DEVELOPMENTS IN ARD REMEDIATION TECHNOLOGIES AT WESTERN HARD ROCK MINES, U.S.

HARRY H. POSEY, Ph.D.
COLORADO DEPARTMENT OF NATURAL RESOURCES
DIVISION OF MINERALS AND GEOLOGY
1313 SHERMAN STREET – ROOM 215
DENVER, CO 80203
harry.posey@state.co.us

ABSTRACT

Federal regulations governing surface water discharges at *active* mines are essentially the same for coal and non-coal mines. Application of those regulations, however, differs for *abandoned* coal and non-coal mines. Abandoned coal mine reclamation falls under OSM jurisdiction and water quality discharges require little beyond construction-based objectives; non-coal mine reclamation however requires full compliance with Clean Water Act standards. As a result of these practices, water quality discharge requirements for the two mine types differ significantly. Metal mines, for instance, must meet strict surface water protection standards while abandoned coal mine reclamation programs usually call simply for monitoring of key elements with no requirement meet water quality standards. These differences greatly influence the choice of cleanup methods.

This paper highlights some of the major reclamation practices that involve water treatment at metal mines. Particular attention is given to water management strategies that, in the water treatment stream, precede classic alkaline amendment-based water treatment. Also discussed are some promising treatment strategies seen in the offing.

INTRODUCTION

In a 1993 Federal District Court case now renowned among western non-coal AML programs, an environmental group – Committee to Save Mokelumne River – prevailed over a California municipal utility district, thus forcing the MUD to meet clean water act discharge requirements from a dam constructed by the MUD to *decrease* pollutant releases from an upstream abandoned metal mine (*Committee to Save Mokelumne River v. East Bay Municipal Utility District et al.; 1993).* As a result of the judgement, sometimes called the Penn Mine case, the defendants installed a water treatment plant and may treat water, some say, in perpetuity. As a further result, some western states have adopted a strategy for abandoned metal mines that says, in essence, “don’t touch polluted water.”

Voluntary cleanup programs, Brownfields, and other EPA-regulated programs that offer incentives for cleaning up point source discharge are still bound to require compliance with federal Clean Water Act standards. Thus, projects that might improve water quality in a watershed by, say, removing some quantity of metals from several point sources in that watershed have been put on hold pending legislation that will allow potential remediation entities to minimally improve water quality without incurring Clean Water Act liability. A "Good Samaritan" provision to the Clean Water Act is now in the sixth year of consideration before Congress, but until such an amendment is passed, metal discharges from orphaned non-coal AML sites will go generally unabated except under CERCLA actions.

This is not to say that non-coal AML programs are avoiding water quality problems at orphan sites altogether. Rather, strategies have been developed to either (a) reduce the flows without reducing the metal loads or (b) reduce metal concentrations and loads by minimizing clean water infiltration of ARD-producing rocks. The following section explains some of these strategies in terms of ARD prevention strategies and ARD control strategies.

ARD PREVENTION STRATEGIES

Short of treating all polluted water from an orphan site, metal mine cleanups seek either to reduce metal and acid concentrations or to reduce metal loads. Where metal concentrations are to be reduced, water treatment of some sort is required. Where metal loads cannot be minimized without incurring CWA liability, some water managers have chosen to segregate "clean" streams from "dirty" streams in clean/dirty mixtures, thus producing a smaller stream of polluted water carrying the same metal load as the original, higher-flow, mixed stream. The purpose of such a strategy is to save unpolluted waters for beneficial uses without "touching" the polluted water and thus incurring CWA liability.

Metal load, it is recalled, is the product of metal concentration times flow:

[Load in pounds per day] = [Concentration in ppm] x [Flow in cfs] x [Conversion factor]

Load may be expressed by other weight/unit time measures, but pounds per day is most common.

Load reduction may be accomplished by passive means, including:

a. upland surface water diversions
b. waste rock caps or
c. waste rock covers.

Metal load reductions however can be accomplished only via some water treatment system. The following sections briefly review these features.

Upland surface water diversions. Upland surface water diversion strategies are well described in both the mining and civil engineering literature. Basically, upland waters are diverted from ARD producing features through ditches or other topographic modifications. In cases where water cannot be diverted, ARD-producing waste rock may be relocated to minimize contact with upland waters.

Caps. Waste rock caps or surface liners are applied generally where the cost of capping is lower than the cost of waste rock relocation and covering (see next section). Caps are engineered surface liner systems which are composed of low permeability soils, permeable soils amended with clay, or artificial membranes – "soil" in this case refers to engineering, not geologic, definitions. Topsoil or growth media may be applied above the liners, but are not everywhere a critical feature.

In extremely cold climates, engineered caps typically are covered with thermal barriers. Barrier thickness designs depend on average or absolute minimum temperature for the region, heat production properties of the covered, ARD-generating material, and liner materials. If the ARD-generating material produces significant heat due to exothermic reactions due to sulfide weathering – the Richmond Hill Deposit, for instance, in South Dakota (Deux, 2000) – then the necessary thermal barrier thickness may be less than otherwise. Frost-heave prevention requirements vary depending on liner materials; where heave is likely to be significant, thermal barriers will need to be maximized.

Covers. Covers differ from caps in that their function is to minimize, not prevent, water infiltration. By controlling precipitation input to ARD-generating rock, the outflow rate of ARD solution thus is also controlled.

Covers control infiltration rates by:

- limiting cover permeability
- limiting surface retention by controlling surface roughness
- promoting surface runoff through sloping and ditching.

Cover designs may or may not include a topsoil/vegetation component. Where vegetation is included, the overall design may take advantage of the water retention and transpiration characteristics of the topsoil/vegetation system.

Evapo-transpiration covers. Evapo-transpiration (E-T) covers are a relatively recent concept in cover design that may have applications in more arid areas. In concept, E-T covers minimize water infiltration to an ARD-generating body by:

(a) storing water for some design period,
(b) allowing some of the stored water to evaporate and
(c) allowing some of the water to be transpired through plants present in the cover itself.

For E-T covers to work effectively, the regional yearly rate of evaporation must exceed the yearly precipitation rate. Depending on local climate and depending on the rate at which ARD may be released from the capped material, if it is allowed to be released at all, E-T covers may need to store the maximum expected yearly precipitation. For instance, if most or all of the yearly precipitation is expected to fall over a short period, the cap may need to hold a full year's precipitation allotment. On the other hand, if yearly precipitation periods alternate with dryer periods, the E-T cap may need to hold only that proportion of the yearly precipitation that falls within the maximum precipitation period.

Where cover vegetation is integral to controlling infiltration rates through the E-T cap, the following characteristics of each vegetation species need to be known:

- percent cover of each vegetation species
- water uptake characteristics
- transpiration rates
- length of growing season
- sun aspect effects on transpiration rates.

Other climatic, physiographic, and anthropogenic features also need to be understood or controlled:

- daily and yearly sun aspect
- daily and yearly shadow effects
- prevailing wind patterns and their effects on transpiration
- effect of burrowers on vegetation
- land use features that affect vegetation cover such as grazing or off-road vehicle use.

Depending on the rooting depth of the various vegetation species and the response of each species to soil solutions, it may not always be necessary to construct all layers of the E-T cover from non-ARD producing materials. An upper rooting zone may be constructed of "benign" materials while deeper levels may be ARD producing.

E-T cap designers should realize that some evaporite minerals which precipitation from ARD solutions actually store metals and acid. Designs should account for the potential buildup of such stored metals and acid over the years, and the potential effects of flushing such materials during storms should be evaluated.

Overall, E-T caps offer promise as "passive" reclamation options in arid climates. Research currently under way at the University of Nevada-Reno Desert Research Institute may offer needed insights into such caps.

ARD WATER TREATMENT AND CONTROL STRATEGIES

Mined land reclamation projects continually strive to adopt walk away solutions; walk away solutions are also the goals of AML reclamation. Perpetual water treatment is incompatible with these reclamation goals so walk away reclamation concepts are being continually being tested. Papers in the recent ICARD volume (ICARD, 2000) reflect fairly well the current directions in ARD-related treatment and control strategies.

"Walk-away" reclamation solutions are not possible for all mines where Clean Water Act water quality compliance and profitability are factors. (Yes, where local circumstances require it, some mines are indeed meant to be run unprofitably – knowingly and deliberately.) When considering the net value of the ore minerals, calculations must include reclamation costs, and reclamation generally must consider whether post-mining water treatment will be required and for how long. Operations requiring perpetual or even extremely extended water treatment can be conducted only under a regulatory climate that allows such extended or perpetual treatment. Typically, this requires a state or some other institution with a guaranteed long life to manage some sort of growth fund. Such mechanisms, currently, are not in place in all the western states.

But whether long-term water treatment is permissible or not, it is still considered good business to close mines by minimizing investment losses due to high reclamation costs. To those ends, walk-away reclamation is desirable. In the absence of the walk-away solution, the most attractive reclamation options are those requiring minimal maintenance and passive treatment. In cases where passive treatment is not possible, active water treatment selected, but as the option of last resort. The following sections mention the more popular active water treatment features, describe in more detail some of the problems with passive treatment systems, and explains some of the developing treatment technologies.

Active water treatment.

Most active water treatment systems at metal mines, abandoned or otherwise, rely on standard alkali-addition procedures. Lime (or other CaO-bearing products), sodium hydroxide, and sodium carbonate remain the alkalis of choice. Such treatment typically involves mixing of alkali and acid-metal water in treatment tanks, mechanical mixing for a fixed period, addition of some drinking water-approved flocculent to promote agglomeration of small precipitated particles, filtration of the precipitate from the water and, usually, some level of drying. (In cases where metals removal depends on adsorption of key metals by ferrihydrite precipitates, ferric chloride may be added to the solution in a polishing step. However, ferric chloride, which is acidic, is not applied where extremely alkaline pH is required to effect metals removal.) Dried filtrates, which typically contain only 10-15 percent solids, are then trucked to landfills or stored on site. Alkali-precipitated filtrates tend to pass even rigorous leach tests such as the EPA Method 1311 procedure – the TCLP (Toxicity Characteristic Leach Procedure) – so can be deposited in ordinary landfills.

Unlike remediation practices at numerous coal mines, metal mines tend not to rely on addition of natural rock carbonate (limestone, dolostone, magnesium carbonate) for water treatment due to the need for meeting standards protective of aquatic life and human health. In addition, slow reaction times and a general inability to push solution pH into the very alkaline range (pH >10) required to effect the levels of metals removal necessary for water quality compliance also preclude reliance on these natural rock carbonates. By extension, the family of limestone drains (SAPS, anoxic limestone drains, limestone channels, etc.) are not generally employed other than to pre-treat low pH waters.

Many metallic elements that, once dissolved in water, can cause environmental problems for aquatic life, agriculture, or human health can be removed to near acceptable levels by mixing very low pH solutions with limestone, dolostone, or magnesium carbonate. (If pH of the pollutant source solution exceeds about 3.5 – 4.0, and metal concentrations still exceed standards, then amendment with natural rock carbonate, which tend to buffer in the range of pH of 8, will cause very little more metal to precipitate from solution.) Dissolved metals that are easily precipitated from solution are those that either quickly form metal hydroxides, metal carbonates, or metals sulfates, or that effectively co-precipitate with or are adsorbed by iron oxyhydroxides. Metals that typically can indeed be removed by carbonate addition include arsenic, cobalt, copper, cadmium, iron and to a lesser extent, lead. Elements that are not readily removed by addition of natural rock carbonates include manganese and zinc. Zinc, for instance, does not easily sorb to ferrihydrite; nor does it readily precipitate as either an hydroxide or a carbonate. Manganese, which is stable as manganese oxide under oxidizing conditions, forms extremely slowly in natural systems and does not readily co-precipitate with Fe-oxides or hydroxides.

Based on the above, geochemical models that predict precipitation (removal) of zinc from solution due to neutralization of acid solutions should be viewed with circumspection; most models implicitly assume equilibrium and do not account for reaction time. Unless precipitation rates are known to be fast, equilibrium assumption-based results may provide very misleading predictions about water quality that can be derived from solution mixtures. The assumption that equilibrium can be achieved in laboratory scale times, or in the time it takes the typical ARD solution to move into "waters of the State or of the United States" are not realistic for the precipitation of manganese oxide, Zn hydroxide, or zinc carbonate. As might be expected therefore, these two metals, manganese and zinc, typically "drive" water treatment mechanics at ARD cleanups because they require extreme pH values to promote rapid precipitation: raise the pH high enough to remove manganese and zinc, and all other metals will have been removed.

Passive or single-pass water treatment.

Passive treatment systems, most notably artificial or manufactured wetland treatment systems, are perhaps talked about more at metal mine cleanups than applied. Where successful, wetland treatment systems appear either to be required to meet permissive cleanup standards, or are applied to remove only minimal amounts of metal from solutions of very constant composition and constant flow. In this author's opinion, wetland treatment systems cannot be expected to work effectively to simultaneously (a) remove multiple metals (b) to regulatory levels (c) in waters of variable composition (d) year round (e) where temperatures range from well below freezing to well above freezing (f) for solution of pH less than about 4.0.

Certainly, the so-called passive wetland treatment systems are not really passive: they require periodic maintenance, sometimes extensively so. But that well-known fact notwithstanding, such systems have not consistently removed metals and compounds to regulatory levels. Moreover, single pass wetlands cannot simultaneously remove multiple metals if such metals require both oxidizing and reducing conditions. For instance, while dissolved Fe and SO_4 both may be removed from an Fe-Mn-SO_4 system through simultaneous sulfate reduction and iron-sulfide precipitation, Mn cannot be removed in real time in such a system because MnO equilibrates with solutions of higher eH.

Mechanisms for metals removal via artificial or manufactured wetlands appear to be poorly studied in general, although there are indeed some fairly complete evaluations. Typical field tests measure metal concentrations going into and coming out of the wetland, yet fail to examine the residence of the metals or sulfur in the wetland. When detectable sulfur odors appear after mine drainage is funneled through a wetland, it is generally assumed, correctly, that sulfate is being reduced to H_2S. Many studies presume further, based on geochemical modeling but without field evidence, that metal sulfides have formed from the dissolved metals and reduced sulfur. Removal mechanisms, particularly adsorption by organics, are not typically considered. A synthesis of total system behavior for various fluid compositions seems yet to have been compiled.

Despite these criticisms of artificial wetlands passive treatment, some passive systems have shown success. The Biopass® system (Mudder et al., 1995) has been successfully used to treat draindown fluids from abandoned cyanide heap leach pads containing cyanide and metal cyanide species in a neutral to alkaline media. These anaerobic systems sometimes require polishing to remove metals to the finer level required for discharge regulations, but alone do not remove manganese (Terry Mudder, pers. comm).

Developing water treatment technologies.

Many systems now being tested are categorized either as "permeable reactive barriers" or "deep aquifer remediation tools." PRB's serve any of several purposes:

- minimize oxygen infiltration by sequestering oxygen, typically in a nutrient laden fine organic material;
- provide organic "food" source to sulfate reducing bacteria to reduce sulfate to sulfide and, perhaps, precipitate metal sulfides
- sequester metals or sulfate in the barrier material by providing critical reactants along a groundwater flow path.

PRB's typically consist of a ditch or trench placed downgradient of a shallow contaminant plume ("upwind" in the case of oxygen consuming PRB's) filled with the reactive material. Such trenches are periodically excavated and re-filled with reactive materials.

Similar systems placed in more deeply-contaminated zones or plumes have been called deep aquifer remediation tools, or DARTS (C.D. Wilkowske, USGS, pers. comm.). These consist of a set of selectively spaced wells filled in the contaminant plume zone with any of a variety of reactive materials, including those described above. Other potential reactants include:

- zero valent iron (to reduce sulfate)
- activated aluminum
- ferric oxyhydroxide coated sand or gravel
- iron-oxide coated sand
- manganese-dioxide coated sand
- ion exchange resins
- lateritic or other reactive soils.

One developing technology that offers promise for in situ remediation of ARD involves application of liquid organic nutrients to promote sulfate reduction and, possibly, metal sulfide precipitation in saturated systems. Liquid organics might consist of methanol, ethanol, dissolved brewers yeast or any of a large family of liquid organics that might serve as an energy source for sulfate reducing bacteria. Organics might be applied to saturated ARD-producing backfill, ARD groundwater plumes, or even pit lakes. One critical criteria for application is that the contaminated fluid be stationary or slow-moving enough to allow adequate reaction time. Applications require solution mixing through injection and withdrawal wells or some other mechanism.

Another developing technology for ARD control that is being viewed with growing interest is "mineral passivation." In theory, reactive mineral surfaces such as sulfide minerals, if coated with long-lasting, un- or weakly-reactive, benign materials, should reduce reaction rates and could promote compliant discharges if the ARD water mixed with and was sufficiently diluted by a clean water source. One such passivation material, potassium permanganate, is being tested by the University of Nevada-Reno. Silicate coatings also have been tested.

One obstacle to overcome, particularly in promoting passivation technologies for older ARD-generating source rocks, is the effect of re-solution of metal and acid-releasing minerals that form upon evaporation of ARD. These easily soluble evaporite minerals, which typically are hydrated iron sulfates, store metals and acid and to tend to quickly release same when re-saturated. If the stored acids thus attack the passivation media, the benefits of passivation might quickly pass.

SUMMARY

The need for "walk away" solutions to mine water problems helps drive research in many directions. Passive or low-maintenance procedures are being developed for both physical barriers and chemically reactive systems. Given the complexity of individual mines and the diversity of metallic mineral deposits, it seems unlikely that a one-size-fits-all solution will be available soon. Before applying any new system, detailed site geology, hydrology and geochemistry must be integrated with properly-scaled laboratory tests to find the most reliable solutions. Controlling water contact with ARD generating materials remains the most apparently reliable means of preventing or minimizing ARD. Pre-mine planning should strongly consider the placement of ARD-generating waste rock relative to water, and evaluate the cost of reclamation as an overall factor in evaluating the worth of a mineral deposit. Perpetual water treatment may be economically feasible for some deposits provided state laws allow such practices. Generally, however, it appears wise to avoid perpetual water treatment and operations that will require such. Physical barriers to ARD generation may offer short term, walk away solutions to ARD whereas long term water management and water treatment requirements provide uncertainty. Developing chemical technologies may reduce the costs of long-term treatment enough to make some deposits economically viable and mine cleanups more feasible.

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