Acid Mine Drainage and Effects on Fish Health and Ecology: A Review

For:

U.S. Fish and Wildlife Service, Anchorage Fish and Wildlife Field Office,

Anchorage, Alaska, 99501

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Purpose

In Alaska, several large mine projects are currently proposed, ranging from open-pit, hard rock mines to strip mines for extracting coal. These large-scale projects have the potential to impact fish and wildlife resources through alteration or removal of vast areas of habitat. The U.S. Fish and Wildlife Service (Service) is responsible for managing fish and wildlife resources for the American public and in carrying out its mission, participates in pre-development activities for industrial projects. This report was commissioned to provide information to the Conservation Planning Assistance branch of the Anchorage Fish and Wildlife Field Office to aid in review of documents required as part of the permit process with the U.S. Environmental Protection Agency (EPA), U.S. Army Corps of Engineers and the State of Alaska.

Acid Mine Drainage Overview

Acid rock drainage (ARD) is produced by the oxidation of sulfide minerals, chiefly iron pyrite or iron disulfide (FeS₂). This is a natural chemical reaction which can proceed when minerals are exposed to air and water. Acidic drainage is found around the world both as a result of naturally occurring processes and activities associated with land disturbances, such as highway construction and mining where acid-forming minerals are exposed at the surface of the earth. These acidic conditions can cause metals in geologic materials to dissolve, which can lead to impairment of water quality when acidic and metal laden discharges enter waters used by terrestrial or aquatic organisms.

Chemistry of Acid Rock Drainage

The reaction of pyrite with oxygen and water produces a solution of ferrous sulfate and sulfuric acid. Ferrous iron can further be oxidized producing additional acidity. Iron and sulfur oxidizing bacteria are known to catalyze these reactions at low pH thereby increasing the rate of reaction by several orders of magnitude (Nordstrom and Southam 1997). In undisturbed natural systems, this oxidation process occurs at slow rates over geologic time periods. When pyrite is exposed to oxygen and water it is oxidized, resulting in hydrogen ion release - acidity, sulfate ions, and soluble metal ions as shown in equation 1. The acidity of water is typically expressed as pH or the logarithmic concentration of hydrogen ion concentration in water such that a pH of 6 has ten times the hydrogen ion content of neutral pH 7 water.

$$2\text{FeS}_{2(s)} + 7\text{O}_{2} + 2\text{H}_{2}\text{O} \rightarrow 2\text{Fe}^{+2} + 4\text{SO}_{4}^{-2} + 4\text{H}^{+}$$
(1)

Further oxidation of Fe⁺² (ferrous iron) to Fe⁺³ (ferric iron) occurs when sufficient oxygen is dissolved in the water or when the water is exposed to sufficient atmospheric oxygen (equation 2).

$$2Fe^{+2} + \frac{1}{2}O_2 + 2H^+ \longrightarrow 2Fe^{+3} + H_2O$$
⁽²⁾

Ferric iron can either precipitate as $Fe(OH)_3$, a red-orange precipitate seen in waters affected by acid rock drainage, or it can react directly with pyrite to produce more ferrous iron and acidity as shown in equations 3 and 4.

$$2Fe^{+3} + 6H_2O <-> 2Fe(OH)_{3(s)} + 6H^+$$
 (3)

$$14Fe^{+3} + FeS_{2(s)} + 8H_2O \longrightarrow 2SO_4^{-2} + 15Fe^{+2} + 16H^+$$
(4)

When ferrous iron is produced (equation 4) and sufficient dissolved oxygen is present the cycle of reactions 2 and 3 is perpetuated (Younger, et al., 2002). Without dissolved oxygen equation 4 will continue to completion and water will show elevated levels of ferrous iron (Younger, et al., 2002). The rates of chemical reactions (equations 2, 3, and 4) can be significantly accelerated by bacteria, specifically *Thiobacillus ferrooxidans*. Another microbe, *Ferroplasma Acidarmanus*, has been identified in the production of acidity in mine waters (McGuire et al. 2001)

Hydrolysis reactions of many common metals also form precipitates and in doing so generate H^+ . These reactions commonly occur where mixing of acidic waters with

substantial dissolved metals blend with cleaner waters resulting in precipitation of metal hydroxides on stream channel substrates (Equations 5 through 8).

$$Al^{+3} + 3H_2O <-> Al(OH)_{3(s)} + 3H^+$$
 (5)

$$Fe^{+3} + 3H_2O <-> Fe(OH)_{3(s)} + 3H^+$$
 (6)

$$Fe^{+2} + 0.25 O_2 + 2.5 H_2 O <-> Fe(OH)_{3(s)} + 2H^+$$
(7)

$$Mn^{+2} + 0.25 O_2 + 2.5 H_2 O <-> Mn(OH)_{3(s)} + 2H^+$$
(8)

Metal sulfide minerals in addition to pyrite may be associated with economic mineral deposits and some of these minerals may also produce acidity and SO_4^{-2} . Oxidation and hydrolysis of metal sulfide minerals pyrrhotite (Fe_{1-x}S), chalcopyrite (CuFeS₂), sphalerite ((Zn, Fe)S) and others release metals such as zinc, lead, nickel, and copper into solution in addition to acidity and SO_4^{-2} (Jennings et al., 2000; Younger et al., 2002).

Acid Mine Drainage

Acid rock drainage occurs when sulfide ores are exposed to the atmosphere, which can be enhanced through mining and milling processes where oxidation reactions are initiated. Mining increases the exposed surface area of sulfur-bearing rocks allowing for excess acid generation beyond natural buffering capabilities found in host rock and water resources. Collectively the generation of acidity from sulfide weathering is termed Acid Mine Drainage (AMD).¹ Mine tailings and waste rock, having much greater surface area than in-place geologic material due to their smaller grain size, are more prone to

¹ As this literature review is focused on mining, the term AMD will be used in the text, yet rocks found in undisturbed environments are similarly able to generate acidity (or ARD) without the anthropogenic influence of mining. The term Mine Influence Water is also synonymous.

generating AMD. Since large masses of sulfide minerals are exposed quickly during the mining and milling processes, the surrounding environment can often not attenuate the resulting low pH conditions. Metals that were once part of the host rock are solubilized and exacerbate the deleterious effect of low pH on terrestrial and aquatic receptors. Concentrations of common elements such as Cu, Zn, Al, Fe and Mn all dramatically increase in waters with low pH. Logarithmic increases in metal levels in waters from sulfide-rich mining environments are common where surface or groundwater pH is depressed by acid generation from sulfide minerals.² These environmental, human health, and fiscal consequences, if not mitigated, can have long-lasting effects. Acid mine drainage continues to emanate from mines in Europe established during the Roman Empire prior to 467 AD (CSS, 2002). Georgius Agricola's De Re Metallica (1556), the first and seminal treatise on mining exhibits detailed woodcut illustrations not only of the known mechanics of 16th Century mining, but also depictions of the devastation of streams. The cost of mitigation of environmental damage from acid mine drainage is great. The U.S. Forest Service (USFS) estimates that between 20,000 to 50,000 mines are currently generating acid on lands managed by that agency; with negative impacts from these mines affecting some 8,000 to 16,000 km of streams (USDA, Forest Service 1993). Many of these mines are small abandoned facilities located in remote areas of the western United States and originating prior to modern environmental controls. However, several large scale mines developed in the latter half of the twentieth century have declared bankruptcy and left tax payers with the responsibility of treating acid waters in perpetuity. Examples include the Zortman Landusky Mine in Montana, the Summitville Mine in Colorado, and the Brohm Mine in South Dakota. The largest and most expensive sites that EPA has listed under the Comprehensive Environmental Resource Compensation and Liability ACT (CERCLA; aka Superfund) are mining sites in the West, including Iron Mountain Mine in California, Bunker Hill in Idaho, and the Butte-Clark Fork River complex in Southwestern Montana. Human health risks and ecological injury, chiefly from elevated metals, have been identified by EPA and natural resource trustees at many of these mega-mining Superfund sites.

Acidic drainage has been identified as the largest environmental liability facing the Canadian mining industry and is estimated at \$2 to \$5 billion dollars (MEND 2001). In response to the challenge presented by mitigation of AMD, 200 technology-based reports were generated to evaluate sampling, prediction, prevention, treatment and monitoring of potentially acid-generating materials and locations. A 1986 estimate for Canada suggests

² Note: The authors recognize that AMD and elevated metal levels in water are inextricably linked, however the purpose of this report is to assess the effect of acidity on fisheries independent from elevated metals.

that acid-generating tailings cover 12,000 hectares plus an additional 350 million tons of mine waste rock were noted (MEND 2001).

Effect of Acid Mine Drainage on Aquatic Resources

Once acid drainage is created, metals are released into the surrounding environment, and become readily available to biological organisms. In water, for example, when fish are exposed directly to metals and H^+ ions through their gills, impaired respiration may result from chronic and acute toxicity. Fish are also exposed indirectly to metals through ingestion of contaminated sediments and food items. A common weathering product of sulfide oxidation is the formation of iron hydroxide (Fe(OH)₃), a red/orange colored precipitate found in thousands of miles of streams affected by AMD. Iron hydroxides and oxyhydroxides may physically coat the surface of stream sediments and streambeds destroying habitat, diminishing availability of clean gravels used for spawning, and reducing fish food items such as benthic macroinvertebrates. Acid mine drainage, characterized by acidic metalliferous conditions in water, is responsible for physical, chemical, and biological degradation of stream habitat.

Water contaminated by AMD, often containing elevated concentrations of metals, can be toxic to aquatic organisms, leaving receiving streams devoid of most living creatures (Kimmel 1983). Receiving waters may have pH as low as 2.0 to 4.5, levels toxic to most forms of aquatic life (Hill 1974). Data relating to specific effects of low pH on growth and reproduction (Fromm 1980) may be related to calcium metabolism and protein synthesis. Fromm (1980) suggested that a "no effects" level of pH for successful reproduction is near 6.5, while most fish species are not affected when the pH is in a range from 5.5 to 10.5. Howells et al. (1983) reported interactions of pH, calcium, and aluminum may be important to understanding the overall effects on fish survival and productivity. Several reports indicate low pH conditions alter gill membranes or change gill mucus resulting in death due to hypoxia. Hatchery raised salmonids can tolerate pH 5.0, but below this level hemeostatic electrolyte and osmotic mechanisms become impaired (Fromm 1980).

A study of the distribution of fish in Pennsylvania streams affected by acid mine drainage (Cooper and Wagner 1973) found fish severely impacted at pH 4.5 to 5.5. Ten species revealed some tolerance to the acid conditions of pH 5.5 and below; 38 species were found living in waters with pH values ranging from 5.6 to 6.4; while 68 species were found only at pH levels greater than 6.4. Further, these investigators reported complete loss of fish in 90% of streams with waters of pH 4.5 and total acidity of 15 mg/L. Healthy, unpolluted streams generally support several species and moderate abundance of

individuals; whereas impacted streams are dominated by fewer species and often low to moderate numbers of only a few organisms. Streams affected by acid mine drainage are poor in taxa richness and abundance. In older studies (Warner 1971), more species of insects and algae were found in unpolluted West Virginia streams (pH > 4.5) compared to those streams polluted by acid (pH 2.8 to 3.8). Reductions of benthic fauna in a West Virginia stream severely affected by acid mine water were reported by Menendez (1978). In more recent studies (Farag et al. 2003), some streams in the Boulder River watershed in Montana impacted by nearly 300 abandoned metal mines are devoid of all fish near mine sources. Populations of brook trout (Salvelinus fontinalis), rainbow trout (Oncorhynchus mykiss), and cutthroat trout (O. clarki) were found further downstream and away from sources of acid mine drainage. In a 2003 study evaluating the effect of localized habitat degradation from a gold mine near the Yukon River (in AK?) on population structure of salmon, it was suggested that coho salmon (O. kisutch) may be at risk of losing genetic diversity due to localized habitat degradation (Olsen et al. 2004). The abandoned Britannia copper mine in British Columbia has been releasing acid mine drainage into local waters for many years. Investigators compared fish abundance, distribution and survival at contaminated and non-contaminated areas (Barry et al. 2000). Chum salmon (O. keta) fry abundance was significantly lower near the impacted waters (pH < 6 and dissolved copper > 1 mg/L) than the reference area. The investigators also reported that laboratory bioassays confirmed acid mine drainage from the Britannia Mine was toxic to juvenile chinook (O. tshawytscha) and chum salmon. Chinook salmon smolt transplanted to surface cages near Britannia Creek experienced 100% mortality within 2 days (Barry 2000).

The scientific literature is replete with studies designed to quantify the adverse environmental effects of acid mine drainage on aquatic resources. Most recent investigations focus on multiple bioassessments of large watersheds. These assessments include water and sediment chemistry, benthic macroinvertebrate sampling for taxa richness and abundance, laboratory acute water column evaluations, laboratory chronic sediment testing, caged fish within impacted streams, and development of models to explain and predict impacts of acid mine drainage on various aquatic species (Soucek et al. 2000, Woodward et al. 1997, Maret and MacCoy 2002, Hansen et al. 2002, Kaeser and Sharpe 2001, Baldigo and Lawrence 2000, Johnson et al. 1987, Griffith et al. 2004, Schmidt et al. 2002, Martin and Goldblatt 2007, Beltman et al. 1999, Hansen et al. 1999, Boudou et al. 2005).

Major Environmental Incidents Caused by Acid Mine Drainage

Releases of acid mine waters containing elevated metal and cyanide concentrations with resulting impacts to landscapes and waterways have been documented by several organizations (UNEP 2002). Fish kills resulting from the uncontrolled release of acid and metals from mine wastes into receiving streams have been reported from world wide areas in which hard rock mining, milling, and smelting activities have occurred. In 1998, a mine flood incident in Spain deposited some 6 million m³ of acid water over the banks of the Guadiamar River with metal and sulfide rich sediments. The U.S. EPA described 66 incidents in which environmental injuries from mining activities are detailed (EPA 1995). Nordstrom and Alpers (1999) reported that millions, perhaps billions, of fish have been killed from mining activities in the U.S. during the past century.

In 1989, a large fish kill (> 5000 salmonids) in Montana's Clark Fork River resulted when acid, metalliferous tailings and efflorescent metal salts were flushed into the river during a thunderstorm event. Within 20 minutes, the acidity of the river water was reduced by several orders of magnitude, and copper concentrations rose dramatically. Fish gill tissue copper levels indicated acute toxicity (Munshower et al. 1997). The Sacramento River in California has experienced several fish kills due to sudden releases of acid water from upstream mine areas; more than 20 fish kills were reported since 1963, and in 1967, at least 47,000 fish died (Nordstrom et al. 1977).

Prediction of Acid Mine Drainage

Accurate prediction of acidic drainage from proposed mines is recognized by both industry and government as a critical requirement of mine permitting and long-term operation. Substantial emphasis has been placed on prediction of acid drainage associated with coal development in the Eastern U.S. (Pennsylvania DEP 1998; Skousen and Ziemkiewicz, 1996), and metal mining in the Western U.S. and in Canada (MEND 2001). The standard protocols for evaluating geologic materials for their ability to produce AMD are generally agreed upon within the scientific community, yet much uncertainty remains in the ability of scientists and engineers to predict the ultimate drainage quality years in the future, as many complex variables influence acid generation and neutralization.

The backbone of predicting acid generating potential from any geologic formation is the ability to characterize the presence and quantity of both acid-forming minerals and

neutralizing minerals in the geologic materials to be unearthed during mining operations. Typically samples are collected by drilling during exploration, analyzed and interpreted with respect to their risk of acid formation. Methods for characterizing acid-forming minerals were developed during the 1970's in areas of the eastern U.S. mined for coal (Smith et al., 1974). Ultimately, these techniques lead to a standardized EPA protocol for characterization of mine soil and overburden (Sobek et al., 1978). In these analytical approaches, the amount of sulfur present in geologic materials is measured and attributed to being either an acid-forming mineral such as pyrite (FeS₂) or non-acid-forming mineral such as gypsum ($CaSO_4$ •2 H_2O). The relative amount of acid-forming minerals is then contrasted to the amount of neutralizing minerals such as calcite (CaCO₃) to develop a prediction of the probability of acid generation. The ratio of neutralization potential (NP) to acid potential (AP) is commonly presented in graphical interpretations with the inference that geologic materials with an abundance of NP are unlikely to generate acidic drainage. In Eastern coal mines NP:AP ratios <1 commonly produce acidic drainage, NP:AP ratios between 1 and 2 may produce either acidic or neutral drainage and NP:AP ratios >2 should produce alkaline water (Skousen et al., 2002). However, this index does not always accurately predict the resultant acid generation from a mine. Of 56 mines evaluated by Skousen and others (2002) 11% did not conform to the expected results based on NP:AP ratios, including four sites with ratios > 2: these sites eventually produced acidic drainage. Furthermore, the applicability of the experimental findings from West Virginia coal deposits hosted in sedimentary rock to metal mines developed in igneous parent material is unknown. Sedimentary sulfide mineralization is caused by diagenetic interaction between microbes, Fe and S in a low temperature saturated environment resulting in formation of poorly crystallized pyrite while igneous pyrite is formed by high temperature magmatic fluids or molten rock cooling slowly to form well developed crystalline structure. Mineralogical variation between each geologic domain causes dissimilar reactivity to weathering conditions and leads to laboratory variability in assessment. Recurrence of inaccurate interpretations between laboratory and field data has caused investigators to reexamine the adequacy of the analytical methods. Because of the challenges inherent in interpreting laboratory data and predictive models, forecasting future water quality impacts from AMD should not be considered routine and robust, rather they should be considered an area of uncertainty and on-going research.

If the rates of weathering and availability of acid-forming and neutralizing minerals are dissimilar the potential exists that acid-generation may overwhelm the pool of resident NP. Slowly reacting neutralizing minerals may lead to generation of acidic water. Sherlock and others (1995) evaluated the rates of weathering of sulfides, carbonates and silicates and determined that sulfide minerals reacted fastest and cautioned that conventional methods of prediction do not consider the specific mineralogy and reaction kinetics are at risk of erroneous interpretations and predictions.

Research has also focused on the presence of minerals which are detected by the NP analytical method, yet do not contribute to production of alkalinity. Siderite (FeCO₃) has been found in mining environments and while contributing to the measured NP, no actual neutralization has been observed in the field (Frisbee and Hossner, 1989). In an evaluation of 31 overburden³ samples containing siderite, pyrite, calcite and quartz using 4 dissimilar methods for NP determination, siderite-containing samples showed wide variation in NP between three laboratories (Skousen et al., 1997). Using the standard Sobek (1978) test for NP, Weber and others (2004) showed that up to 432 hours may be required for complete hydrolysis of siderite-containing samples in laboratory testing, implying that inaccurate interpretations of NP are common for rock containing this siderite since routine laboratory tests would not be run for such a great length of time. The limitations of laboratory testing for NP without supporting mineralogical characterization can often lead to overestimation of NP (Lawrence and Scheske, 1997; Paktunc, 1999). Conventional laboratory methods for determination of NP employ wet chemical methods where the presence of carbonates in soil is made based on titration of a sample with acid followed by back titration with a base. No determination of the mineralogical source of carbonate is made by the NP test. Similarly, quantification of acid-forming minerals is challenging in a laboratory setting. Analysis of total sulfur levels is routinely accomplished using standardized laboratory equipment, however the typical Sobek method employs subsequent acid extractions to distinguish between acidforming minerals containing sulfur and non-acid sulfur minerals. In research using pure mineral samples, Jennings and Dollhopf (1995) showed that conventional analytical methods failed to accurately characterize acid-forming minerals. Incomplete recovery of sulfur-bearing minerals has been observed using the Sobek method since a residual sulfur fraction is commonly observed in laboratory testing implying the standard method of dissolution failed to solubilize or dissolve the sulfide found in the sample. Regional variation is observed in the interpretation of residual sulfur leading to non-standardized findings. The residual sulfur component is commonly characterized as non-acid forming organic sulfur in sedimentary rock and as acid-forming sulfide in metal mining samples. Collectively, the static tests described have significant limitations in accurately predicting whether acidic drainage will form.

Kinetic⁴ tests are commonly run as a companion to static⁵ testing to measure the weathering behavior of geologic material when exposed to field conditions. Kinetic tests

³ Overburden is defined as geologic material overlying a resource of interest. In surface mining overburden is typically removed as waste material.

⁴ Kinetic tests of mine waste are typically accomplished by monitoring the chemical constituents in water resulting from simulated laboratory weathering or actual field site weathering of mine waste materials over a period of months to years. Water is leached through the geologic material and recovered as drainage.

may be run in a laboratory column or in the field in large containers. The quality and quantity of leachate is subsequently evaluated to offer a supporting interpretation to static testing. Six large columns each containing 1.6 tons of waste rock were evaluated over a period of 3 years showing two pH controls: 1) sulfide oxidation with calcite dissolution sustaining a neutral pH, and 2) simultaneous silicate and sulfide weathering occurring at an equilibrium pH of 3-4 (Stromberg and Banwart, 1999). During the period of investigation the columns either remained at near-neutral pH or became acidic after 0.5 to 3 years lag time. The lag time in appearance of low pH was caused by mineralogical reactions occurring in the waste rock that either neutralized the acidity formed until exhausted or rendered non-reactive, or the acid reactions required a period of time to initiate. In a companion study Stromberg and Banwart (1999) showed there was a large difference in weathering rates based on particle size. In the columns particles smaller than 0.25 mm were responsible for approximately 80% of both the sulfide oxidation and silicate dissolution. Calcite particles larger than 5-10 mm were found to react too slowly to neutralize acid produced by sulfide oxidation. Similar unique reaction kinetics has been observed at the Bingham Canyon Mine in Utah where fresh waste rock exhibits a paste pH^6 of 7.0. Within 6 years the pH of the waste rock dumps declines to 4.7 further decreasing to pH 3.7 after 50 years of weathering (Borden 2001). Scharer and others (2000) observed that NP was strongly related to particle size and particles greater than ¹/₄ inch (6.4 mm) were only 20% consumed at the onset of acid conditions. Kinetic data on the depletion rate of NP supplemented by geochemical modeling suggests that waste rock with NP/AP ratios as high as 5 may turn acidic in the long term: this is much different than the results mentioned above by Skousen (2002) who identified 2 as the ratio below which NP/AP ratios would generally not become acidic. If neutralizing minerals are depleted or non-reactive long-term generation of acidic drainage may be initiated with potentially dire ecological consequences if untreated.

Notable uncertainty exists in the long-term predictions of acid generation from geologic materials found in mining environments. Evaluation of Environmental Impact Statements from 25 mines performed by Kuipers and others (2006) showed 15 of 25 mines (60%) exceeded surface water quality standards for metals and pH after permitting.

⁵ Static testing is the laboratory analysis of geologic materials for chemical characteristics such as total metal levels, pH or total S. Static testing is the analysis of the bulk concentrations in rock or soil material.

⁶ Paste pH or saturated paste pH is the measurement of pH in a slurry of soil or rock with deionized water after allowing time for reaction of the slurry. Paste pH is a measure of the soil solution indicative of the acidity of soil water in the context of plant growth or leaching to groundwater.

Similarly, kinetic tests performed using humidity cells⁷ over a 3 to 7 year period showed that rates of acid generation have a 50% chance of stabilizing within one year while the remainder of the humidity cells fluctuated significantly throughout the test periods (Morin and Hutt, 2000).

Assessment of Acid Rock Drainage and Metals Release

Canada's Mine Environment Neutral Drainage (MEND) Program was implemented to develop and apply new technologies to prevent and control acid drainage. Recognizing acid drainage as the greatest environmental problem facing the mining industry and the regulatory agencies' responsibility to protect the environment and safeguard human health, the MEND Program was funded jointly by Natural Resources Canada and The Mining Association of Canada. In 2005, MEND released a report titled *List of Potential Information Requirements in Metal Leaching/Acid Rock Drainage Assessment (ML/ARD) and Mitigation Work* (Price 2005). The purpose of this document is to improve the assessment and mitigation of metal leaching/acid rock drainage. It achieves this goal by providing a comprehensive list of information and data necessary to assess the potential for ML/ARD, and multiple strategies for mitigation. The document is intended to be used as a general guide for the mining industry, regulators, environmental advocacy groups, and other stakeholders. The MEND program uses the term 'Acid Rock Drainage' to describe the acidic water drainage from mines.

The MEND report (Price 2005) recommends a set of informational variables and data that should be generated and developed so that informed decisions can be made with respect to the potential for acid drainage and toxic metal release. These recommendations were intended to mitigate the consequences of sulfide mineral oxidation caused by mining, milling, and other process involved in metal resource development. These information requirements are summarized in the following statements:

<u>General site characteristics</u>: location, access, climate, ecology, history of previous mining, waste materials, geology, hydrology, mineralogy, descriptions of all materials that will be excavated or exposed, soils, reclamation objectives, end land uses, data tables, relevant figures, and other pertinent information. This is not exhaustive and site-specific information and data will be required.

⁷ Humidity cells are laboratory equipment to simulate weathering of rock in a small benchtop enclosure where soil or rock is repeatedly wetted and dried over a period of months to years to monitor changes in drainage water quality. A humidity cell is a specialized type of kinetic testing.

<u>Specific material characterization and predictions of ML/ARD</u>: The ability to accurately predict the potential for ML/ARD requires a careful and complete characterization of all materials and waste types under the probable weathering (oxygen, bacteria, moisture, volumes of materials, etc.) conditions. Representativeness and adequacy of samples collected, measures of variability and uncertainty, and analytical procedures selected need to be appropriate. Industry-regulatory quality assurance and quality control procedures need to be followed. To be complete, predictions and assessments are to be made pre-mining (baseline data), during the operational phase, post-mining, and long-term. The document defines specific tests to define the geological and mineralogical properties of materials.

<u>Static and kinetic tests</u>: Static tests require appropriate sampling intensity, sample preparation, determinations of elemental concentrations (total and water soluble), and full acid-base accounting. Kinetic tests are recommended to evaluate reaction rates and to predict and measure drainage chemistry. Humidity cell, column test and actual field verification tests should be conducted. Monitoring of site drainage (seeps, mine drainage, pit lakes, etc.) should include parameters to be evaluated and the frequency of monitoring during and post-mining.

<u>Assessments of waste materials</u>: Waste materials may include waste rock, tailings, treatment wastes, low grade ore and overburden materials. All media require assessments and predictions for acid drainage and releases of metals. Post-disposal weathering of waste piles, including changes in pH, carbonate content, soluble weathering products (acid water and metals). Thermal properties, pore gas composition, and oxygen concentrations may be significant parameters in the assessments of long-term water quality degradation.

The MEND document (Price 2005), also provides an approach to interpretation and display of the above characterization data. Identification of ARD generating materials is important, but toxicity from metals with neutral pH can be significant factors and are not to be overlooked. Predicting drainage chemistry is based on data and information gathered and their proper interpretation. Factors include the weathering environment and climate, data predicting ARD/ML potential, anticipated rates of leaching from mine wastes and mine workings, metal releases based on kinetic tests and geochemical modeling. Additional issues are in stream alkalinity, dilution, and natural attenuation.

Estimating environmental and ecological impacts should be based on identifying potential receptors, endangered species, sensitivity and distributions of selected species and forms of exposure. A conceptual site model can be useful in determining mechanisms of contaminant release, contaminant pathways and receptors of concern. Acute and

chronic toxicity testing of identified aquatic and terrestrial receptors and pre- and postmining monitoring programs are recommended.

In the United States, the National Research Council (1999) took up the issue of metal mining recognizing the controversy associated with permitting and compliance of hardrock mining. The committee was well versed on the potential deleterious impacts of mining and spent most of their deliberations contemplating the weaknesses of the existing regulatory framework. Recommendations were put forward for the Federal agencies consideration suggesting greater coordination and use of the best available scientific practices. This report did not explore technical topics such as AMD in detail, rather the recommendations were policy oriented.

Water Quality and Acid Mine Drainage: Pre-mine Predictions and Post-mine Comparisons

A major and unique study (Kuipers et al. 2006) was conducted comparing predicted and actual water quality at several mines in the United States. The overall purpose of this study was to examine the reliability of pre-mining water quality predictions at hard rock mining operations. The approach included reviews of the history and accuracy of water quality predictions in Environmental Impact Statements (EISs) for major hard rock mines and then examined and compared actual water quality to the predictions postulated in the EISs. A total of 183 mines were identified, with 71 having reviewed EISs. The investigation focused on 25 mines for in-depth analysis. Nearly all of the EISs reviewed reported that they expected acceptable water quality (concentrations lower than relevant standards) after mitigation was taken into account. Data analyses in this report, in general, refuted these EIS predictions. The following are major findings of the investigation:

<u>Surface water:</u> Sixty percent of the case study mines (15/25) exceeded surface water quality standards due to mining-related activities. Of these, four (17%) noted a low potential to exceed standards, seven (47%) a moderate potential, two a high potential, and three had no information in their EISs for surface water quality impacts in the absence of mitigation measures. The specific water quality parameters exceeding standards varied between sites and were not specifically identified in the report.

<u>Ground water</u>: The majority (64% or 16/25) of the case study mines also exceeded drinking water standards in groundwater. At three of the mines, all in Nevada, the elevated concentrations of metals that did not meet the standards may be related to baseline conditions. However, due to mining activities, 52% of the case study mines

clearly exceeded standards in surface water. In terms of post-mitigation groundwater quality impacts, 77% (10/13) of the mines that predicted low groundwater quality impacts in their EISs were above the water quality standards. Most mines predicted no impacts to groundwater quality after mitigation were in place, but in the majority of case study mines, impacts have occurred.

<u>Metals of Concern</u>: Elements that most often exceeded standards or that had increasing concentrations in groundwater or surface water included toxic heavy metals such as copper, cadmium, lead, mercury, nickel, or zinc (12/19 or 63% of mines), arsenic and sulfate (11/19 or 58% of mines for each) and cyanide (10/19 or 53% of mines).

<u>Acid mine drainage:</u> The majority of the case study mines (18/25 or 72%) predicted low potential for acid drainage in one or more EISs. Of the 25 case study mines, 36% have developed acid drainage on site to date. Of these 9 mines, 8 (89%) predicted low acid drainage potential initially or had no information on acid drainage potential. The Greens Creek Mine in Alaska initially predicted moderate acid drainage potential but later predicted low potential for acid drainage for an additional waste rock disposal facility. Therefore, nearly all the mines that developed acid drainage either underestimated or ignored the potential for acid drainage in their EISs.

Factors Leading to Failures in Predicting Post-Mine Water Quality and Acid Mine Drainage

In the report comparing predicted and actual water quality at hard rock mines (Kuipers et al. 2006), the authors identified two types of characterization failures that led to differences between predicted water quality as speculated in EIS documents and the actual water quality either during or after mining began. The two characterization failure types were: 1) insufficient or inaccurate characterization of the hydrology, and 2) insufficient or inaccurate geochemical characterization of the proposed mine. Inaccurate pre-mining characterization and interpretation can, therefore, result in a failure to recognize or predict water quality impacts. The authors reported primary causes of hydrologic characterization, overestimations of discharge volumes, and underestimations of storm size. The primary causes of geochemical characterization failures were identified as: lack of adequate geochemical characterization, in terms of sample representativeness and sample adequacy.

In the 25 case study mines, the authors identified mitigation failures with the following primary causes: mitigation measures were not identified or they were inadequate, or not

implemented; waste rock mixing and segregation was not effective, liners leaked, tailings were spilled, or embankments failed, and land application discharge was not effective. The authors provided a table summarizing these failures (Table 1) for the 25 case study mines.

| Failure Mode | Root Cause | Examples |
|---------------------------------|--|---|
| Hydrologic Characterization | Lack of hydrologic characterization | Royal Mountain King, CA; Black Pine, MT |
| | Dilution overestimated | Greens Creek, AK; Jerritt Canyon, NV |
| | Amount of discharge underestimated | Mineral Hill, MT |
| | Size of storms underestimated | Zortman and Landusky, MT |
| Geochemical Characterization | Lack of adequate geochemical characterization | Jamestown, CA; Royal Mountain King, CA; Grouse Creek, ID; Black Pine, MT |
| | Sample size and/or representation | Greens Creek, AK; McLaughlin, CA; Thompson Creek, ID; Golden Sunlight, MT; Mineral Hill, MT; Zortman and Landusky, MT; Jerritt Canyon, NV |
| Mitigation | Mitigation not identified, inadequate, or not installed | Bagdad, AZ; Royal Mountain King, CA; Grouse Creek, ID |
| | Waste rock mixing and segregation not effective | Greens Creek, AK; McLaughlin, CA; Thompson Creek, ID; Jerritt Canyon, NV |
| | Liner leak, embankment failure or tailings spill | Jamestown, CA; Golden Sunlight, MT; Mineral Hill, MT; Stillwater, MT; Florida Canyon, NV; Jerritt Canyon, NV; Lone Tree, NV; Rochester, NV |
| | Land application ineffective | Beal Mountain, MT |

Table 1. Water Quality Predictions Failure Modes, Root Causes and Examples from Case Study Mines (Kuipers et.al, 2006).

Treatment of Acid Mine Drainage

Water treatment for elevated metal levels and acidity is a common outcome of acid mine drainage. The effectiveness and feasibility of water treatment is highly variable depending on the treatments employed and unique site characteristics. Water treatment installations may include both passive and active systems. Passive water treatment systems, typically wetlands, operate without chemical amendments and without motorized or mechanized assistance. In contrast active water treatment systems are highly engineered water treatment facilities commonly employing chemical amendment of acid mine water to achieve a water quality standard specified in a discharge permit. In-depth evaluation of AMD treatment options was not performed as part of this literature review; rather emphasis was placed on prevention of AMD formation. Active treatment systems are operational at the Berkeley Pit, Butte, Montana; Britannia Beach, British Columbia; Iron Mountain Mine, Shasta County, California; and, Idaho Springs/Clear Creek, Colorado. Passive treatment systems are most frequently employed in Appalachian coal mining regions for control of acidic drainage. Semi-passive treatment systems are also in use where alkaline amendments are added to surface water at remote sites such as the Summitville Superfund site, Colorado.

Recommendations for Acidic Drainage Minimization

Acidic drainage from mines is observed at many mine sites and the undesirable consequences of acidification are well known. Every effort should be employed to minimize the causes of acid generation. Because mineralogy and other factors (particle size, reactivity of NP and presence of oxidizers) that influence AMD formation are highly variable from one mine to another, and among different geologic materials within a proposed mine site, accurate prediction of future acid generation is difficult at best. Predicting the potential for AMD formation is costly, and of questionable reliability (Kuipers et al. 2006). In addition, concern has arisen over the lag time between waste emplacement and observation of an acid drainage problem. With acid generation, there is no general method to predict its long-term duration or to predict when acidic drainage will commence. There are historical, and now modern mining examples of long-term AMD generation requiring active treatment in perpetuity. There are two primary approaches to addressing AMD: circumvent mining sulfide rich ore deposits with high AMD potential, and implementing mitigation measures to limit potential AMD impacts. It is noted that avoiding mining of sulfide ores with the potential to form AMD may be difficult because they are most often associated with the mineral resource of interest.

Selective handling and avoidance of sulfide ore and overburden is a strategy for minimizing the risk of future acid generation (Skousen et al., 1998). In a review of selective handling of acid-forming materials in coal mining in the Eastern U.S., Perry and others (1997) found that selective handling had not eliminated acid formation due in part to the inherent difficulty in segregating benign overburden from acid-forming waste. In some mining operations acid-forming minerals can be avoided through the mine planning process or through using underground mining rather than surface mining.

Mine waste isolation and avoidance of oxidizing conditions can be performed using several methods that keep sulfides isolated from oxygen. Subaqeous disposal of tailings and waste rock below the water table is commonly practiced in Canada as a protocol for mine reclamation (Samad and Yanful, 2004). Paste backfill is a mining methodology for minimization of acid formation by backfilling mine workings using a mixture of mine tailings, Portland cement and other binders to create a waste disposal option that is both geotechnically stable and geochemically non-reactive since sufficient NP can be added to neutralize any future acidity (Benzaazoua, T.B. and B. Bussiere, 2002). Depyritization of tailings can be accomplished to remove sulfide minerals from waste products to create a benign sand fraction suitable to use as a general backfill and a companion low-volume sulfide concentrate requiring careful disposal. Most mine tailings contain small amounts of sulfide minerals that can be readily separated from non-acid forming silicate minerals using conventional mineral processing equipment to create a cleaned material with sufficient NP to ameliorate any future acidity (Benzaazoua, B. et al., 2000).

In many cases, the measures described above are most effective when used in combination and adapted to the situation at a specific site. For the most part, only limited data are available to document the long-term effectiveness of any of these controls. The Kuipers Report (2006) provides a unique view of the failure to predict the formation of AMD at many hardrock mines. There are many research investigations being conducted by university, government, and industrial entities to develop new treatment strategies for AMD. The transfer of laboratory data to site-specific conditions (climate, geology, physical properties of ores, etc.) can be problematic and significantly impact their feasibility and performance in the field.

Thorough baselines studies of the biological, hydrologic, and geochemical conditions characteristic of the unique site are required to provide a basis for long-term monitoring and provide an insight into mechanistic processes involved in AMD evolution (Edwards et al., 2000). Associated financial assurances for resource mitigation in the event of default of a mine property are also required (NRC, 1999) to ensure both short-term and long-term mitigation of AMD and the associated impacts to water quality and fisheries.

Based on review of the acid mine drainage literature it is clear that severe world-wide ecological consequences, especially for aquatic resources, have resulted from mining ore deposits with acid-forming minerals. Accurate prediction of the onset and aggressiveness of low-quality acidic water discharge is perilously difficult using the best available science. Multiple complex geochemical, biological and hydrologic factors create a daunting task for mining engineers to profitably recover mineral resources while preventing discharges of metals and acidity to surface and ground water. The deleterious effects of elevated metals levels and acidity to salmonids are clearly reported in the scientific literature. The inevitability of impacts to fisheries from AMD caused by mining is an open question and dependent on the outcome of complex geochemical reactions and human attempts to understand and mitigate their consequences. The track record of industry is replete with problems, thus little comfort is afforded by extensive pre-mine studies.

Summary

Acid mine drainage commonly forms as a result of natural geochemical processes that oxidize metal sulfides exposed at the earth's surface by mining. Oxidation of sulfur and hydrolysis of iron result in acid-sulfate waters which have been observed at thousands of historic mine sites and at operational mines where mitigation measures have failed to prevent the release of acid mine drainage to down-gradient surface waters. Resultant low pH conditions mobilize metals from waste materials resulting in degradation of water quality and impairment of aquatic health. Acid mine drainage and associated weathering products commonly result in physical, chemical and biological impairment of surface water. Pre-mine characterization of the risk of AMD formation is often inaccurate leading to notable post-mine risk to fisheries. Fisheries have been impaired world-wide by releases of AMD from mining areas. The mining industry has spent large amounts of money to prevent, mitigate, control and otherwise stop the release of AMD using the best available technologies, yet AMD remains as one the greatest environmental liabilities associated with mining, especially in pristine environments with economically and ecologically valuable natural resources. Problematic to the long-term operation of large scale metal mines is recognition that no hard rock surface mines exist today that can demonstrate that AMD can be stopped once it occurs on a large scale. Evidence from literature and field observations suggests that permitting large scale surface mining in sulfide-hosted rock with the expectation that no degradation of surface water will result due to acid generation imparts a substantial and unquantifiable risk to water quality and fisheries.

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