THE SELECTIVE OXIDE SYSTEM™: ACID DRAINAGE TREATMENT THAT AVOIDS THE FORMATION OF SLUDGE

Harry R. Diz, Ph.D.
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute and State University
Blacksburg, Virginia, 24061-0246

A. INTRODUCTION

B. A new approach to treating acid mine drainage (AMD) has been developed which avoids the formation of metal hydroxide sludge, and holds the promise of being more economical than conventional treatment. Current chemical treatment technologies are either impractical or too expensive to be used at abandoned mine lands (AML), and all approaches generate large volumes of metal hydroxide sludge requiring further treatment and/or ultimate disposal.

Contaminated water is continually discharged from many AML sites day after day with no treatment at all. The negative impact on the aquatic habitat is significant. The states of Pennsylvania and West Virginia, for instance, have identified AMD as the #1 water quality problem in their waters. Localized point sources account for most of the pollution. Therefore, a point-source system may be useful in treating these polluted discharges.

C. BACKGROUND

When pyritic minerals are exposed to the atmosphere, oxidation of sulfide produces sulfuric acid and releases iron and other metals to solution. The characteristics of AMD include low pH, high specific conductivity, high concentrations of iron, aluminum, and manganese, and variable concentrations of toxic heavy metals.

Various approaches have been used to ameliorate AMD and its effects. In general, attempts to prevent moisture, oxygen, and microorganisms from reaching the disturbed pyrite surfaces have met with relatively little success (Unz and Dietz, 1986). The bulk dumping of limestone in streams was once thought to be capable of neutralizing the acidity of the water, but typically the limestone became coated with iron oxyhydroxides, slowing its dissolution and thus limiting its effect on stream pH (Hedin and Watzlaf, 1994). It was found that pH neutralization by limestone was successful so long as the water was anoxic (anoxic limestone drains - ALDs). However, once the neutralized water was exposed to the atmosphere, iron oxidized and hydrolyzed, and more acid was generated. Since the iron then precipitated in the stream or in settling ponds, the lack of an iron removal mechanism is a significant shortcoming of this approach.

When anoxic limestone drains were combined with natural or constructed wetlands, some treatment success was achieved (Wildeman et al., 1994). However, wetlands have shown a limited ability to cope with intermittent low pH events, and can be overwhelmed by high flow (Tarutis and Unz ,1995). Some metals, such as manganese, are often not effectively removed by wetlands. A recent innovation (Skousen, 1995) is known as an alkalinity producing system (APS), which is an engineered downflow system in which organic matter is layered on top of limestone. The overlying organic layer depletes the water of dissolved oxygen, and contributes alkalinity due to microbial metabolism. As the anoxic water flows to the limestone layer, dissolution of the limestone contributes additional alkalinity. Head loss increases as the pore spaces within the layers become filled with particulates, and thus sufficient freeboard must be designed into the system. The effluent of the APS is then routed to a settling pond, in which iron becomes oxidized and precipitates, forming an iron hydroxide sludge. Clarified supernatant is then allowed to flow into a receiving water. The advantage of this approach is that relatively inexpensive limestone is employed as the primary source of alkalinity. However, settling ponds are still required where the uncontrolled precipitation of iron results in the profuse generation of iron sludge, and manganese is not effectively removed. The long term reliability of downflow passive systems has not been established, and there is a likelihood of clogging.

Chemical treatment systems have generally only been used at active mine sites. These typically consist of pH adjustment with caustic soda (NaOH) or lime (CaO), followed by settling ponds. New source performance standards developed for National Pollutant Discharge Elimination System permits by the USEPA for the coal mining industry stipulate total iron of 3 mg/L, total manganese of 2 mg/L, total suspended solids of 35 mg/L, and pH between 6 and 9 units (30 day averages) (USEPA, 1976) with similar requirements imposed by the Surface Mining Control and Reclamation Act of 1977.

An activated sludge system for treatment of AMD was evaluated in England in the mid-1960's with little success (Whitesell et al., 1971). In Japan, *Thiobacillus ferrooxidans* was employed at an abandoned mine discharging 20 m^3 min^{-1} of water with a pH of 1.6 containing 795 mg/L of total iron (Murayama et al., 1987). Total detention time in the system was approximately 8.5 h. The operational cost of treatment was approximately one-third that of the previous all-chemical process. There were considerable problems in recirculating the clay slurry used for the immobilization of the bacteria, and oxidized iron was still captured as a sludge in settling ponds.

D. SYSTEM CONFIGURATION

The Selective Oxide System™ takes advantage of the tendency of ferric iron to form mineral coatings, uses inexpensive limestone, and avoids the formation of iron hydroxide sludge. The requirement for sedimentation basins is thus eliminated along with the need for storage and disposal of sludge.

At low pH, ferrous iron oxidization is due to microbial activity; above about pH 4.5, abiotic oxidation is sufficiently rapid that microbial activity is less critical. Once oxidized, the very low solubility of ferric iron results in precipitation of oxyhydroxide minerals if pH exceeds 3.0. In a previous phase of the work (Diz and Novak, 1997a), it was shown that ferrous iron could be oxidized in a bioreactor while maintaining the iron in a dissolved state since the bioreactor operated below pH 3.

The precipitation of ferric iron is not instantaneous upon addition of alkalinity to the solution. However, when sufficient base is added to a ferric iron solution to exceed a threshold level, precipitation of iron oxyhydroxides is inevitable (Figure 1), although the time from the addition of the base to the time of appearance of a precipitate, the

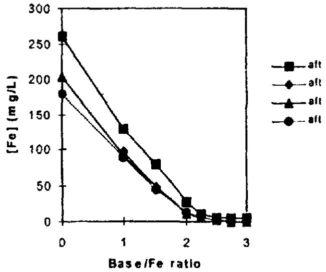

Figure 1. Dissolved iron concentration at various ba ratios at various times after addition of the base.

so-called "induction period", may last from seconds to months (Dousma and de Bruyn, 1979). During the induction period, changes occur within the solution which eventually result in precipitate formation. This process, described in detail elsewhere (Diz, 1997), appears to involve a reversible increase in polymerization of Fe/OH units, resulting in the formation of many critical-sized nucleii. Once critical size is achieved, the nucleii continue to grow by incorporation of additional Fe/OH growth units until the concentration of dissolved iron becomes low and the rate slows significantly. Over time, small particles may join together, a process referred to as agglomeration (Mullin, 1993). As particles grow in size, the number of particles decreases, and growth by agglomeration slows; precipitation, usually defined as the appearance of filterable particles, may occur at some point in this process.

It was hypothesized that this sequence could be interrupted if dissolved iron units and/or very small iron particles could be removed from solution at an early stage by exposing the solution to a mineral surface. If the growth units and/or very small particles preferentially united with the pre-formed surface, the continued growth and agglomeration of the iron nucleii could not occur, thus avoiding the formation of precipitated iron.

Since AMD typically contains dissolved species other than iron, the effect of those dissolved species on iron solubility and precipitation kinetics would be important in determining the success of such a treatment system. In a previous phase of the work (Diz, 1997), it was found that aluminum and manganese did not exert any measurable effect on precipitation rates. However, sulfate had a major effect, increasing iron solubility and slowing precipitation rates.

Diz (1997) investigated the performance of a packed bed bioreactor using expanded polystyrene beads to immobilize iron-oxidizing chemolithotrophic bacteria for the conversion of reduced ferrous iron to the ferric state at low pH (about pH 2.3). It was found that good oxidation efficiency (98 %) could be expected at influent ferrous iron concentrations up to 10 mM (558 mg L^{-1}) and detention times as short as 0.5 h. It was also found that temperature exerted a significant effect on oxidation rates, and that dissolved oxygen concentration should be maintained above about 2 mg L^{-1}. Supplementation with carbon dioxide did not result in increased oxidation rates.

The new active treatment process presented in this report is relatively simple in design and operation (Figure 2). The unit operations of the system include a bioreactor for the oxidation of ferrous iron, a fluidized bed reactor for the precipitation of iron onto the surfaces of seed particles, and a trickling filter for the oxidation and precipitation of manganese at high (>9) pH, with final neutralization of the effluent by passage through a calcium carbonate bed. The technology avoided the generation of iron sludge and the necessity for sedimentation basins. Other than electrical power to operate the system, the only maintenance requirements would be the replacement of sand media in the fluidized bed, the periodic replenishment of the concentrated caustic soda (NaOH) for the trickling filter stage, and the addition of limestone to the carbonate bed. The requirement for caustic soda would be much lower than in conventional treatment, since most of the acid-neutralizing power is provided by the carbonate bed, a much cheaper source of alkalinity. The NaOH is only required to increase the pH from ~7 to >9. An additional cost and operational advantage is that it would not be necessary to remove the iron-coated sand from the site unless there was some productive use for it elsewhere. It is, after all, simply rust-coated sand, and poses no threat to aquatic life.

For design purposes, a detention time in the bioreactor of about 0.5 to 1 h is sufficient to oxidize essentially all of the influent ferrous iron (up to a concentration of 10 mM Fe II). Depending on the specific AMD characteristics of the site, the detention time could possibly be even shorter. The bacteria which inhabit the system are naturally occurring, grow slowly, require no artificial input of nutrients, and produce very little biomass. Thus, the disposal of biomass would not appear to be necessary. Since the oxidation rate is affected by dissolved oxygen (DO) concentration, the aeration system needs to be properly sized to maintain DO at a minimum of about 2 mg L^{-1}. Temperature has a major impact on rates, and thus it is important to maintain reactor temperature as high as practical,. If the system is located close to the point of discharge from below ground (at the mean annual sub-surface temperature), reactor temperature would probably remain in an acceptable range. Otherwise, supplemental heating might be necessary.

Iron loading to the fluidized bed reactor was found to be the most important design parameter (Diz and Novak, 1998). Sufficient surface area (a function of the mass and diameter of sand grains) is required to prevent iron loading from exceeding 0.20 mg Fe m^{-2} h^{-1}. Above this loading, dispersed iron particulates form, resulting in a turbid effluent. The limiting loading rate appears to be a function of the collector efficiency of the seed particles and the growth rate of the particles while in the reactor environment. Based on iron precipitation kinetic studies (Diz 1997), it was found that a detention time of less than 1 h within the fluidized bed would result in a dissolved iron concentration of less than 10 mg L^{-1} at pH 3.5. The solubility and rate of precipitation of iron are closely related to pH, the sulfate/iron ratio, and to some extent, to the iron concentration itself. Site-specific AMD characteristics therefore influence the optimal operating parameters for the system. Below the optimal pH value, the dissolved iron concentration increases in a clear effluent; above this value, a turbid effluent develops due to the presence of particulate iron.

Detention time in the carbonate bed was about 2 h. Effluent pH was in the range of pH 6.3 - 7.2. Iron remaining in the fluidized bed effluent was largely removed in the carbonate bed, and a final effluent iron concentration of less than 3 mg/L was routinely produced.

Cu, Mn, Ni, and Zn) when added to the feed solution is shown in Figure 3 (Diz and Novak, 1997). There was removal in the fluidized bed reactor (FBR) as well as in the trickling filter (TF), where pH >9 caused manganese to oxidize and precipitate (96% removal); removals of copper, nickel, and zinc (initial concentrations ranging from 5 to 15 mg L^{-1}) appeared to be due primarily to sorption onto oxide surfaces. Removals averaged 97% for copper, 70% for nickel and 94% for zinc.

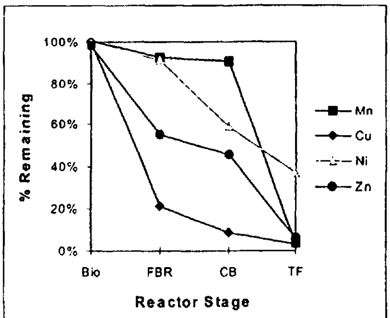

Figure 3. Heavy metal removal in various stages of the Selective Oxide System.

OTHER POTENTIAL APPLICATIONS

It is conceivable that this system could be employed to remove heavy metals in wastewaters which are not rich in iron and/or manganese. Low concentrations of iron, manganese, and/or acid could be added to the influent at a rate just sufficient to slowly generate new oxide surfaces. The alternating environments of low pH in the fluidized bed and high pH in the trickling filter would provide a combination of environments which would strongly sorb both anions and cations, in a fashion similar to sequential anion/cation-exchange resins. Several toxic elements form oxyanions, such as arsenate, selenate and chromate, and may be efficiently removed in the fluidized bed where iron oxides at low pH have positively charged surfaces. Cationic heavy metals are strongly attracted to the negatively charged MnO_x surfaces of the trickling filter (Singh and Subramanian, 1986). A drawback to ion-exchange resin systems is that they require periodic regeneration by flushing with concentrated saline or acid/base solutions, thus creating contaminated backwash waters. This new treatment system would not require such a step. For example, in the case of the removal of radionuclides from low-level radioactive wastewaters, this new process might operate over long periods of time without the generation of radioactive backwash waters. Also, since the additions of iron and manganese would be modest, the seed particles would not require replacement over long periods.

COST COMPARISONS

Primary benefits for this new approach compared to conventional treatment include:

- Use of limestone instead of lime or NaOH for pH adjustment. Based on the approach of Phipps et al. (1991), the chemical cost savings per ton of acidity (Figure 4) would be approximately $17/ton compared to lime (34%) and $247/ton compared to NaOH (88%).
- No sludge generation, thus no need for settling ponds and sludge disposal.
- *Savings since re-acidification (to pH < 9) is not* necessary for final discharge.

The capital cost of a new installation would probably be equivalent to that of conventional lime treatment plants. However, capital savings would accrue due to lower land requirements (no need for settling basins), and the fact that sludge dewatering/ handling/disposal equipment would not be required. Depending on the presence of trace metals in the raw water, the oxides generated may have commercial value.

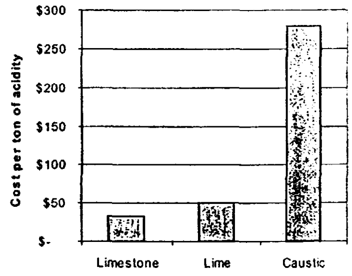

Figure 4. Relative cost to neutralize a ton of acidity using three sources of alkalinity (based on US DOE data).

CONCLUSION

The feasibility and economics of this technology for AMD is yet to be established through pilot-scale studies, but it offers the potential of compact, economical treatment suitable for concentrated AMD seeps, drainage from acidic tailings ponds, active mine effluent, and acidic iron-rich industrial wastewater. Applicability to other contaminated waters is being investigated.

E. REFERENCES

Diz, H.R., 1997. Chemical and Biological Treatment of Acid Mine Drainage for the Removal of Heavy Metals and Acidity. PhD dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Va.

Diz, H.R. and J.T. Novak, 1997. Heavy Metal Removal in an Innovative Treatment System for

Acid Mine Drainage. Proceedings of the Mid-Atlantic Industrial and Hazardous Waste Conference, Roanoke, VA.

Diz, H.R. and J. T. Novak, 1998. A Fluidized Bed for Removing Iron And Acidity From Acid Mine Drainage. J. Environmental Engineering (in press).

Dousma, J. and P.L. de Bruyn, 1979. Hydrolysis-Precipitation Studies of Iron Solutions. III. Application of Growth Models to the Formation of Colloidal αFeOOH from Acid Solutions. J. Colloid Interface Sci. 72(2):314-320.

Hedin, R. S. and G. R. Watzlaf, 1992. The Effects of Anoxic Limestone Drains on Mine Water Chemistry. Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA. April 24-26, 1994, pp. 185-194.

Mullin, J. W. 1993. Crystallization, Third Edition. Butterworth-Heinemann Ltd., Oxford.

Murayama, T., Y. Konno, T. Sakata, and T. Imaizumi, 1987. Application of Immobilized *Thiobacillus ferrooxidans* for Large-Scale Treatment of Acid Mine Drainage. Meth. Enzymol. 36:530-49.

Phipps, T., J. Fletcher, and J. Skousen, 1991. A Methodology for Evaluating the Costs of Alternative AMD Treatment Systems. Proc. 12th Annual West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV.

Singh, S. K., and V. Subramanian, 1986. Hydrous Fe and Mn Oxides: Scavengers of Heavy Metals in the Aquatic Environment. CRC Critical Reviews Environmental Control 14(1): 33-90.

Skousen, J. G. 1995. Douglas Abandoned Mine Land Project: Description of an Innovative Acid Mine Drainage Treatment System. In: J.G. Skousen and P.F. Ziemkiewicz, Eds. Acid Mine Drainage: Control & Treatment. West Virginia University, Morgantown, WV.

Tarutis, Jr., W. J. and R. F. Unz, 1995. Iron and Manganese Release in Coal Mine Drainage Wetland Microcosms. Wat. Sci. Technol. 32(3):187-192.

Unz, R.F. and J.M. Dietz, 1986. Biological Applications in the Treatment of Acidic Mine Drainages. In: H.L. Erhlich and D.S. Holmes (Editors), Biotechnology for the Mining, Metal-Refining, and Fossil Fuel Processing Industries. John Wiley & Sons, Inc., NY, pp. 163-170.

US EPA, 1976. Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Coal Mining Point Source Category. EPA 440/1-76/057a, pp.288.

Whitesell, Jr., L., R.L. Huddleston, and R.C. Allred, 1971. Microbiological Treatment of Acid Mine Waters. Water Pollution Control Research Series 14010 ENW 09/71, USEPA. p 78.

Wildeman, T.R., D.M. Updegraff, J.S. Reynolds, and J.L. Bolis. 1994. Passive Bioremediation

/

of Metals from Water Using Reactors or Constructed Wetlands. In: J. L. Means and R. E. Hinchee (Editors), Emerging Technology for Bioremediation of Metals. Lewis Publishers, Boca Raton. pp.13-25.