ADVANCES IN PASSIVE TREATMENT OF COAL MINE DRAINAGE 1998-2009[1]

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Abstract. This report updates the review of passive treatment prepared by the Acid Drainage Technology Initiative (Skousen et al., 1998). Important advances since that report include:

1. Measured and calculated acidities are net acidities that are robust measures of this parameter.
2. Removal rates of Fe at pH>5 can be enhanced by CO_2 degassing, by catalysis by solid Fe phases and by specialized aerators; at pH<5, low pH Fe oxidation by bacteria can be helpful in treating high-Fe acidic discharges.
3. For low-Fe-Al AMD, oxic limestone drains can be effective for treatment, but effectiveness declines over years owing to accumulation of precipitate.
4. For high Fe or Al AMD, limestone beds with timed flushing devices can remove large amounts of metals, though eventual cleaning of the limestone may be needed.
5. Addition of limestone sand or lime to streams can be a cost-effective method of restoring watersheds
6. Vertical flow ponds (VFP's, SAPS) can be sized using a loading factor of 25-35 g of acidity/m^2/d.
7. Manual flushing of VFP's removes only a few percent of accumulated Al precipitate, but timed flushing can be much more effective.
8. Common problems of VFP's include inadequate size, accumulation of Fe precipitate on compost, deterioration owing to Al coatings, and construction defects.
9. Sulfate reduction in passive systems involves a complex community of microbes, with long-term rates dependent on cellulose degrading microbes. Mixtures of fresh organic matter with high-cellulose material appear to provide good performance in lab tests, but more data on longer-term behavior is needed.
10. Sulfate-reducing bioreactors process Al better than older VFP's.
11. Steel slag and chitin hold promise for effective treatment of AMD.
12. A relation for sizing of limestone beds for Mn removal has been developed.
13. Fe precipitate from sludge is being successfully sold for pigment production, and Mn-rich concentrate has been recovered from limestone beds.
14. A revised flow chart for selection of treatment method has been prepared, and the AMDTreat computer program allows easy costing of passive treatment.

Additional key words: acidity, iron, oxic limestone drains, flushing, limestone sand, vertical flow ponds, SAPS, sulfate reduction, sulfate-reducing bioreactors, steel slag, chitin, Mn removal.

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Introduction

In 1998, the Coal Group of the Acid Drainage Technology Initiative (ADTI) released the Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage (Skousen et al., 1998). Chapter 5 of this Handbook described methods for passive treatment of coal mine drainage, as then recognized. Since 1998, passive methods have been extensively applied, and in 2008 the ADTI group decided that an update on passive treatment was appropriate. The author agreed to undertake this update, which has progressed slowly, to generate the current manuscript.

The approach has been to cover all significant advances known to the author, and to compile a bibliography of all relevant papers from the Proceedings of the American Society of Mining and Reclamation (ASMR) for 2005 through 2008. Papers in the journal Mine Water and the Environment were also compiled. In addition, relevant citations in the reference lists of papers in the ASMR Proceedings were compiled. Papers mainly relevant to heavy metal mine discharges have generally not been covered, unless they seemed relevant to coal mine drainage. The significant advances from this bibliography have been incorporated in this review. Comments and suggestions from colleagues also contributed to the discussion to follow.

A general reference covering prevention and remediation of mine drainage is Younger et al. (2002). Reviews of methods for treating mine drainage are provided by Johnson and Hallberg (2005), Skousen et al. (2000) and Watzlaf et al. (2004), and a recent publication summarizes methods from the metal-mine aspect (Gusek and Figueroa, 2009).

The purpose of this review is to summarize and discuss advances in passive treatment of coal mine drainage since 1998. The topics are covered in the order outlined in the abstract.

Acidity

Acidity is a key parameter in evaluating and treating AMD. It represents the quantity of alkaline material that must be dissolved into an AMD in order to neutralize it to a certain pH endpoint, such as 8.3. Acidity is used to design passive treatment systems, so it is important that it be measured correctly and reproducibly.

The acidity method used for AMD is usually a hot peroxide method (American Public Health Assoc., 1998a, b = Standard Methods 1998), in which pH is first decreased to <4 to convert HCO_3^- to dissolved CO_2, then H_2O_2 is added to oxidize Fe^{2+} and Mn^{2+} to higher oxidation states and the solution is heated to drive off CO_2, followed by titration with NaOH to pH 8.3 (APHS, 1998b; U.S. E.P.A., 1979). The equivalents of acid used to decrease pH to 4 are subtracted from the equivalents of base added in titrating to pH 8.3, making the result essentially a net acidity.

Cravotta and Kirby (2004), Kirby and Cravotta (2005a, 2005b) and Hedin (2006) showed that a reliable net acidity can be obtained from the hot peroxide acidity (Standard Methods, 1998), or by calculation from the pH, Fe, Al, Mn and alkalinity concentrations:

$$\text{Acidity (mg/L } CaCO_3) = 50(10^{(3\text{-pH})} + 2C_{Fe}/55.8 + 2C_{Mn}/54.9 + 3C_{Al}/27) - C_{Alk(mg/L\ CaCO3)} \quad (1)$$

where C is the concentration of the subscripted species in mg/L (or mg/L $CaCO_3$ in the case of alkalinity). The use of the coefficient 2 for all Fe is a good approximation because most of the ferric Fe is complexed as $Fe(OH)^{2+}$ in solution. Also, they showed that aged samples that had oxidized and precipitated $Fe(OH)_3$ produced essentially the same measured hot acidity as fresh samples. This result indicates that acidity is a relatively robust measure in terms of storage conditions. However, in order to have a valid acidity by eq. (1), the sample as collected in the field must be either filtered or contain negligible suspended Fe, Al and Mn solids that would otherwise count as acidity. This calculation is included in the toolkit of the computer program AMDTreat (Means et al., 2004).

These results indicate that the previous procedure of calculating net acidity as measured acidity minus measured alkalinity is incorrect, because the hot peroxide acidity is already a net acidity. Cravotta and Kirby (2004) urged labs and others to use the Standard Methods (1998) procedure and to report negative acidities when obtained.

Iron Oxidation and Removal

Iron occurs in two oxidation states in natural waters: Fe^{2+} and Fe^{3+}, and as solid phases in several oxides, hydroxides and hydroxysulfates (Fig. 1). The diagram shows that ferric iron (Fe^{III}) is soluble only at pH less than about 3 and oxidizing conditions (high Eh), in the form of Fe^{3+}, $FeSO_4^+$ and $Fe(OH)_2^+$. At higher pH, it precipitates as some form of ferric hydroxide or related compound. Ferrous iron (Fe^{II}) is soluble as Fe^{2+} under more reducing conditions and up to pH about 8.

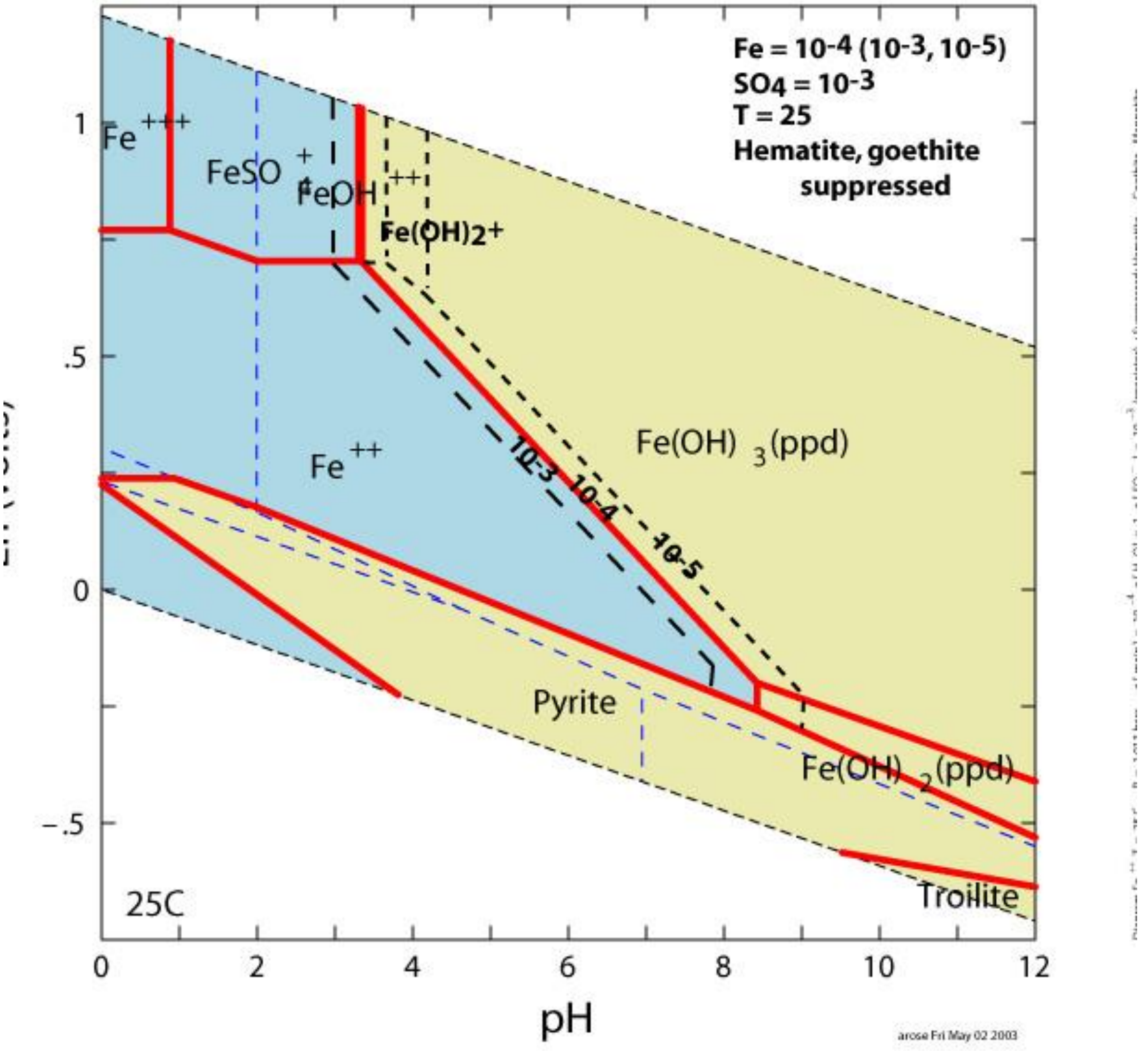

Figure 1. Eh-pH diagram for iron, showing fields of solubility of dissolved species (blue) and solid species (tan). Upper boundary is open air, lower boundary reducing. Conditions: 10^{-4} Fe ~ 6 mg/L, 10^{-3} SO_4 ~ 96 mg/L.

In general, precipitates from AMD between pH 2.8 to 4.5 are found to be schwertmannite (Fe_8O_8 $(OH)_{5.5}(SO_4)_{1.25}$); precipitates at less than 2.8 are jarosite ($(K,Na,H)Fe_3(SO_4)_2(OH)_6$); precipitates between pH 4.5 to 6 are mixtures of schwertmannite and ferrihydrite ($Fe_5O_8H \cdot 4H_2O$); and above 6 are ferrihydrite and goethite (FeOOH) (Bigham et al., 1996).

Sulfate-bearing phases, such as schwertmannite and jarosite, can be considered “acid salts” that can release acidity on exposure to higher pH waters.

For near-neutral waters treated in wetlands, Hedin et al. (1994a) suggested that Fe was removed at a rate of 20 g/m^2/d. However, application of this relation to ponds and other facilities for Fe oxidation and settling has led to discrepancies at some sites. For example, Cravotta (2007) reported Fe removal of only 3.7 g/m^2/d for AMD at pH 6.2 and Fe of 11.3 mg/L flowing through a pond and wetland at the Otto discharge. Kirby et al. (1999) thoroughly reviewed the literature and used data from 6 field sites to generate and test more complex relations (Fig. 2).

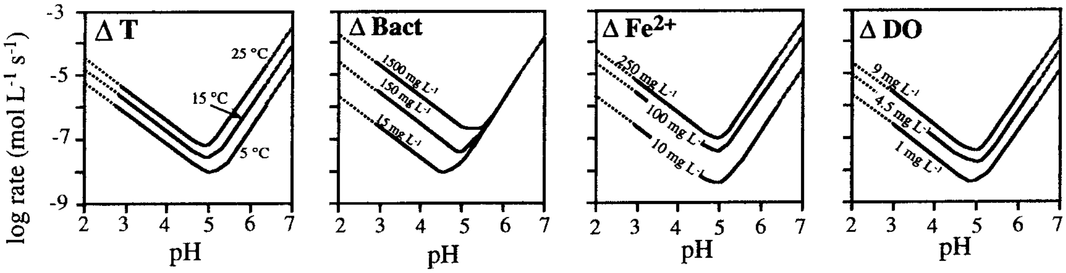

Figure 2. Rate of Fe^{2+} oxidation vs. pH as calculated by Kirby et al. (1999), showing effect of changes in pH, temperature, bacterial abundance, Fe concentration and dissolved O_2.

In most cases, the rate-controlling step in removal of dissolved Fe from solution is its oxidation to Fe^{3+} (Singer and Stumm, 1970). In the pH range from 5 to 6.4, Fe^{2+} oxidizes abiotically at a rate that increases as $1/(H^+)^2$, so that Fe removal is relatively rapid and effective at pH near neutrality.

A key catalyst in Fe^{II} oxidation at near-neutral pH can be adsorption on pre-existing Fe^{III} hydroxides and oxides (Dempsey et al., 2001). Conversely, at pH 2.8 to 5, abiotic Fe oxidation is very slow, but specialized bacteria, such as *Thiobacillus* sp., catalyze oxidation (Kirby et al., 1999). In this range, the rate is inversely proportional to pH:

$$d[Fe^{2+}]/dt = k_{bio}C_{bact}[Fe^{2+}][O_2][H^+] \qquad (2)$$

where C_{bact} is the concentration of bacteria. Removal of Fe in this pH range has been termed “low-pH Fe removal” (Burgos et al., 2008).

Low-pH iron removal occurs naturally at some sites, and may be enhanced to partially treat low-pH waters (Hilton, 2005; Burgos et al., 2008). The rate of Fe oxidation and removal is dependent on bacterial metabolism and on the surface area for bacterial attachment, and probably other variables. At a few sites, almost complete removal of Fe is observed. The precipitation of

Fe is accompanied by decrease in pH. The H^+ in the resulting water is more readily treated than high Fe contents.

In ponds, several effects may complicate Fe oxidation. Kirby et al (1999) found dissolved O_2 concentrations only 10 to 30% of saturation at the Howe Bridge pond, with concentrations decreasing downward from the surface in this 1 m deep pond. Ponds may become stratified owing to temperature gradients (warm water on top of cold water) or higher density AMD underlying more dilute solution. A factor that has not been investigated is ice cover as an inhibiting effect of oxygen transfer on oxidation-settling ponds in winter time.

Sapsford et al. (2007) describe experiments with a tank in which net alkaline water with about 7 mg/L Fe overlies a bed of precipitate through which the water flows down into an underdrain. Iron precipitation from the AMD is accelerated by the catalytic effect of the pre-existing Fe hydroxides. The tank and associated wetlands have a very small footprint compared to conventional wetlands.

Another major factor in Fe removal is the pH-buffering effect of dissolved CO_2 in effluent of underground mines. This dissolved CO_2 ($=H_2CO_3$) represents acidity and buffers the pH in the vicinity of 6.4. If it can be degassed, then the pH increases, the acidity decreases, the concentration of total CO_2 and HCO_3^- decreases, and the oxidation rate of Fe^{2+} is greatly increased:

$$CO_2(aq) + H_2O = H_2CO_3(aq) = CO_2(g) + H_2O = HCO_3^- + H^+ \qquad (3)$$

The potential benefits of degassing and aeration for net alkaline discharges (and potentially for net alkaline effluent of VFP's and ALD's treating net acidic water) have been demonstrated by Kirby et al. (2008). Aeration experiments at two net alkaline discharges with pH ~ 5.7 and Fe ~ 16 mg/L produced increases in pH to greater than 7, and decreases in Fe to <0.05 mg/L by the combined effects of degassing CO_2, increase of dissolved O_2 to saturation, and oxidation and precipitation of Fe.

For some waters, relatively complete degassing of CO_2 is crucial. Lab tests incorporating aeration of water from the Otto discharge were able to degas CO_2 to near atmospheric levels and added dissolved O_2 (Cravotta, 2007). The dissolved Fe oxidized and precipitated to negligible values. However, a field treatment system consisting of an oxidation pond followed by 2 wetlands and an oxic limestone drain removed only about 35% of the Fe. The CO_2 was only partly degassed, leaving the pH <7, and a much slower Fe oxidation rate than the lab experiment. The Fe removal rate in the combined pond and wetlands was only 3.7 $g/m^2/d$, with the wetlands being more effective than the pond.

Specialized equipment for aeration and oxidation includes the Maelstrom oxidizer, which utilizes a complex of flow diverters and air injectors to effectively introduce O_2 and degas CO_2 (Budeit, 2007. A spray reactor nozzle that accomplishes rapid oxidation of Fe^{II} is described by Klein and Neufeld (2005).

Jarvis and Younger (2001) and Sapsford et al. (2006) describe trickling filters termed SCOOFI reactors (Surface Catalyzed Oxidation of Ferrous Iron). In these reactors, the water trickles down over a support with a large surface area. Ferric solids precipitate on the support and catalyze oxidation of ferrous iron, leading to rapid precipitation of additional ferric solids.

Oxic Limestone Drains (OLD), Anoxic Limestone Drains (ALD) and Flushed Limestone Beds

Contact of limestone with AMD containing appreciable dissolved Fe or Al results in precipitation of Fe and Al as a coating on the limestone surface and as pore-filling accumulations. As a result, the neutralization rate has been expected to decrease because of the coating. However, tests by Cravotta et al. (2004) show that this is not necessarily true.

Anoxic Limestone Drains

Based on experiments in cubitainers and on full scale limestone drains, Cravotta and Watzlaf (2002) and Cravotta (2003) derived rates of neutralization for limestone drains, and recommended a method for sizing drains. Mukhopadhyay et al. (2007) extended this work. Huminicki and Rimstidt (2008) investigated calcite dissolution rates and precipitation of gypsum (CaSO4·2H2O) on limestone surfaces exposed to SO4-rich solutions.

In general, anoxic limestone drains are very successful in treating waters with low Al and ferric Fe. ALD's are regarded as a reliable, predictable technology by BAMR (2009).

An anoxic limestone drain constructed within a mine shaft in Oklahoma generated >400 mg/L alkalinity (LaBar et al., 2008). This type of application within an underground mine appears applicable elsewhere for AMD with low Al and ferric Fe..

Oxic Limestone Drains

Cravotta and co-workers have experimented with oxic limestone drains and beds for treatment of several large flows of AMD with low contents of Fe and Al (Cravotta and Trahan, 1999; Cravotta et al., 2004; Cravotta and Ward, 2008; Cravotta, 2007, 2008; Cravotta et al., 2008). In these oxic systems, aerated AMD flows through a bed of relatively coarse limestone to neutralize the relatively low acidity. Fe and Al precipitate as loose flocs and coatings during this process. Table 1 summarizes the performance of these systems.

Table 1	Characteristics of oxic drains and beds					
Site	Flow	Fe	Al	Acid.	pH	Result
	L/s	mg/L	mg/L	mg/L		
Orchard	18	1	1	35	3.5	Without flushing, plugged in 7 years. Reconstructed in 2007 as upflow bed with flush pipes
Hegins	526	0.2	5	47	3.5	Partial treatment; decline over 4 years, CO_2 loss. Modified in 2005 with addition of compost cover
Buck Mtn.	534	13	0.6	28	4.5	OK for 11 years. Additional limestone added in 2001 and 2005 to replenish 25 tonnes/year dissolved
Bell	870	2.2	1.4	20	3.9	Partial treatment by Downflow beds, only1 yr of data. In 2008, limestone was reworked to improve flow and high-Ca limestone was added
Reevesdale	15	2.5	1	9	4.7	Deteriorated within 9 months because of inflow blockage. In 2008, inflow excavated to restore treatment.
Otto	92	9	<0.2	-10	6.5	Plugged in 1 month, lack of CO_2 degassing in preceding wetland led to excessive loading of Fe

In general, lab experiments and field units studied by Cravotta and coworkers indicate that much of the Fe and Al precipitate was either washed out of the drains or had limited effect on inhibiting limestone dissolution, so that good neutralization and metal removal continued for periods of many years at some systems. However, if the flow was channelized within the bed or had higher Fe contents, the limestone beds could become plugged. Also, retention of CO_2 was important to develop adequate alkalinity in the acidic inflows, but thorough degassing to lose CO_2 was crucial in the net alkaline case.

Lab experiments on neutralization of Fe solutions by calcite, using influent of pH 4 to 4.8 and 100 mg/L Fe show the development of layered coatings of Fe phases on calcite (Santomartino and Webb, 2007). At the conclusion of experiments after 750 hr, a void space of 60 µm separated calcite from an inner porous Fe coating 60 µm thick, overlain by a 20 µm thick layer of denser goethite and lepidocrocite. The calcite continued to react despite this coating, though at a decreasing rate. Because of the void space, the coating was easily removed from the limestone by mild abrasion.

Flushed Limestone Beds

Extensive experiments with flushing and cleaning of limestone beds are reported by Hedin Environmental (2008). Net acidic AMD with high Al but lower Fe from two sites was investigated with flushable limestone beds in roll-off trash containers and in a large tank. The beds were flushed either by a siphon system when full or by a timed flushing system (Agridrain Smart Drainage, Fig. 3). The timed flushing system allowed the AMD to flow through the full bed for several days before flushing, and was more effective than the siphon flushing system. A rapid flow and complete flush of the bed were more effective than the partial flushes usually conducted manually. Although not all Fe and Al were removed, the outflow was more easily treated by other methods.

At suitable loadings of acidity and Al, the flushed limestone maintained treatment for up to 2 years, with flushing of about 50% of the Al-Fe-Mn precipitate in either normal outflow or flushing water. Net alkaline water was generated for many months at acidity loadings of 90 to 190 $g/m^2/d$, from influent AMD of pH 3, acidity 225 mg/L, Al 27 mg/L and Fe 8 mg/L. Flushing on a timed schedule was an improvement over flushing by a siphon-type system, because in the latter case, much of the AMD had been in contact with the limestone for only a short time, and had not had time to react.

Methods for cleaning the coating and sludge from the bed were developed using agitation with an excavator in a water-filled depression in the bed, and in separate containers (Hedin Environmental, 2008). The coating on limestone was easily scaled off by agitation, and loose sludge was washed off. The cleaned limestone produced treatment rates similar to fresh limestone. Under these conditions, fine limestone (2 cm size) performed better than coarser limestone.

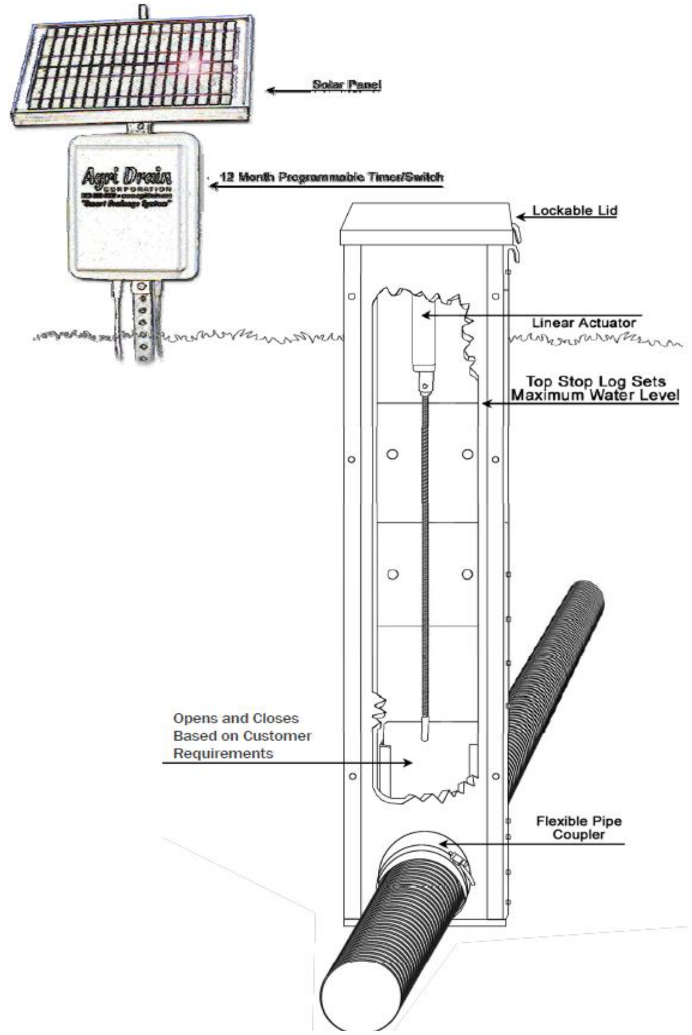

Figure 3. Diagram of Agridrain Smart Drainage Unit

In 2007, a limestone upflow pond about 140 x 18 m area was constructed at Strattanville, PA, with 5 ft of aggregate and timed flushing. This system treats AMD with pH 5, acidity 400 mg/L, Fe 220 mg/L, Al 7 mg/L at 400 to 600 L/min. Effluent recently averages pH 5.9, acidity 260 mg/L, Fe 133 mg/L and Al 0.2 mg/L, a considerable improvement. The system flushes 3 hours per day, controlled by a Smart Drainage System. Effluent flows to a settling pond and then to a large sulfate-reducing bioreactor for further treatment.

The Keystone system in SW Pennsylvania has a large limestone upflow pond (~61 x 23 m) built in late 2004, treating influent with typically 150 mg/L Fe at pH 3.3, Al 9 mg/L and acidity 140 mg/L at a flow rate of about 190 L/min (Helfrich, 2009). During the first two years, the effluent of the pond was mostly net alkaline with pH 6 to 7, <30 mg/L Fe and < 0.5 mg/L Al. However, the limestone clogged several times, and was replaced with coarser limestone in 2007. Recent data indicate effluent acidities of 30 to 50 mg/L and Fe < 20 mg/L.

These examples indicate that strongly flushed limestone beds have the potential to treat extremely metal-rich waters to the point that other methods can handle them. After several years, the flushed limestone beds may require reworking to remove the Fe or Al coatings, but this can be accomplished relatively inexpensively.

Other Limestone Bed Methods

Another method, using fine limestone coated onto wood chips, was studied the lab by Rotting et al. (2008a). Natural AMD with pH 2.8, Fe 250 mg/L, Al 106 mg/L and acidity 1727 mg/L was flowed through columns packed with the limestone-coated wood chips. The outflow pH was 6 to 7 with alkalinity 230 to 300 mg/L. Plugging was not a problem. A pilot field test treated AMD with pH 3.3, acidity 1400 to 1650 mg/L, Fe 317 mg/L and Al 74 mg/L (Rotting et al, 2008b). The system generated effluent with pH 6.2 and alkalinity 180 mg/L, but clogged after about 4 months because of an Al hardpan just below the surface. The authors suggest that with a lower Al loading in the range 5 to 10 $g/m^2/d$ the system could avoid plugging problems.

Simple limestone beds have been used to add alkalinity to relatively clean water which is then mixed with AMD. Thorne and Pitzer (2003) describe two sites that successfully used such beds to add alkalinity and bring back fish populations.

Other workers have used limestone beds on the outflow of other passive systems to clean up minor Fe and Al and to remove Mn (Hilton et al., 2003). As an alternative to limestone, Bernier (2005) has suggested serpentinite as a relatively alkaline material.

Limestone Sand and Limestone Dosing

In West Virginia, a program of annual dumping of limestone sand has been conducted on about 300 miles of streams affected by acid precipitation, with good results in restoring fisheries (Brown, 2005). After an addition of twice the acidity load in the first year, the sand is added annually in amounts approximating the annual acidity load. The pH of the Middle Fork at its mouth improved from 4.9 to 6.8, with conversion from net acidic to net alkaline. A stream length of 119 miles was restored to trout fishery by the limestone sand additions. The technology is more cost efficient than passive treatment of AMD at source discharges.

In Maryland, continuous addition of limestone sand or hydrated lime from a silo through an automatic feeder (doser) has shown good results (Mills, 2009). Dosers on severely contaminated streams have led to fish recovery in the Potomac River and several tributaries contaminated by severe AMD discharges. The stream immediately below the doser is impacted by Fe and Ca sludge, but farther downstream, the stream is greatly improved. Dosers have been installed on several streams and discharges in Pennsylvania.

Vertical Flow Ponds (VFP's, SAPS, RAPS, Vertical Flow Wetlands)

The VFP technology has been widely used to treat net acidic AMD. It was initially described by Kepler and McCleary (1994) as Successive Alkalinity Producing System (SAPS), and has also been termed Reducing and Alkalinity Producing System (RAPS, Watzlaf et al., 2000), and Vertical Flow Wetland (VFW), but the author prefers Vertical Flow Pond (VFP) which will be used in this review. A typical system consists of a pond, with a layer of organic matter underlying the water. The organic matter in turn is underlain by a limestone bed in which perforated underdrain pipes are embedded. AMD flows into the pond and down through the organic matter, where dissolved oxygen is consumed, ferric iron reduced to ferrous, and some SO_4 reduced to sulfide with generation of alkalinity and precipitation of FeS. The water then flows down into the limestone, providing further neutralization and alkalinity, and out through the underdrain into a pond or wetland where the dissolved ferrous Fe is oxidized and precipitated with the dissolved alkalinity.

A modified design has been developed by Jarvis and England (2002). In this system, the AMD flows down through organic matter and then laterally through pipes to an upflow limestone bed. This design allows for more convenient addition of organic matter and limestone.

Sizing of VFP's

Initially, these systems were generally sized to allow 16 to 24 hours of retention time in the limestone layer, as recommended by Hedin et al. (1994b) for anoxic limestone drains. Watzlaf et al. (2000) provided data on 6 VFP's showing acidity removal rates of 20 to 62 $g/m^2/d$, where acidity is measured as $CaCO_3$. Data on Ca increases and SO_4 decreases indicated that limestone dissolution dominated the neutralization process.

Case studies of about 30 systems showed that few systems exceeded a removal rate of about 40 g of acidity ($CaCO_3$) per meter^2 of water surface per day (g/m^2/d), with lower rates typical for units treating the effluent of an initial system (Rose and Dietz, 2002). Later evaluation with more reliable acidity treatment indicated that 35 g/m^2/d is a more accurate limit (Rose, 2004; Rose, 2006). Rates for newly constructed systems can be higher in the first 6 months to a year, but typically decrease to the rates described above. If fine limestone is added to the organic layer, rates can be somewhat higher.

Typically, 0.3 m or more of organic matter is placed in the pond, underlain by enough limestone to neutralize 20-25 years of acidity, usually at least 0.6 m of limestone. The limestone should be high calcium (>85% $CaCO_3$). Early ponds used limestone of about 2.5 cm size to maximize reaction surface, but more recently, well graded 5 to 8 cm sizes have been used to minimize plugging. Also, 10 to 25% of fine limestone has commonly been mixed with the organic matter to help keep pH in this layer at more favorable values for sulfate reducers, and to accomplish neutralization.

Modeling of chemical reactions in VFP's showed that the areal removal limit (35 g/m^2/d) depends strongly on the amount of dissolved carbonate species generated in the AMD as it passes through the organic matter, and on the amount of Al and Fe that is precipitated within the organic and limestone layers to generate H^+ and dissolve $CaCO_3$ to provide CO_2 species (Rose, 2007). High concentrations of dissolved CO_2 when the water reaches the limestone lead to higher amounts of bicarbonate alkalinity in the effluent. This alkalinity is then available to neutralize the H^+ generated by precipitation of Fe oxyhydroxides on exposure to air in the oxidation-settling pond (Eq. 3). In particular, the organic layer should be thick enough and effective enough to reduce appreciable amounts of SO_4 (which releases alkalinity) in order to reach optimum levels of acidity removal.

Investigations of Processes in VFP's

A number of studies have examined processes within bioreactors and VFP's. Thomas and Romanek (2002a,b) conducted lab tests of highly acid ferric-rich AMD treated in columns filled with a mixture of stable waste containing wood shavings, plus minor spent brewing grains and cricket manure mixed with 25% fine limestone. This mixture was termed a limestone-buffered organic substrate (LBOS). The influent AMD typically had pH 2.4, 142 mg/L Fe, 84 mg/L Al and 1300 mg/L acidity. Effluent was circum-neutral, with removal of 90% of the Fe and 100% of Al and acidity. Flow rates of 15-28 ml/min through the 92 cm diam. columns generated acidity removal averaging 58 $g/m^2/d$.

Examination of the columns after 2 years showed several zones of progressive reaction of the AMD within the column. From the top, these were 1) an orange layer of organic matter with Fe oxyhydroxide precipitation, 2) a lighter colored layer of Al hydroxysulfate accumulation with some gypsum, 3) a dark zone of Fe sulfide precipitation, and 4) unreacted substrate. Limestone was dissolved from layer 1 and partly dissolved from layer 2. The columns did not plug, though some concern was expressed about potential formation of a hardpan zone in layer 2. Analysis of pore water from within the columns indicated the advance of “reaction fronts” downward through the columns. In the lower part of layer 1, ferric Fe precipitated as a result of pH increase by dissolution of limestone. In layer 2, Al precipitated owing to further increase in pH from limestone dissolution. In layer 3, sulfate reduction led to precipitation of ferrous Fe as Fe sulfides.

AMD with elevated Al concentrations (30 to 237 mg/L) was tested in bench-scale bioreactors by Gusek and Wildeman (2002). The bioreactors were filled with various mixtures of wood chips, sawdust, manure, mushroom compost, hay and limestone. The reactors removed Al effectively and the reactors did not plug. No specific Al phase was detected. The authors inferred that removal might be as Al silicates or hydroxysulfates.

At several sites, Rose et al. (2004, 2007) found that the limestone immediately beneath the compost was coated by an amorphous Al phase accompanied in places by gypsum ($CaSO_4 \cdot 2H_2O$), even though the water in the limestone was undersaturated with gypsum. The gypsum was attributed to formation in a Ca-rich diffusion zone adjacent to the limestone. The gypsum is inferred to have slowed neutralization reactions. This process appears to occur only where dissolved SO_4 exceeds about 2000 mg/L.

Flushing of VFP’s

Accumulation of Al precipitates in limestone beds and coating of limestone are recognized as problems for Al-bearing AMD. Other precipitates, such as Fe oxyhydroxides and sulfides, may also be problems. Kepler and McCleary (1997) proposed flushing VFP’s to remove Al from the limestone bed. Kepler and McCleary (1997) and others found that flushing improved the effectiveness of VFP's and extended their useful lifetime.

Four main designs of flushing facilities have been used. The simplest is a large manually operated inline valve in a large pipe connected to the perforated pipe underdrain system and its outlet manifold. Another common method is the use of an irrigation control box (such as Agridrain Inline Water Control Structure). This consists of a vertically elongated box with inflow and outflow pipes near the bottom, separated by stop-logs running up the middle of the box. By adding or removing stop-logs, the water level and flow rate can be adjusted to flush the system.

Vinci and Schmidt (2001) proposed use of automatic flushing siphons to increase flushing frequency from manual flushing, typically on a monthly schedule. These systems trigger when the pond fills to its maximum level, and flush to a lower level. Such flushing siphons have been successfully used at several sites.

A more recent flushing technology is the Agridrain Smart Drainage system (Fig. 3). This system operates a valve that is programmable to flush at certain intervals, times or water levels, using a solar panel for power, as described above. This technology has recently been applied to VFP's.

Watzlaf et al. (2002) evaluated the effectiveness of manual flushing at four VFP's and found that less than 5% of the accumulated Al precipitate was flushed during a flushing event. This result, confirmed by others, plus the decreasing effectiveness of several flushed VFP's with appreciable influent Al loads, suggests that manual flushing is not a complete answer to treatment of Al-bearing AMD over time. Watzlaf et al. (2002) suggest that the Al accumulation may be in a band at the top of the limestone bed, as observed at some sites, and that flushing may not be dislodging Al precipitate in critical locations.

In an attempt to improve flushing, more elaborate designs of underdrain systems have been devised. Weaver et al. (2004) evaluated processes removing precipitate during flushing, such as flow velocity, and provided design criteria for double-layer flushing-underdrain systems that provide maximum flow velocity. The upper layer of pipes is near the top of the limestone layer where Al is presumed to accumulate. A pilot experiment using an automatic flushing siphon flushed about 80% of the Al precipitate from a limestone bed, in contrast to the <5% found for manual flushing at monthly or similar intervals. Danehy et al. (2002) describe systems with 2 layers of underdrain pipes in the limestone bed, divided into as many as 8 subsystems capable of being flushed separately.

Case Studies of VFP's

Case studies have been conducted of a number of VFP's. Demchak et al. (2001) sampled influent and effluent at 4 VFP's monthly for a year. Performance was highly variable among the 4 sites, which had functioned for 2 to 7 years prior to study. The McKinley site, with the lowest influent acidity (57 mg/L) and metals (5 mg/L Fe, 3 mg/L Al) generated net alkaline water. Filson 1 removed acidity at a high rate (51 $g/m^2/d$) but suffered from low permeability of the compost, possibly due to compaction by equipment. It failed by overflowing a year or so later. Howe Bridge, receiving influent with very high Fe of 172 mg/L but no Al, removed major amounts of Fe but largely plugged after about 8 years of operation due to about 9 inches of Fe precipitate on top of the compost. The Sommerville site received high Al (42 mg/L Al) and had problems with short-circuiting owing to thin compost over part of the limestone bed. It plugged with Al after a couple of years. Sampling of water chemistry at a series of depths down through the compost at the 4 sites indicated that for these sites, about 50 cm of compost was desirable to ensure reducing conditions in water entering the limestone.

Jage et al. (2000, 2001) monitored 8 VFP's for 24 months or longer. All systems removed acidity but at most the removal was incomplete. The amount of acidity removed was proportional to the log of retention time in the limestone layer. They also detected strong seasonal variations in the acidity removal rate and in SO_4 removal.

At the Pot Ridge site, influent AMD contained acidity of 500 to 1000 mg/L, Fe of 160 to 230 mg/L, Al of 21 to 70 mg/L at pH 3 to 3.5 and flow of 60 to 120 L/min (Rose et al., 2001). At the TEST system, most of the acidity and metals were still being removed after 10 years of operation, but the effectiveness was declining. At the C system with higher Fe, the initial VFP was largely plugged with Fe precipitate on top of the compost after 8 years. Similar plugging problems occurred at the A system. The systems removed acidity at rates of 35 to 50 $g/m^2/d$. During summer and fall, the TEST system removed sulfate, but in winter it released it, probably because the compost was not able to maintain reducing conditions in the 1 foot thickness of compost.

Over 5 years, the Tangascootack #1 VFP was never able to satisfactorily treat AMD with acidity 235 mg/L, pH 4, Fe 3.7 mg/L, Al 24 mg/L and Mn 68 mg/L (Rose et al., 2004). The system removed acidity at 45 to 60 g/m^2/d, indicating that incomplete treatment resulted mainly from inadequate size of the system. Excavation of the system showed that limestone for several inches beneath the compost was coated with Al and gypsum, as noted above, and that compost was very thin (3 in.) in some sections.

Rose (2003, 2004b) compiled information on performance and problems at VFP's, based mainly on "autopsies" at several sites plus observations at other localities. Major problems were identified as follows:

1. The VFP was not large enough to treat the influent acidity load, using the acidity removal criterion of 35 g/m^2/d.
2. In high-Fe systems, Fe precipitate accumulated by low-pH Fe precipitation on top of the compost and eventually limited flow down through the compost and limestone, leading to overflow.
3. Al precipitate accumulated in the limestone layer and coated the limestone fragments, leading to reduced rates of reaction with limestone and possibly eventual plugging.
4. Short circuiting through the compost layer owing to thin compost, and penetrations along cleanouts and inflow riprap led to incomplete treatment.
5. Possible plugging of compost by FeS precipitate.
6. Plugging of the outflow pipe by cattail roots.
7. Inadequate vertical relief .

For sites with limited relief near the discharge, Behum and Kim (2004) suggest piping the flow lower down the drainage. Although problems can occur with plugging of piping, this procedure may be useful at some sites with limited space. Plugging problems can be minimized by designing the intake structure to prevent contact of the AMD with air.

Another helpful technique is the mixing of alkaline water with the AMD. The alkaline water can be obtained from naturally alkaline sources (Behum et al., 2008) or by limestone or slag beds, as discussed later in this review.

Evaluation of VFP Performance and Cost Effectiveness

As indicated above, many VFP's have only incompletely treated their discharge or have plugged. In view of this result, Bureau of Abandoned Mine Reclamation (2009) considered that VFP's are not a reliable technology. Their "Risk Analysis" table deducts significant points for discharges with Fe+Al > 25-50 mg/L, or flow exceeding 100 gal/min. Others, including the author, consider this conclusion oversimplified, largely arising from inclusion in their database of older sites with inadequate size and with design flaws of the type listed above. An evaluation of performance is summarized on the following paragraphs.

Several compilations of VFP performance have been published. Rose and Dietz (2002) and Rose (2004a, 2006) followed more than 30 VFP's for periods of 5 to 13 years. Of 40 sites reported in 2006, about half were performing entirely satisfactorily. Most of the remainder were treating at a moderate level, but not up to original expectations. Six sites had essentially ceased to treat. Problems were those listed above. Regarding plugging by Al, longevity of treatment at several VFP's suggested that these systems could handle water with influent Al up to about 20 mg/L for many years. At several sites, the inadequate size of the VFP was due to inadequate pre-construction flow and chemical data.

Performance and cost/benefit comparisons have been presented by Ziemkiewicz et al. (2002, 2003a, b) for 137 passive systems of various types. Of 19 VFP's, 16 removed acidity. Costs of treatment systems were compared with active treatment by NaOH, taken as $500/ton of acidity removed, counting only the cost of the NaOH, but not the costs of ponds, sludge handling and other routine maintenance. The systems were assumed to have a life of 20 years. Nine systems had costs lower than the NaOH cost, and several more were less than $1000/ton, a cost that more fully represents caustic treatment (see below).

In a similar study, Skousen and Ziemkiewicz (2005) evaluated 116 sites, of which 16 were VFP's. Ten of the VFP's generated net alkaline effluent, and 3 more had only slightly acid output. All removed major proportions of the influent acidity except for three systems that do not appear to require VFP design because they received net alkaline influent or had influent pH exceeding 6. Costs of acidity removal at about half were less than $500/T of acidity removed, and 11 were less than $1000/ton. Two of the 5 higher-cost systems were those with net alkaline influent or pH exceeding 6.

Rose (2006) also compared systems in cost of acidity removal. Costs were estimated with the AMDTreat program, and compared with a cost of $1000/ton by NaOH treatment including construction of ponds, chemicals and labor, but not sludge disposal, as calculated by AMDTreat (Means et al., 2004). At a few sites, a cost of renovation was included. At 19 of 22 systems, cost of acidity removal was less than $1000/ton, assuming 20-year life of the system. Of the 3 systems with high costs, Somerville had essentially failed because of Al plugging, and Hortert was treating water with mainly Mn which is not removed in VFP's. At the third site, data is very incomplete.

Ji et al. (2008) evaluated 29 passive treatment systems in South Korea, of which 19 revealed problems. Twenty systems were vertical flow ponds (SAPS). Problems included overflow owing to excess inflow or accumulation of Fe on the organic layer, leakages, and clogged and broken pipes. Most systems removed Fe, Al and acidity at efficiencies greater than 90%.

Based on this data, properly designed and constructed VFP systems usually are a competitive method of treating AMD but may require maintenance and rehabilitation during their life. At high Fe discharges (>50 mg/L), special methods may be needed, such as low-pH Fe removal ahead of the VFP or mixing with alkaline water. Use of organic layers with added fine admixed limestone is recommended, especially for high Al systems, along with advanced flushing technology.

Organic Materials

Compost and many other types of organic material play a prominent part in many passive treatment systems for AMD. Organic materials are the main components in Sulfate-Reducing Bioreactors, and form the upper layer in typical Vertical Flow Ponds (SAPS). Organic materials are added in anaerobic wetlands. The major function of these materials is to act as a reducing agent, but they also generate alkalinity and have appreciable adsorbent properties for contaminants. In treating AMD from coal mines, the organic materials function to reduce Fe^{3+} to Fe^{2+} and to furnish organic reactants for sulfate-reducing bacteria (SRB). The sulfate reduction reaction consumes H^+:

$$SO_4^{2+} + 2CH_2O + 2H^+ = H_2S + 2CO_2 + 2H_2O \qquad (4)$$

where CH_2O represents a typical organic matter. In AMD from metallic mining sites, the H_2S generated by SRB is very effective in precipitating many heavy metals, such as Pb, Zn and Cu.

Because of the attractive potential of SRB's to remove metals, much research has been conducted in recent years on sulfate reduction by various kinds of organic matter. The goal has been to evaluate various organic materials, environments and systems for efficient AMD treatment. Recent reviews of this research are by Neculita et al. (2007) and Place et al. (2006). An updated table of experiments on organic materials is available in Rose (2009).

It is now generally recognized that microbial species in organic layers occur as several sequential bacterial facies that are dependent on redox state (Chapelle, 1993; Chapelle et al., 1995, Lovley et al., 1994). For oxygenated waters flowing or diffusing into an organic environment, the initial set of microbes acquire energy for their metabolism by reacting dissolved oxygen with organic matter, until dissolved oxygen is depleted. If nitrate is available, another set of bacteria use the organic matter to reduce it to ammonia. If Fe^{3+} is available, it is next reduced to Fe^{2+}. On exhaustion of Fe^{3+}, the sulfate reducers utilize simple organic compounds to metabolize the SO_4^{2-} to S^{2-}. During and after consumption of sulfate, fermenting and methanogenic microbial species can obtain metabolic energy from the organic matter, and break down the complex organic compounds to simple compounds usable by sulfate reducers.

Research clearly indicates that SRB require relatively simple organic compounds, such as lactate or ethanol, for their metabolism. The cellulose that makes up a large proportion of most natural organic matter is not directly metabolizable by SRB. They are therefore dependent on other microbes to break down cellulose and ferment it to simple compounds. In typical AMD treatment systems using organic matter, the SRB are a trace to minor component of the bacterial population (Logan et al., 2005; Hiibel et al., 2008). Most of the bacterial population is degrading cellulose and converting complex organics to simple organics that can be used by the SRB (Fig. 4). After initial consumption of any simple organic compounds, the rate of sulfate reduction is commonly dependent on the rate of cellulose breakdown by these other microbes.

Tests using organic matter amended by glucose show greater sulfate reduction rates than un-amended organic matter or those amended with lactate or acetate (Buccambuso et al., 2007). This result suggests that fermenting bacteria, which can use glucose, is the key for sulfate reduction, and that the microbial community is carbon- limited. Methanogens were relatively inactive in these experiments, indicating that sulfate- reducers can out-compete methanogens.

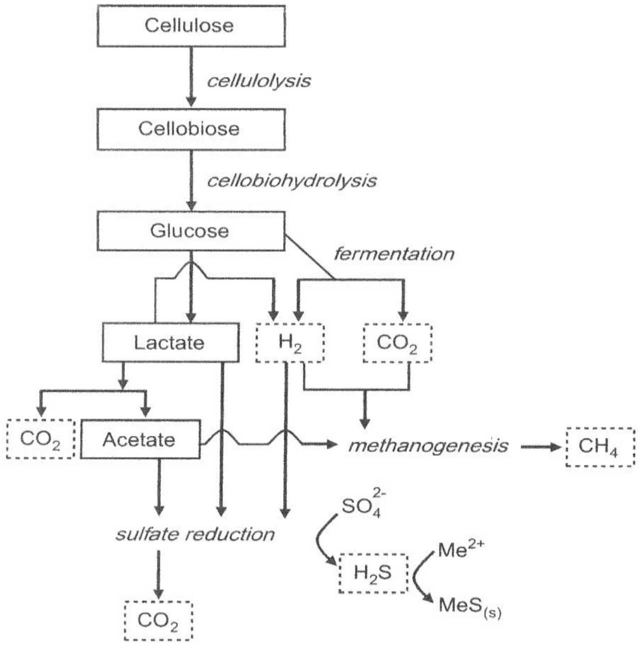

Figure 4. Sequence of microbial processes to degrade cellulose into compounds metabolizable by sulfate reducers (Logan et al., 2005)

A wide range of organic materials have been tested for effectiveness of sulfate reduction. The chemical components in these organic materials can be classified as 1) easily available substances (soluble sugars, starch, amino acids, some proteins), 2) cellulose and hemicellulose and 3) lignin (Gibert et al., 2004). The first group are utilized relatively easily and rapidly by SRB's and their associated microbes and are commonly depleted during the first months of AMD treatment in an organic bed (Place et al., 2006). Cellulose is degraded slowly to simpler organic compounds by fermenting bacteria and other cellulose degraders. The rate of cellulose breakdown by these bacteria probably determines the longer-term rate of sulfate reduction. Lignin is degraded slowly if at all.

Some researchers have found that composted materials perform less well than "fresh" organic matter, but in Pennsylvania, spent mushroom compost works well in most cases. Probably the extent to which simple organic compounds have been consumed is a major determinant in the effect of composting. Also, compost may contain a well developed community of cellulose-degrading bacteria.

Many types of organic matter have been tested as sulfate-reducing media by many investigators. As concluded by Neculita et al. (2007), no clear answer is evident on the best material to use. In part, the uncertainty may derive from the varied length of the testing, which in many cases extended only a few weeks, so that they reflected only the readily available organic compounds. Parameters such as % organic C, C/N, and easily available organics may be helpful in rejecting some materials, but do not provide a final guide. Several workers found that mixtures of materials performed better than the individual pure materials (Waybrandt et al., 1998; Zagury et al., 2006). The easily available organics appear to enhance initial performance. Cellulose accompanied by appropriate conditions for cellulose degraders are essential for long-term performance.

Many workers have stated that pH above about 5 is critical for sulfate reduction, but other workers have observed sulfate reduction at pH down to less than 3 (Praharaj and Fortin, 2004; Gyure et al, 1990; Elliot et al., 1998; Kolmert and Johnson, 2001; Kuyucak et al., 2006; Willow and Cohen, 2005). Some authors report the presence of acidophilic sulfate reducers in these waters.

Low temperatures slow sulfate reduction but do not stop it. Reactors successfully continue treatment at temperatures of 2 to 6^{o}C (Gusek, 2004; Kuyucak et al., 2006).

A number of researchers have attempted to model sulfate reduction. An optimum sulfate-reduction rate of 0.1-0.3 moles/d/m^3 of substrate has been observed by several researchers (Neculita et al., 2007; Wildeman et al., 1998).

In general, the experiments indicate that a mixture of relatively fresh plant material (hay, straw, cornstalks, garden waste) with cellulose-rich material (mushroom compost, sawdust, wood chips, leaf compost) provides good long-term treatment. Addition of manure provides sulfate reducing bacteria. Addition of other types of bacteria needs to be investigated.

Sulfate-Reducing Bioreactors (SRBR) and Permeable Reactive Barriers

Numerous sulfate-reducing bioreactors have been constructed in recent years for treating AMD. Most are for heavy-metal-bearing AMD at metallic mines, but some have been constructed at coal mines for removal of Fe and Al and addition of alkalinity. In a few cases, removal of SO_4 is the goal, but limited success has been achieved toward this goal.

An SRBR is a bed of organic material through which AMD is percolated for treatment. The dominant treatment process is sulfate reduction. Beds may be upflow, downflow or lateral flow.

The sulfate-reducing bacteria in an SRBR consume organic matter and release sulfide that precipitates Fe and heavy metals as sulfides, and also generate alkalinity that increases pH. For some elements, such as Al, the pH increase from alkalinity generation or from limestone included in the bioreactor leads to metal removal by precipitation of hydroxides. An additional process is adsorption of metals and other solutes, though over the longer term the adsorption capacity is saturated and this process no longer operates, or can even be reversed to release adsorbed species.

Experiments on effectiveness of a wide variety of organic materials are summarized in the section on Organic Materials. Commonly relatively fine grained limestone or some other form of $CaCO_3$ (mussel shells, calcareous soil, etc.) is added to help maintain the pH in a better range for sulfate reducers and to help neutralize the acidity. Amounts added range from a few percent to many tens of percent. Properly designed SRBR's are effective even with low pH AMD. They are particularly adapted to removal of heavy metals such as Zn, Cd, Ni, Cu, As and Se, which precipitate as sulfides or in elemental form.

Reactors are sometimes affected by compaction of the bed, reducing permeability, and by short circuiting. Many workers have added larger strong particles such as gravel, sand, walnut shells, wood chips and similar materials to the organic matter to minimize compaction and maintain permeability. Nordwick et al. (2006) describe a horizontal flow reactor that decreases compaction by minimizing the vertical dimension and supporting the active material in modular units in a cellular network.

Start-up of SRBR's can be slow, while the bacterial system adapts to the AMD composition and substrate. For this reason, the bed is commonly maintained in a stagnant condition for weeks or months before flow is initiated. Inoculation with bacteria from other systems or with manure commonly supplies the sulfate reducers. To date, little attention seems to have been paid to establishment of the other microbial species that degrade organic matter to the simple compounds used by sulfate-reducers.

A side effect which has been little noted is that SRBR's can release significant concentrations of soluble organic compounds, reduced S compounds and N compounds in their effluent. Aerobic treatment of the effluent should follow the SRBR to degrade these compounds.

Several large SRBR's have recently been constructed in Pennsylvania. At Strattanville, a "limestone buffered organic substrate" bed treats effluent from an upflow limestone pond (Helfrich, 2009). Design flow is 750 L/min but is occasionally exceeded. Influent has acidity of 200-300 mg/L, pH 5.7 to 6, Fe 80 to 230 mg/L, and Al generally less than 1 mg/L. Effluent during 2008-9 was generally net alkaline with pH 6.5 to 7.8, Fe < 10 mg/L, and Al < 1.

At the Reed site near Strattanville, a discharge of 190 to 570 L/min is being treated by a large SRBR (Golembiewski, 2009). Influent AMD has acidity about 500 mg/L at pH 3, with 140 mg/L Fe and 26 mg/L Al. This flows into a "limestone-buffered organic substrate" bed about 300 m long, 25 m wide and 1.2 m thick. The bed is composed of 40 % by weight shredded wood, 30% No. 10 limestone aggregate, 10% manure, 10% sawdust and 10% alfalfa hay. After 1 year, typical effluent is net alkaline or slightly acidic, with the slightly acidic effluent formed during winter at higher flow.

At a remote site in northern Quebec, a bed of wood chips, hay, manure and limestone with a surface area of 100 m^2 and a depth of 1.7 m received AMD from a tailings pile at a flow rate of 11 to 22 L/min (Kuyucak et al., 2006). The influent had typical pH of 3.4, Al 43 mg/L, Fe 13 to 32 mg/L and acidity 300 mg/L, with elevated Cu and Zn. The system started treating in fall, and successfully treated through the winter. Typical effluent had pH 6.5, Fe <1 mg/L, Al 10 to 20 mg/L, alkalinity 400 mg/L and negligible heavy metals.

Extremely acid water (acidity 2000-4000 mg/L, pH 2.4) was treated satisfactorily at a rate of 4 L/min in a pilot SRBR 20 m square at the Fran Mine site in Pennsylvania (Gusek et al., 2004). Effluent alkalinity of 900 mg/L was generated, and 250 mg/L Al was reduced to <1 mg/L without plugging by Al precipitates.

Permeable Reactive Barriers

A permeable reactive barrier (PRB) is an engineered subsurface system that treats a flow of contaminated groundwater. The plume of contaminated groundwater flows through the barrier and continues as treated groundwater. For AMD, several such systems are reported, mainly at sites with heavy metal pollution.

A PRB at the Nickel Rim mine near Sudbury, Ont. was successful in treating AMD with pH 5 to 6, 1000-4000 mg/L SO_4, 200-1000 mg/L Fe, and up to 30 mg/L Ni (Benner et al., 2000) over a period of 5 years. The PRB was constructed in 1995 in unconsolidated material above bedrock, and contains 20% municipal compost, 20% leaf compost, 9% wood chips, 1% limestone and 50% pea gravel. Groundwater downflow from the PRB contains <100 mg/L Fe, <0.2 mg/L Ni and increased alkalinity.

At a site in British Columbia, treatment in a PRB of 84% gravel,15% leaf compost and 1% limestone removed Cu, Cd, Ni, Pb and Zn as sulfides to low values (Ludwig et al., 2002; McGregor et al., 2000) in a retention time estimated at 6 days. Influent water had pH 6.4.

Steel Slag Beds

Beds, channels and dams of steel slag have been used to generate alkaline water which is then mixed with AMD. Direct contact of AMD has also been attempted with less consistent success. Slag from electric arc steel-making is the best material. Ziemkiewicz (1998) and Ziemkiewicz and Skousen (1998) have shown that the hard glassy fragments are capable of maintaining permeability through a bed, except in the finest sizes. Neutralization potential of steel slags studied by them ranges from 450 to 780 t/1000t (45 to 78% $CaCO_3$ equiv.). Columns of 3 mm slag particles filled to depths of 10 to 60 cm gave initial alkalinities of over 2000 mg/L $CaCO_3$ on daily leaches with 0.5 L of distilled water. The alkalinities declined with time as the finer particles were dissolved, but the 24 inch bed maintained alkalinities above 1000 mg/L for 8 months of daily leaches. Feeding AMD into beds of steel slag tends to rapidly cause coating and plugging due to precipitation of Fe and Al on the fragments; therefore, clean water is preferred for continuing generation of alkaline water.

In a study at the McCarty Highwall site, Simmons et al. (2002) used check dams made of fine slag and limestone, in combination with open limestone channels, to treat several small flows of acidic water with acidities of 12 to 30 mg/L, pH 4.1 to 5.0 and Al 0.6 to 2.5 mg/L. The limestone-slag system generated outflow with net acidities of negative 170 to 225 mg/L at pH 8 to 9.5 over a year.

In Ohio, extensive reclamation efforts at the Broken Aro Mine have utilized slag beds receiving both AMD and clean water. The slag beds, containing about 10,000 tons of slag, have contributed large amounts of alkalinity. The acidity load from the area has decreased by

700 kg/d. Similar success utilizing slag and other techniques has been attained at the Huff Run watershed in Ohio (Hamilton et al., 2007).

Lab experiments on three sizes of slag showed that sand size and 6 mm size slag generated high alkalinities (600 to 1100 mg/L as $CaCO_3$) in about 4 hours of circulation of relatively clean stream water (Mills, 2009). Slag of 5 to 8 cm size generated only about 30 mg/L alkalinity.

Chitin as a Treatment Material

Chitin is the skeletal material produced by arthropods (insects and crustaceans), mollusks and fungi. It is an organic material, a polysaccharide with the formula $C_8H_{13}NO_5$, and is recovered as a waste product from crab and shrimp processing. In these shells, chitin is thinly and intimately interlayered with $CaCO_3$. Experiments show that the organic component is very effective as an electron donor for sulfate reduction, and as an adsorbent for a wide range of organic and inorganic species. The very fine $CaCO_3$ is effective in neutralizing acid, and the N may act as a nutrient for some microbial activities. The effluent from chitin treatment can contain significant amounts of N species, which need to be evaluated with this material as well as other organic materials.

Daubert and Brennan (2007) tested AMD in microcosms with crab shell chitin. The pH increased from 3.2 to 6.8, and alkalinity from 0 to 235 mg/L $CaCO_3$ while acidity decreased from 192 to negative 114 mg/L in 9 days of contact. Iron, Al and Mn also decreased.

In lab experiments comparing chitin with lactate and compost, Robinson-Lora and Brennan (2008) showed that chitin was much more effective than either lactate or compost in facilitating sulfate reduction, neutralization and metal removal from three sources of AMD. At the National Tunnel in Colorado, AMD containing Fe and heavy metals was successfully treated for 6 months by flow at 23 L/d through 120 L chitin-filled barrels (Venot et al., 2008b.

In summary, chitin has unusual effectiveness in treatment of AMD, and also represents consumption of a waste material.

Limestone Beds for Mn Removal

Most passive systems such as ALD's and VFP's do not remove appreciable Mn. Vail and Riley (1995, 1997, 2000) reported a patented technology for removal of Mn from AMD discharges using the "Pyrolusite Process". The method utilizes inoculation of specialized Mn-oxidizing bacteria into a bed of limestone. The Mn^{2+} in AMD flowing through the bed is oxidized to Mn^{3+} or Mn^{4+} by the bacteria at pH values of 6 to 8, and precipitated on the limestone as an Mn oxyhydroxide (todorokite or birnessite). Many such inoculated limestone beds have been constructed to remove Mn..

Rose et al. (2003a, 2003b) and Means and Rose (2005) provide information on the effectiveness and sizing of these beds. The oxidation of Mn is catalyzed by bacteria and by auto-catalysis by pre-existing Mn-oxyhydroxide surfaces. The oxidation proceeds by approximately the following reaction:

$$Mn^{2+} + 0.5\ O_2 + H_2O = MnO_2 + 2H^+ \qquad (5)$$

At constant pH and oxygen, the rate of Mn oxidation is proportional to Mn concentration. Based on field studies of 6 field sites, the area of limestone bed needed to treat a given concentration of Mn was determined

Field observations of limestone beds for Mn removal indicate that the beds work well but tend to accumulate silt and leaves, and also Al-Fe precipitate if the influent water contains any (Rose et al., 2003a). Accumulation of these constituents leads to plugging and flow of water across the surface of the bed. Also, beds that were not inoculated with special bacteria are as effective as beds inoculated with special bacteria. The water entering the beds should be well oxygenated, and essentially devoid of dissolved Fe and Al. because the Mn is chemically displaced by Fe^{2+}, and precipitates of Fe and Al interfere by plugging the bed.

Denholm et al. (2008) successfully recovered an Mn-rich sludge from a limestone bed that had been removing Mn for several years. A small pond was excavated in the bed, and the Mn-coated limestone was agitated below water level in the pond inside a perforated drum mounted on an excavator. The recovered Mn has been sold for use in ceramics and other purposes.

Selection of Method

A key step in passive treatment is selection of the optimum method for the AMD chemistry and the site. Figure 5, modified after Hedin et al. (1994a), provides an updated approach to selection based on technology discussed in this report. The key initial choice is between net alkaline and net acidic waters, as derived from measured acidity (Standard Methods 1998), or a calculated acidity (eq. 4) on a filtered or clear sample. For net acidic AMD, a number of choices are available, depending on site conditions and chemistry.

Several other writers have provided similar diagrams. Figure 6 shows selection diagrams by the PIRAMID group (PIRAMID Consortium, 2003)).

A very useful computer program for evaluating cost of treatment methods is AMDTreat, developed by the US Office of Surface Mining in collaboration with state regulatory agencies (Means et al., 2003). It is available at amd.osmre.gov. This program requires method selection by a procedure such as that shown above, but can then predict approximate costs for various sets of treatment steps.

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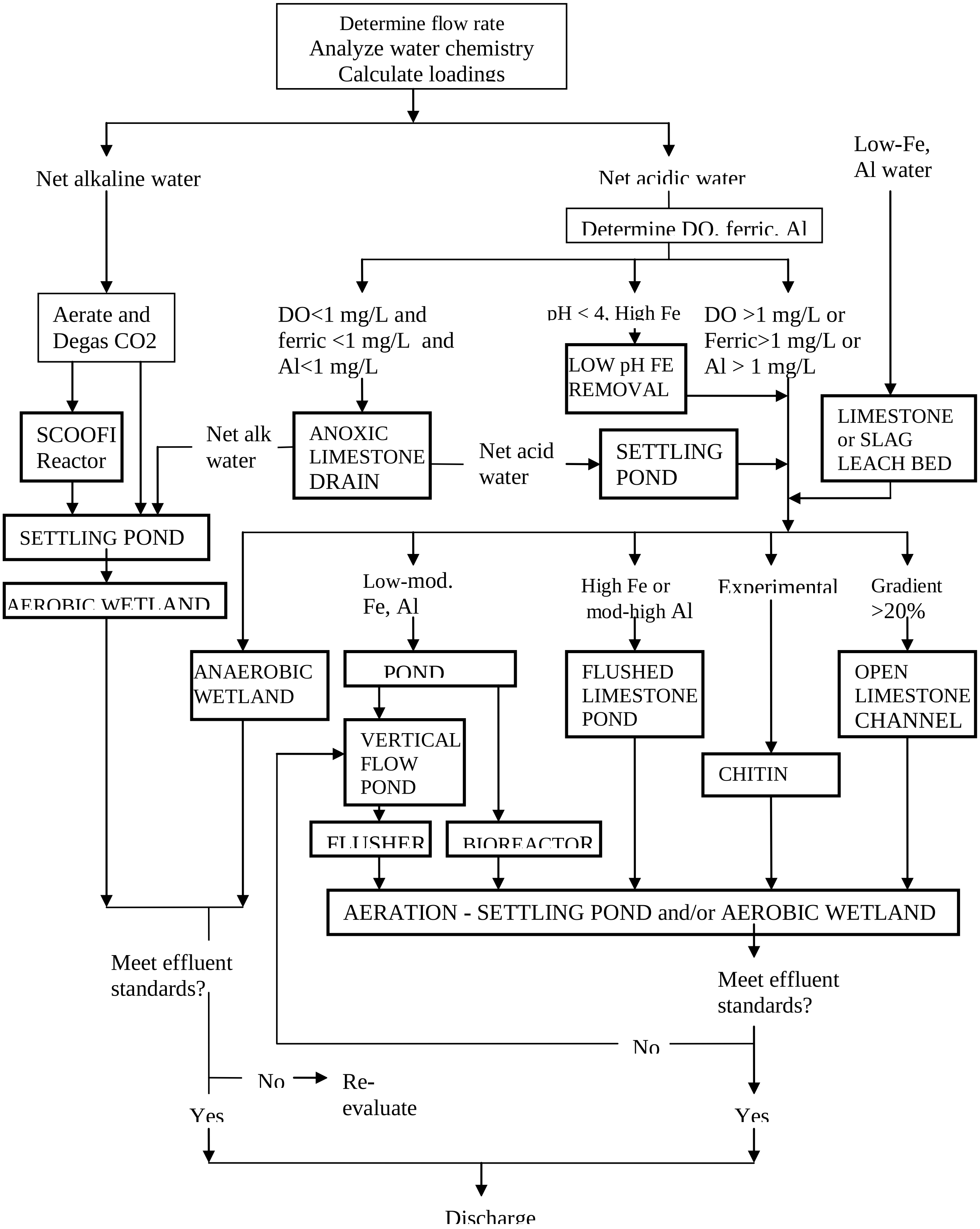
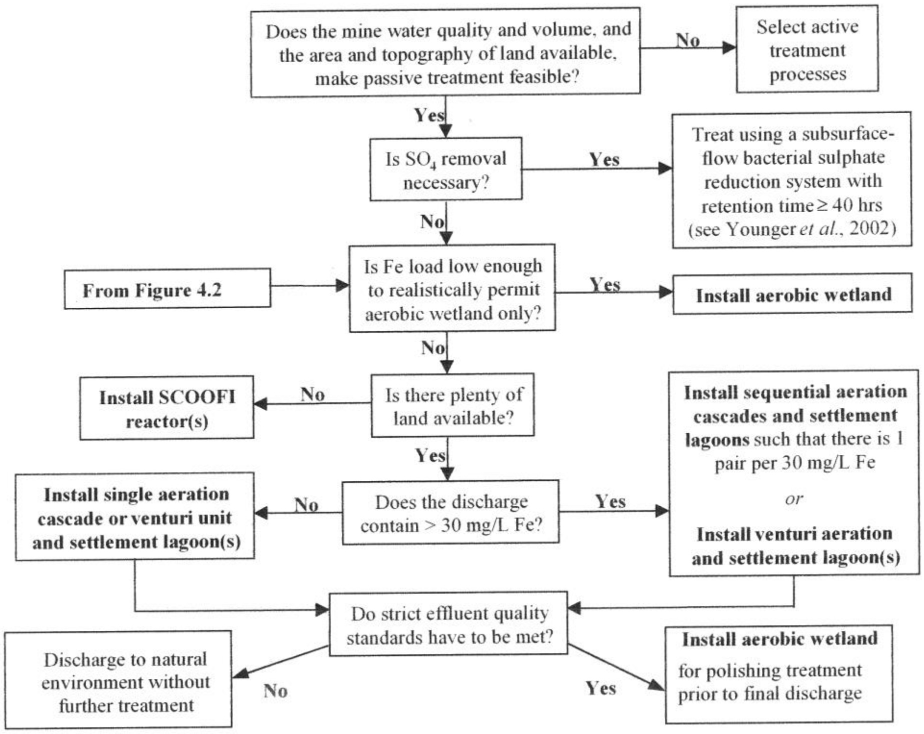


Figure 5. Flow chart for selection of passive method.



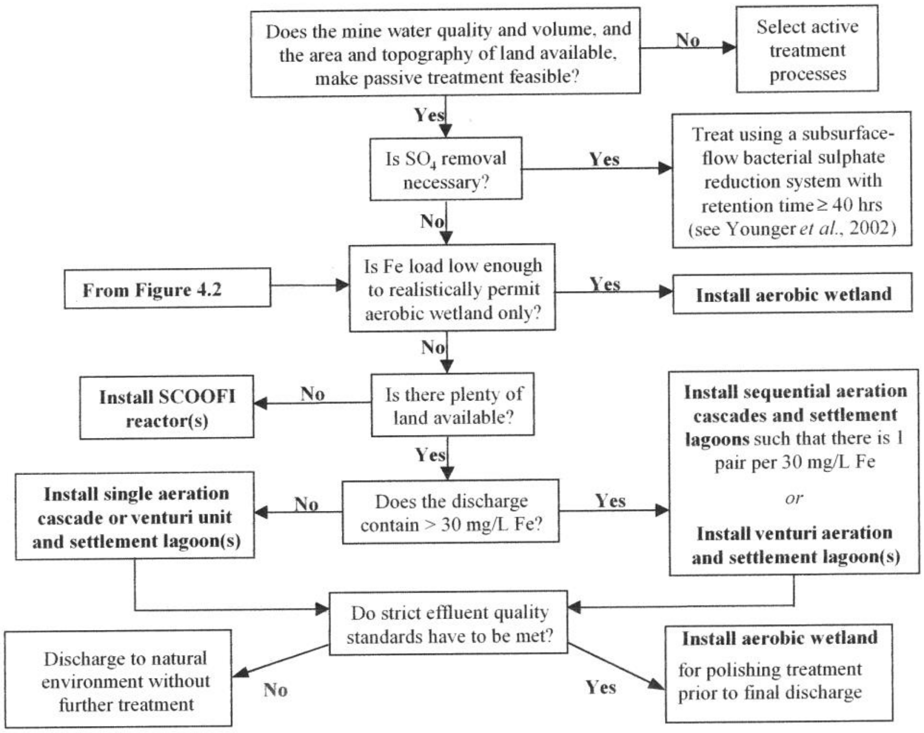


Figure 6. Flow chart for method selection, after PIRAMID (2003)

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