and a similar decrease in Fe, Mn, and Al. The results indicate that the process works, but improvements in organic material injection and the establishment of a reliable saturated zone in the backfill are needed for maximum development.

The Pyrolusite process uses selected groups of microorganisms growing on limestone to oxidize Fe and Mn into their insoluble metal oxides (Vail and Riley 1997). On a field site in PA using a limestone bed inoculated with microorganisms, Fe was decreased from 25 mg/L to <1 mg/L, Mn went from about 25 mg/L to <1 mg/L, while pH and alkalinity in the effluent were increased.

5.8 Diversion Wells

The diversion well is a simple device initially developed for treatment of stream acidity caused by acid rain in Norway and Sweden (Arnold 1991). It has been adopted for AMD treatment in the eastern U.S. A typical diversion well consists of a cylinder or vertical tank of metal or concrete, 1.5-1.8 m in diameter and 2-2.5 m in depth, filled with sand-sized limestone. This well may be erected in or beside a stream or may be sunk into the ground beside a stream. A large pipe, 20-30 cm in diameter, enters vertically down the center of the well and ends shortly above the bottom. Water is fed to the pipe from an upstream dam or deep mine portal with a hydraulic head of at least 2.5 m (height of well). The water flows down the pipe, exits the pipe near the bottom of the well, then flows up through the limestone in the well, thereby fluidizing the bed of limestone in the well. The flow rate must be rapid enough to agitate the bed of limestone particles. The acid water dissolves the limestone for alkalinity generation, and metal flocs produced by hydrolysis and neutralization reactions are flushed through the system by water flow out the top of the well. The churning action of the fluidized limestone also aids in limestone dissolution and 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. The limestone must be replenished as it is used, commonly weekly.

Case Studies:

Arnold (1991) used diversion wells for AMD treatment in PA and reports that three wells increased pH from 4.5 to 6.5, with corresponding decreases in acidity. For example, one diversion well located at Lick Creek treats about 1000 L/min of slightly acid water. After passing through the diversion well, the pH changes from 4.5 to 5.9 and the net acid water

(8 mg/L as CaCO₃) changes to net alkaline water (6 mg/L as CaCO₃). Similar results are found for several other sites in PA.

A diversion well has also been constructed in the Casselman River Restoration Project (Ziemkiewicz and Brant 1996). This large diversion well has a retention time of about 15 min for a 360-L/min flow of moderately acid water. The diversion well reduces the acidity from 314 to 264 mg/L as CaCO₃, Fe from 83 to 80 mg/L, and Al from 24 to 20 mg/L.

At the Galt site in WV, a diversion well changes a 20-L/min flow from a pH of 3.1 to 5.5, acidity from 278 to 86 mg/L as CaCO₃, Fe from 15 to 2 mg/L, and Al from 25 to 11 mg/L (Faulkner and Skousen 1995).

5.9 Limestone Sand Treatment

Sand-sized limestone may also be directly dumped into AMD streams at various locations in watersheds. The sand is picked up by the stream flow and redistributed downstream, furnishing neutralization of acid as the stream moves the limestone through the stream bed. The limestone in the stream bed reacts with acid in the stream, causing neutralization. Coating of limestone particles with Fe oxides can occur, but the agitation and scouring of limestone in the stream bed keep fresh surfaces available for reaction.

Case Studies:

The WV Division of Environmental Protection treats 41 sites in the Middle Fork River, including the headwaters of 27 tributaries (Zurbuch 1996). The first year's full treatment was based on four times the annual acid load for non-AMD impacted streams and two times the load for AMD tributaries. During subsequent years, the limestone sand application will be an amount equal to the annual acid load, or about 2,000 tons/yr. About 8,000 tons of limestone were deposited in 1995. The cost was \$25/ton delivered to the treatment sites. Water pH has been maintained above 6.0 for several miles downstream of the treatment sites. The anticipated precipitate coating on limestone was not observed. It is predicted that treating the river with limestone sand will be necessary three times a year to maintain water quality for fish populations.

Questions for Continuing Investigation

As can be inferred from the above discussion, the use of passive systems is relatively new and our understanding is incomplete. The following lists some questions for future investigation.

1. What is the long term success of these passive treatment methods? For wetlands, data for periods greater than 10 years are available, some ALDs have over 5 years of data, but SAPS and OLCs, have only a few years of data available at most. Many systems have only initial data reported during the first or second year of operation. Revisiting these systems to evaluate long term success or failure is needed. What design features or water characteristics are responsible for failure/success?
2. Plugging by precipitation of Al is a major problem for ALDs and a potential problem for SAPS. What are the limits of Al in the influent for successful use of these methods? Can designs be developed to alleviate the Al problem?
3. Water of low pH may react more rapidly with limestone than water of the same acidity but higher pH. This factor also interacts with the amount of Al and ferric iron. How does this affect the appropriateness and design of ALDs, SAPS, and OLCs?
4. How does one design for flow through the organic layer in SAPS? What is the saturated hydraulic conductivity of various types of organic matter? How thick should the organic layer be? How can storm events and other high-flow periods be handled? What head difference across the SAPS is reasonable? How does the required head change with time?
5. What types of organic matter are best for SAPS? How long will the organic layer function as a reducing layer and provide satisfactory hydraulic conductivity?
6. How important is bacterial sulfate reduction in anaerobic wetlands and SAPS? Does it introduce large amounts of alkalinity?
7. How can Mn be removed most effectively in passive systems? Can this be done with well-aerated channels or wetlands in contact with limestone?
8. How do the designs change by the presence of heavy metals, like drainage from metal mines?

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