

The Potential for Acid Mine Drainage and other Water Quality Problems at Modern Copper Mines Using State-of-the-Art Prevention, Treatment, and Mitigation Methods

A Report by the Center for Science in Public Participation
November 20, 2014

INTRODUCTION

Northeastern Minnesotans for Wilderness asked the Center for Science in Public Participation to assess current state-of-the-art mining practices and technologies to determine whether it is possible at this time to eliminate risks to water quality and other natural resource values in the immediate and downstream areas of sulfide ore mines, should they be developed in the vicinity of the Boundary Waters Canoe Area Wilderness. This report examines several areas of mining practice and technology and acknowledges that while it is possible to reduce the risk of water contamination, it is not possible to eliminate the risks to local water resources. In addition, the track record of copper mines in North America for containing contaminants, and even for preventing large-scale releases of contaminants, suggests that these events must be carefully considered in analyzing risk to water resources.

The report is focused on copper mining, and the water quality problems that are typically encountered in the mining and concentration of copper ores. Descriptions of mine processes assume current best practices for environmental protection. Copper mining and concentrating operations are assumed to use either underground and/or open pit mining and copper concentration via flotation processing. It is further assumed that the ore being mined comes from a disseminated orebody with little acid-buffering capacity, generally leading to the need for water treatment if a discharge is required in a net precipitation area, such as northeastern Minnesota. Waste disposal is also an important issue to consider, since a significant portion of the mining waste is potentially acid-generating. Mining waste typically constitutes over 99% of all of the material that is mined, and will remain permanently on the minesite.

This report draws heavily on existing public sources of information on copper deposits and copper mining technologies. As such, this is not an original piece of research, but a compilation of information from a number of existing sources, which are referenced in this document.

COPPER DEPOSITS & COPPER MINING

Chemistry and Associated Risks of Disseminated Copper Deposits (USEPA 2014)

Exposure to hazards associated with mining disseminated¹ copper deposits (Miller 2011) can pose risks to aquatic and terrestrial ecosystems and to human health. These risks can range from insignificant to extremely harmful depending on a variety of factors that control the hazards, including site geology (both local and regional), hydrologic setting, climate, and mining and ore processing methods. There are a variety of geochemical models and approaches to understand and predict the water quality of releases to the environment. However, our ability to make predictions is limited because of data insufficiency and the inherent complexity of natural materials and their environment.

Sources of hazards from disseminated copper mines can be grouped into four broad, interrelated categories: acid-generating potential, trace elements and their mobilities, mining and ore processing methods, and waste disposal practices. The relative importance of these categories will vary from deposit to deposit, but some generalizations can be made for disseminated copper deposits as a whole.

¹ In this report the term “disseminated” copper deposits is used to refer to both magmatic Cu-Ni PGE (USGS 2012) and Cu-Au-Mo porphyry deposits (USGS 2008), which typically occur as low grade sulfide mineralization disseminated in a host (usually igneous) rock.

Mining processes expose rocks and their associated minerals to atmospheric conditions that cause weathering, which releases minerals (e.g., iron and copper sulfides) from the rock matrix. The blasting of ore and waste, and the grinding methods used in these processes create materials that have high surface areas, which accelerates the rate of weathering. Disseminated copper deposits are characterized by the presence of sulfide minerals, and oxidation of sulfide minerals creates acidity, sulfate, and free metal ions (e.g., iron in the case of pyrite). In addition, the acid produced can further accelerate weathering rates. Because most metals and other elements become more soluble as pH decreases, the acid-generating or acid-neutralizing potentials of waste rock, tailings, and mine walls are of prime importance in determining potential environmental risks associated with exposure to metals and certain elements in the aquatic environment.

In general, the rocks associated with disseminated copper deposits tend to straddle the boundary between being net acidic and net alkaline, as illustrated by Borden (2003) for the Bingham Canyon porphyry copper deposit in Utah. Acidic rock for disseminated copper deposits typically correlates with the distribution of pyrite.

Ore Processing (USEPA 2014)

Generally, two streams of materials come from a mine: ore and waste rock. Ore is rock with sufficient amounts of metals to be economically processed. Waste rock is material that has little or no economic value at the time of disturbance, although it may have recoverable value at a future time (i.e., under different technological or economic conditions).

The most profound influence that ore processing can have on long-term management of a mine site centers on the fate of pyrite (Fuerstenau et al. 2007). Traditionally, alkaline and acidic tailings were discharged together, thereby contributing to the acid-generating potential of the tailings storage facility. It is possible to use a technique called selective flotation to separate most of the pyrite into the cleaner circuit tailings (acidic) with the rougher tailings comprising predominantly alkaline minerals. The acidic tailings would need to be stored separately and kept isolated from oxygen.

Final products of the flotation process are a concentrate which typically includes gold and platinum group metals (PGEs), perhaps a molybdenum concentrate, and pyritic tailings (secondary or cleaner tailings). The gold in disseminated copper deposits is partitioned among the copper-sulfide minerals (chalcopyrite, bornite, chalcocite, digenite, and covellite), pyrite, and free gold (Kesler et al. 2002). Gold associated with the copper minerals would stay with the copper concentrate and be recovered at an off-site smelter. Gold associated with pyrite would end up in the tailings storage facility unless a separate pyrite concentrate were produced, and gold could be recovered from this concentrate by a vat leaching cyanidation process (Logsdon et al. 1999; Marsden and House 2006).

The process for removing metal sulfides from ore is not 100% efficient. At some point the cost of recovering more metals exceeds their value, so the amount of metals left in the tailings represents a tradeoff between revenues from more complete ore processing and extraction costs. The residual metals remaining with the tailings would be discharged to a tailings storage facility along with the residue of blasting agents, flotation reagents, and inert portions of the ore.

Wastewater Treatment / Treatment Plant Failures (USEPA 2014)

Under any mine scenario water in contact with tailings, waste rock, ore, product concentrate, or mine walls would leach minerals from those materials. In addition, chemicals would be added to the water used in ore processing. Most of the water used to transport tailings or concentrate or used in ore processing would be reused. Leachates collected from tailings storage facilities or waste rock piles would be stored in the tailings storage facility or treated for use or discharge, but leachate that escaped collection would flow to groundwater, and could likely affect streams. Waste rock used in the construction of

berms, roads and other mine structures would be leached by rain and snowmelt, but that source is small relative to the waste rock piles and dams. Waste rock is generally tested in humidity cells, and the leachate produced is assumed to have the mean concentrations reported in these tests. Mine pit water would also likely be used or treated for disposal. Treatment of surplus water on the site would be required to meet applicable standards and other permit limits for discharge. In the environmental assessment process it is always assumed, after considerable review, that the treatment processes will perform as planned. However in practice water treatment is a much more fickle process, and normally requires considerable fine tuning to adequately treat the actual (rather than theoretical) chemical composition of the contaminants.

An even larger problem with an actual mine is collecting all the seepage that is produced. It is one thing to project that a collection well, cutoff wall, or collection trench will intercept the contaminated water, and it is another thing to make this happen at the required efficiencies in the real world of complicated geomorphology and wide-swings of the hydrologic cycle.

Water treatment generates sludges or brines containing material removed from the wastewaters plus materials added to the water, such as precipitating agents. These materials are usually deposited in a tailings storage facility. Copper and other metal concentrations in these wastes would be high, so they likely would be significantly toxic if spilled into surface waters by a tailings pipeline failure (a high-probability but typically low-impact occurrence) or a tailings dam failure (a low-probability but high-impact occurrence).

If a gold-processing facility is part of the processing, a separate water treatment system would typically be required to decompose or recycle the cyanide used in the separation of gold. That system would have the potential to fail, releasing the cyanide solution to a stream or groundwater. Cyanide in the tailings would flow to a tailings storage facility, where it could degrade or combine with copper or other metals.

Probability of Contaminant Releases (USEPA 2014)

Water collection and treatment failures are a common feature of mines. A review of the 14 porphyry copper mines that have operated for at least 5 years in the United States found that all but one (93%) had experienced reportable aqueous releases (the definition of a reportable release is determined by local regulations and differs among mines), with the number of events ranging from 3 to 54 (Earthworks 2012). Mine water releases range from chronic releases of uncaptured leachate to acute events caused by equipment malfunctions, heavy rains, or power failures. The USEPA has observed that some operators continue to discharge when they know that treatment is ineffective and not meeting standards. Hence, the record of analogous mines indicates that releases of water contaminated beyond permit limits would be likely over the life of any mine.

The probability of a waste water treatment plant failure cannot be quantitatively estimated. However, it is plausible that such an event could result from equipment failures, inadequate storage or human errors. It is more likely that a partial failure (e.g., incomplete treatment) would occur. Although any one of the innumerable incomplete treatment scenarios is unquantifiable, in the aggregate the potential for one or more episodes of incomplete treatment is high.

During mine operation it is legally incumbent on a mine operator to fix water treatment problems expeditiously in order to maintain their operating permit. However after mine closure, if long term (i.e., perpetual) water treatment is required, the only non-taxpayer source of funding to address changes or failure in water treatment would be the long-term operating fund set up during mine operation. These funds seldom provide a contingency for unpredicted events, often leaving the public to meet the cost of spills, treatment miscalculations, or acts-of-god (e.g., the Zortman-Landusky mine in Montana).

Copper Standards and Criteria (USEPA 2014)

Although the ore and waste rock from disseminated copper mines contain a mixture of metals, copper is a major resource metal and is particularly toxic to aquatic organisms. Hence, it is the most likely to cause toxic effects, and the toxicity can be increased by co-occurring (synergistic) metals like zinc.

The federal government has developed National Ambient Water Quality Criteria for Protection of Aquatic Life for copper (USEPA 2007). These criteria are calculated using the Biotic Ligand Model (BLM), which derives the effects of copper as a function of the amount of metal bound to biotic ligands on gills or other receptor sites on an aquatic organism. The ligands bind free copper ions and, to a lesser degree, copper hydroxide ions. Copper competes for ligands with calcium and other cations. The competitive binding model for the biotic ligand requires input from a metal speciation sub-model and user-input values for basic water chemistry parameters (e.g., pH, temperature, DOC, humic acid, calcium, magnesium, sodium, potassium, sulfate, sulfide, chloride, and alkalinity). While the BLM is an advance over the hardness model for copper because it more fully accounts for the mechanisms controlling variance in toxicity, it is still not totally protective of all aquatic species, especially those susceptible at low chronic toxicities. (Dew et al. 2012; Ning, et al. 2009; Wang, et al. 2009; Pyle and Wood 2008).

Copper Exposure-Response Uncertainties (USEPA 2014)

Copper criteria are based on a large body of data and a mechanistic model of exposure and effects. Hence, at least with respect to acute toxicity, it is one of the best-supported criteria. However, it is always possible that it would not be protective in particular cases due to unstudied conditions or responses. Because the most sensitive taxa are aquatic invertebrates, unknown aspects of invertebrates are most likely to be influential. In particular, field studies, including studies of streams draining metal mine sites, show that Ephemeroptera (mayflies) are often the most sensitive species and that smaller instars are particularly sensitive (Kiffney and Clements 1996, Clements et al. 2000). However, the copper criteria do not include any Ephemeroptera in the sensitivity distribution (USEPA 2007). If the mayfly, stonefly, caddisfly, or other invertebrate species in the streams draining the mine footprints are more sensitive than cladocerans (crustaceans, the most sensitive tested species), then they may not be protected by the criteria.

In addition, the BLM chronic copper criterion is derived by applying an acute-to-chronic ratio to the BLM-derived final acute value (USEPA 2007). Because of the complex dynamics of chronic uptake, distribution, and sequestration of metals in aquatic insects, the BLM, which focuses on binding to a surface ligand, may not adequately adjust chronic toxicity (Luoma and Rainbow 2005; Buchwalter et al. 2008). Brix et al. (2011) reviewed the toxicity testing literature and found that aquatic insects are highly sensitive to copper and some other metals in chronic (relative to acute) exposures and may not be protected by current criteria. Because the EPA did not have enough test data to meet the requirement for a minimum of at least one species of freshwater animal in at least eight different families, the BLM derives the chronic criteria from an empirically-established relationship to the acute criteria, rather than through direct testing to determine the chronic criteria (USEPA 2007). Thus, the protectiveness of the BLM chronic criterion is more uncertain than that of the acute criterion.

In comparing the chronic criteria derived by the BLM method to that derived from the hardness-dependent criteria (the old method), the BLM criteria generally have lower limits at low hardness values (typical of uncontaminated streams), but higher limits at high-hardness values typical of streams with discharges from industrial or agricultural use.

The Criterion Maximum Concentration, which typically is the most sensitive of the criterion used to determine a water quality standard, is intended to protect “... 95 percent of a group of diverse genera, unless a commercially or recreationally important species is very sensitive.” (USEPA 2010). So water quality standards are not designed to protect all species, and it is possible some species could be harmed unless species-specific testing is conducted.

COPPER DEPOSITS & COPPER MINING in the DULUTH COMPLEX

Copper Geological Resources of the Duluth Complex

The Duluth Complex consists of 12 mafic sub-intrusions emplaced into the older rocks during continental rifting over a 10 to 12 million year period about 1.1 billion years ago. It covers an area of 6,500 km².

Large resources of low-grade, disseminated copper-nickel sulphides that locally contain anomalous Platinum Group Element (PGE) mineralization occur in the basal zones of the South Kawishiwi and the Partridge River intrusions. Nine deposits have been delineated in these intrusions.

The mineralization consists of 1% to 5% disseminated chalcopyrite (CuFeS₂), cubanite (CuFe₂S₃), pyrrhotite (Fe_(1-x)S), and pentlandite ((Fe,Ni)₉S₈) in a tabular zone parallel to the contact. Better grades of copper, nickel, and PGEs (platinum, palladium, gold, bismuth, tellurium, arsenic) are associated with more mafic units near the top of the mineralized zone (SWRPA 2009).

Disseminated copper-nickel sulfide mineralization and basal massive sulfide mineralization are presently known to occur in the Duluth Complex. Large resources of low-grade copper-nickel sulfide ore that locally contain anomalous PGE concentrations are well documented by drilling in the basal zones of the South Kawishiwi and Partridge River intrusions. The nine deposits that have been delineated occur in the basal 100 to 300 meters of both intrusions (Miller et. al. 2002). The mineralization consists predominantly of disseminated sulfides that collectively constitute over 4.4 billion tons of material averaging 0.66 percent copper and 0.2 percent nickel (Listerud and Meineke 1977).

Types of Mining in the Duluth Complex

Both open pit (MN DNR 2013) and underground (AMEC 2014) mining have been discussed as possibilities for mining the disseminated copper-nickel deposits in the Duluth Complex. Since the grade of the Duluth Complex deposit minerals are similar, the determination between an open pit and underground mine will probably rely primarily on the proximity of the ore to the surface. Shallower deposits will be mined by open pit methods, and deeper deposits that would require the removal of large amounts of overburden, which would be uneconomic if mined by the open pit method, will be mined by underground mining methods if the economics are favorable.

Tailings Disposal in the Duluth Complex

So far tailings disposal has been proposed for both an existing iron tailings storage facility (MN DNR 2013), and potentially an existing mined-out iron pit (AMEC 2014). In some locations construction of a new tailings storage facility could be required. In order to protect groundwater from tailings seepage contamination, liners with leak detection would be the best option. Impermeable cutoff walls are the next best option, assuming there is low-permeability bedrock into which the cutoff wall can be anchored. The final option is a combination of seepage collection trenches and seepage collection wells. This option is both expensive to operate and subject to the vagaries of local hydrology. None of these alternatives is perfect in collecting seepage (all liners leak), but the goal is to minimize the amount of contaminated seepage that escapes to ground or surface waters.

Potential issues exist for the use of old tailings storage facilities, typically constructed without the use of a confining liner, which has led to sulfate contamination issues. The dams that confine these iron tailings were typically constructed using the upstream-type dam construction method, which is the least stable dam construction type for long term seismic and flood event considerations. Over the long-term, and even in a geologically stable area, this type of tailings dam construction poses additional risk of dam failure. Tailings disposal in abandoned iron mine pits also carries the risk of both sulfate and metal contamination moving down-gradient via rock fractures, since the pits will not be lined.

Duluth Complex Tailings Geochemistry (MN DNR 2013)

The assumptions regarding the environmental behavior of the flotation tailings at NorthMet, which probably have similar characteristics to tailings from other Duluth Complex ore bodies, were based on 21 humidity cells (14 for coarse tailings and seven for fine tailings) generated in the pilot-plant processing tests conducted to refine the metal recovery process. The estimates of tailings effects on water quality at NorthMet are based largely on the results from these humidity cell tests at the point when they had run continuously between 90 and 300 weeks, and can be expected to yield results roughly similar to those from tailings processed at other Duluth Complex ore bodies. The mineralization of the Maturi, Maturi Southwest, Birch Lake, and Spruce Road deposits, which contain sulfides at higher concentrations than NorthMet, could be expected to produce the same contaminants as at NorthMet, but at higher rates and concentrations due to the lower pH the higher amounts of sulfide mineralization will yield.

Tailings samples subjected to humidity cell tests included a range of sulfide-sulfur concentrations (0.06 to 0.14 percent sulfur) and size fractions selected to represent the ranges expected under various depositional environments in the tailings storage facility.

Results of the humidity cell tests on pilot-plant tailings at NorthMet had sulfate release rates increasing roughly in proportion to total sulfur, and declining sulfate production over time as the sulfide minerals are consumed. The pH of effluent from oxidizing tailings is predicted by modeling to be between 6 and approximately 8.3, though the pH in effluent from tailings with sulfur similar to that of the NorthMet Tailings Basin (sulfur approximately 0.12 percent) is generally above 7. In most samples of tailings subjected to humidity cell testing, decreases in pH are associated with increases in the concentrations of some metal cations, such as nickel. Under oxygenated conditions at room temperature, oxidation of the tailings released about 5 mg SO₄ per kg tailings per week, and the range in most tests was between approximately 2 and 8 mg SO₄ per kg tailings per week. As above, since the mineralization of the Maturi, Maturi Southwest, Birch Lake, and Spruce Road deposits contain sulfides at higher concentrations than NorthMet, the concentration levels of sulfate and metal contaminants could be higher than those predicted for NorthMet.

Ore processing in the Duluth Complex

Flotation processing is aimed at separating the sulfide-bearing minerals from the silicate minerals. Although the results are not perfect, the “rougher” tailings can be expected to be low, but not entirely missing, in sulfide mineralization, as discussed in the tailings geochemistry section above.

One output from the flotation process would be a concentrate, or several concentrates (e.g. a copper concentrate and nickel concentrate) that would be shipped off site for smelting. In this situation most of the sulfide mineralization, including the pyrrhotite, would be removed from the primary tailings. This would leave the waste rock as the most problematic material because it would still retain its sulfides. However, at least some of the Duluth Complex mines are anticipating at least one further process stage which would produce copper at the mine site, resulting in a secondary waste that would contain a number of easily mobilized metal contaminants (MN DNR 2013). For this waste a smaller, fully lined tailings storage facility would be required. And although much smaller than the bulk tailings facility, it does represent another facility with long term monitoring requirements, and the potential to fail if not properly maintained.

Waste Rock Disposal in the Duluth Complex (MN DNR 2013)

The mechanism most responsible for the release of contaminants from waste rock and tailings is oxidation of sulfide minerals, primarily pyrrhotite (Fe_(1-x)S). The sulfide-oxidation reaction produces sulfuric acid, and releases soluble metals (e.g., cobalt, copper, iron, and nickel) that were bound in sulfide minerals. At the NorthMet deposit, the only Duluth Complex sulfide copper deposit that has been studied in any detail,

secondary effects include leaching of some metals (primarily nickel and chromium) from silicate minerals, particularly where acidic pore waters increase silicate solubility.

Mine-related blasting and excavation dramatically increases the surface area and porosity of the rock, which allows rapid introduction of atmospheric oxygen and flushing of solutes by water. Within the pit walls and underground workings, the blasting effects increase the surface area available for oxidation for approximately 50 feet surrounding the blast holes (Kempton et. al. 2010).

At NorthMet key environmental characteristics of the waste rock include the following:

- most of the waste rock and pit wall rock would contain some sulfide sulfur, mainly as mineral pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), which can produce acid leachate and soluble metals when it oxidizes;
- there are essentially no acid-neutralizing carbonate minerals in the waste rock;
- even though some mafic silicate minerals could neutralize acid, metalloids like arsenic, selenium, thallium, and antimony, could be liberated if present;
- sulfide-bearing rock from the NorthMet Project may oxidize for several years before producing acidic leachate;
- the rate of sulfide mineral oxidation in excavated NorthMet waste rock would be approximately proportional to the total sulfur content of the material, and the rate could increase several fold if the pore water were to become acidic; and,
- if the pore-water pH were to shift from neutral to acidic, then the rate of sulfide mineral oxidation and associated release of some metal cations (e.g., nickel and copper) would increase dramatically.

A problem with waste rock storage in the Duluth Complex is that the terrain is relatively flat and it is difficult to find large areas where bedrock is shallow or exposed. Groundwater flow is more complicated and less restricted in both depth and area in comparison to a mountain site. Containing and/or collecting groundwater is more difficult and expensive as the terrain flattens out. In the case of the NorthMet Project, they propose to construct impermeable slurry walls from the surface down to bedrock to restrict the flow of contaminants from waste rock and tailings to outside surface and ground waters. This is theoretically possible, but is dependent on a good “seal” with the underlying bedrock, and probably has not been attempted on this scale before (never at a mine site, but possibly at a very large contaminated waste disposal facility).

Water Treatment Technologies and Efficiencies

There are dozens of different treatment technologies available to water treatment plant operators, each with its own advantages, limitations, costs, reliabilities, and degree of effectiveness. And, like most mineral extraction technologies, it is generally not possible to say how well a given treatment system will perform on a given mine effluent until that effluent is available to conduct laboratory and field testing.

No fundamentally new water treatment technologies have been developed in the last several decades. There have been refinements of existing technologies, especially in the biotreatment field, in combining different treatment technologies to achieve lower contaminant discharge levels, and in the wider application of selective treatment technologies like arsenic and sulfate removal (e.g. see MEND 2000).

Theoretically the water treatment methods described below (and others) can treat mine effluent to discharge levels that meet or exceed state and federal water quality standards. However, treatment effectiveness varies by site, and cleaning mine effluent to water quality standards can become very expensive. Treatment cost is most often the limitation on treatment effectiveness.

Chemical Treatment

Sulphide oxidation leads to the solubilization of metals. The most common form of water treatment is chemical treatment to raise the pH and precipitate metals.

Chemical treatment involves the addition of an alkali material to raise the pH of the acidic mine drainage stream to levels that cause the solubilized metals to precipitate. Most chemical treatment facilities use reagents derived from limestone.

The acid mine drainage stream pH usually needs to be raised substantially above 6 to effectively precipitate metals. Hydrated lime is the most commonly used reagent for raising the pH. The neutralization effectiveness of lime is dependent upon its CaO content and reactivity. The neutralization of acid mine drainage causes dissolved metals to precipitate from solution through the formation of metal hydroxide/carbonate precipitates which settle to form sludge. The characteristics of treatment sludge vary depending on the properties of the acid mine drainage, and the treatment process and neutralizing reagents used. Most metals precipitate as hydrated metal complexes. The solubilities of these metal hydroxides are related to the pH of the treated water. In general, minimum solubilities of metal hydroxides occur in the pH range of 7 to 10, but can vary considerably in complex systems such as acidic drainages.

Lime-based metal precipitation technology is proven, and has been shown to be effective in consistently providing acceptable effluent quality under normal operating conditions (MEND 2000). In some cases lime precipitation may not be able to remove all metals to meet water quality standards, for example cadmium, and it has little effect on the removal of metalloids (arsenic, selenium, thallium, and antimony) and cyanide. For these and other additional contaminants, for example nitrates and sulfate, other treatment technologies may be necessary.

Membrane Treatment Systems

A number of separation processes utilizing membranes have been developed and are typically used for the removal of dissolved salts from water. All membrane processes separate the feed stream into a permeate (the desalinated water that passes through the membrane) and a concentrate (the stream in which the salts are concentrated). Membrane processes can be distinguished based on the driving force for removal and the size of molecules rejected by the membrane. Reverse osmosis (RO) has a pore size of < 0.002 micron; nanofiltration also has a pore size of < 0.002 micron, but typically operates at lower pressures than reverse osmosis and is used to separate larger molecules such as sugars and divalent salts; ultrafiltration (pore size 0.02-0.2 micron) can retain proteins and colloids; and, microfiltration (pore size 0.02-4 micron) is used for sterilization and removal of suspended material.

Membrane systems are susceptible to fouling by particulates, gas bubbles and other fouling contaminants and therefore the feed must be pretreated. Fine particulates and colloidal silica are usually removed by microfiltration. Scaling agents such as iron salts, silica, calcium sulfate and calcium carbonate can also cause problems as saturation conditions may be met at the membrane surface resulting in precipitation of solids on the membrane. Calcium removal by ion exchange or soda softening and the addition of anti-scaling agents are used to alleviate some of these scaling problems. Pre-treatment systems can be expensive and may account for as much as half of the desalination cost depending on the extent of pre-treatment required.

Another drawback to using membranes for wastewater treatment is the production of highly concentrated brine that must be treated prior to final disposal. The brine is often evaporated using a distillation and crystallization process or evaporation ponds (only practical in arid locations). Safe disposal of the dry salts can also be problematic and requires specially constructed disposal facilities.

Reverse Osmosis (RO)

One of the treatment technologies that is often discussed is reverse osmosis. RO can be used as a secondary treatment to chemical precipitation to further reduce the level of contaminants in a waste discharge.

Reverse osmosis is also known as hyperfiltration and is the finest form of filtration. It allows the removal of particles as small as ions from a solution. The process uses a semi-permeable membrane that allows purified fluid to pass through while rejecting the contaminants that remain. It utilizes pressure to reverse the flow of fluids towards a state of equilibrium, usually with a pump (USEPA 2004). At some sites RO is used with nanofiltration for pre-treatment to avoid RO membrane clogging, fouling, or damage. Fouling is a broad, generic term used to identify a multitude of time-dependent phenomena, which, singly or in combination, impact membrane performance.

Reverse osmosis occurs when the water is moved across the membrane against the concentration gradient, from lower concentration to higher concentration. To illustrate, imagine a semi-permeable membrane with fresh water on one side and a concentrated aqueous solution on the other side. If normal osmosis takes place, the fresh water will cross the membrane to dilute the concentrated solution. In reverse osmosis, pressure is exerted on the side with the concentrated solution to force the water molecules across the membrane to the fresh water side, leaving the larger ions and molecules on the high pressure side of the membrane.

Several systems have been developed to flush or vibrate the concentrate off the membrane to prevent it from plugging. The concentrate must then be collected and disposed of. This can be done by drying it in solar ponds or with heaters, or it can be slurried or transported to a lined disposal site for burial as hazardous waste.

Reverse osmosis is expensive because the semi-permeable membranes tend to plug up or wear out, each membrane can only process a small amount of water, and the concentrated waste must be collected and managed. Typically, the waste product stream is about 15 percent of the total volume treated. If the water is highly acidic the pH must still be adjusted before the water can be released.

Ion Exchange

Ion exchange is extensively used in metallurgical applications and MEND has assessed the extracting capabilities of ion exchangers and the feasibility of improving the economic and environmental aspects of lime neutralization through its use. There are two main groups of ion exchangers: organic (resins); and inorganic (zeolite). Ion exchangers are typically classified into three main groups: anionic, cationic and chelating. Ion exchange utilizes resins and zeolites that are helpful in extracting targeted metals. (MEND 2000)

Ion exchange resins consist of an insoluble support that has active functional groups attached to it. Undesirable ions in solution are substituted for these mobile ions during the ion exchange reaction. Loaded resins are regenerated with acid or caustic, depending on the type of resin, to produce concentrated brine containing the ions removed from solution.

A number of natural materials exhibit ion exchange capabilities such as zeolites (a class of aluminosilicate minerals), coal, metallic oxides and some types of algae and bacteria. Hundreds of synthetic ion exchange resins have been developed and they tend to be more efficient than natural ion exchangers, have higher capacities, and can be designed to be highly selective.

In theory, ion exchange can be applied for the removal of any dissolved contaminants related to mining. Exchange resins have been developed for the removal of heavy metals, calcium and magnesium, radionuclides, sulfate and ammonium. Although ion exchange process can remove contaminants

effectively, their application is generally limited by high capital and operating costs, process complexity requiring highly skilled operators and the need for additional treatment of spent regenerant.

In general, ion exchange is not economically feasible for treating large volumes of concentrated wastewater due to the high cost of regeneration agents and the need to treat a concentrated regeneration brine. Ion exchange may have applications as a secondary treatment step to selectively remove specific contaminants such as heavy metals, ammonia, radionuclides or calcium sulfate (SENES 1999).

Long-Term Water Quality Issues

Mines in the Duluth Complex would almost certainly require waste water treatment due to the amount of precipitation in the area and the geochemical nature of the waste rock. For at least some mines, water treatment in perpetuity is a likely scenario.

As previously mentioned in the general discussion of Copper Deposits & Copper Mining, it is not possible to quantitatively predict the probability of a water treatment plant failure. In general this is due to the fact that there is only a relatively short operating history of these facilities – a few have been in operation for 50 years or more, but the projected operating time frame for many water treatment plants is thousands of years. Even if we assume that treatment will never be affected by catastrophic weather events, human error, or other unforeseeable problems, there are two fundamental questions that must be answered in order to address the issue of the probability of water treatment failure:

- first, can we correctly calculate what the long-term costs of treatment will be so that this money can be put aside during mine operation; and,
- second, will the money set aside for water treatment in perpetuity be managed by a responsible organization in perpetuity?

The Catholic Church and the Roman Empire are among the longest lasting institutions in human history, which itself has a self-documented history of 7,000 – 10,000 years. It is likely that treating some acid-generating waste may be required for longer periods than this, so whether it is even possible to have an institution that can account for funds, and/or be responsible for managing the treatment is questionable.

At the present time we have a fairly good understanding of the causes and sources of metal contaminants to water. However, our ability to predict what metals will be released, and at what rate, is much more primitive. Like forecasting the weather, there are a number of variables that can have a significant impact on metals releases, and the amount of data required to further quantify this problem is not being collected, and it is not likely that it will ever be economically viable to do so. And even if we knew the answer to these questions, there are still assumptions in the financial calculations which we cannot predict in advance (e.g. the future rate of return on investment return, and the future inflation rate), so the basic calculations themselves will always have a significant margin of error.

And even if the calculated long-term treatment monies are either calculated correctly or err on the side of having too much money set aside, there is still the issue of whether that money will be present/viable over the long-term, or will disappear in a major financial collapse or a political upheaval that reorganizes our economic society.

Concluding Comments

It is not feasible, given today's or tomorrow's technology, to reduce the risk of impacting waters downstream from a copper/nickel mine in a sulfide ore body to zero. There will always be some risk, and that risk will be borne not by the direct benefactors of the mineral development, but mostly by future generations who might have to bear the consequences of our resource development decisions.

REFERENCES:

- AMEC 2014. Duluth Metals Limited, Maturi, Maturi Southwest, Birch Lake, and Spruce Road Cu-Ni-PGE Projects Ely, Minnesota USA, NI 43-101 Technical Report, AMEC, 10Apr14
- Borden, R. K. 2003. Environmental geochemistry of the Bingham Canyon porphyry copper deposit, Utah. *Environmental Geology* 43(7):752–758.
- Brix, K. V., D. K. DeForest, and W. J. Adams. 2011. The sensitivity of aquatic insects to divalent metals: a comparative analysis of laboratory and field data. *Science of the Total Environment* 409:4187–4197.
- Buchwalter, D. B., D. J. Cain, W. H. Clements, and S. N. Luoma. 2008. Using biodynamic models to reconcile differences between laboratory toxicity tests and field biomonitoring with aquatic insects (vol. 41, pg 4821, 2007). *Environmental Science & Technology* 42:3117–3117.
- Clements, W. H., D. M. Carlisle, J. M. Lazorchak, and P. C. Johnson. 2000. Heavy metals structure benthic communities in Colorado mountain streams. *Ecological Applications* 10:626–638.
- Dew et al, 2012. "Effects of Continuous Copper Exposure and Calcium on the Olfactory Response of Fathead Minnows." *Environmental Science & Technology* 46(16): 9019-9026
- Earthworks 2012. U.S. Copper Porphyry Mines Report: The Track Record of Water Quality Impacts Resulting from Pipeline Spills, Tailings Failures and Water Collection and Treatment Failure. Washington, DC.
- Fuerstenau, M. C., G. Jameson, and R. H. Yoon (eds.). 2007. *Froth Flotation: A Century of Innovation*. Littleton, CO: Society of Mining, Metallurgy, and Exploration.
- Kempton et. al. 2010. Kempton, H., Bloomfield, T.A., Hanson, J.L., and Limerick, P. 2010. Policy Guidance for Identifying and Effectively Managing Perpetual Environmental Impacts from New Hardrock Mines *Environmental Science & Policy*, Volume 13, Issue 6, October 2010, Pages 558-566
- Kesler, S. E., S. L. Chryssoulis, and G. Simon. 2002. Gold in porphyry copper deposits: its abundance and fate. *Ore Geology Reviews* 21(1–2):103–124.
- Kiffney, P. M., and W. H. Clements. 1996. Size-dependent response of macroinvertebrates to metals in experimental streams. *Environmental Toxicology and Chemistry* 15:1352–1356.
- Listerud and Meineke 1977. Listerud, W.H., and Meineke, D.G., 1977, Mineral resources of a portion of the Duluth Complex and adjacent rocks in St. Louis and Lake Counties, northeastern Minnesota: Hibbing, Minn., Minnesota Department of Natural Resources, Division of Minerals Report 93, 74 p.
- Luoma, S. N., and P. S. Rainbow. 2005. Why is metal bioaccumulation so variable? *Biodynamics as a unifying concept*. *Environmental Science & Technology* 39:1921–1931.
- Marsden, J. O., and C. I. House. 2006. *The Chemistry of Gold Extraction*. 2nd edition. Littleton, CO: Society of Mining, Metallurgy, and Exploration.
- MEND 2000. MEND Manual Volume 5 – Treatment, MEND 5.4.2e, December, 2000
- Miller et. al. 2002. *Geology and Mineral Potential of the Duluth Complex and Related Rocks of Northeastern Minnesota*, James D. Miller, Jr. John C. Green, Mark J. Severson, Val W. Chandler, Steven A. Hauck, Dean M. Peterson, Timothy E. Wahl, Minnesota Geological Survey, Report of Investigations 58, ISSN 0076-9177, Saint Paul, 2002
- Logsdon, M. J., K. Hagelstein, and T. I. Mudder. 1999. *The Management of Cyanide in Gold Extraction*. Ottawa, ON: International Council on Metals and the Environment.

- Miller 2011. Geology and Mineral Deposits of the Duluth Complex, Minnesota, Jim Miller, Department of Geological Sciences, University of Minnesota Duluth, Powerpoint Presentation, 22Sep11
- MN DNR 2013. NorthMet Mining Project and Land Exchange Supplemental Draft Environmental Impact Statement, prepared by Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, November, 2013
- Ning, W., et al. 2009. "Evaluation of acute copper toxicity to juvenile freshwater mussels (fatmucket, *Lampsilis siliquoidea*, in natural and reconstituted waters." *Environmental Toxicology and Chemistry* 28(11): 2367-2377.
- Pyle, G. and C. Wood 2008. "Radiotracer studies on waterborne copper uptake, distribution, and toxicity in rainbow trout and yellow perch: A comparative analysis." *Human and Ecological Risk Assessment* 14(2): 243-265.
- SENES 1999. SENES Consultants Limited, 1999. Report On Technologies Applicable To The Management of Canadian Mining Effluents. Report to Environment Canada, March 1999
- SWRPA 2009. Preliminary Assessment of The Nokomis Project, Minnesota, U.S.A., NI 43-101 Report, Scott Wilson Roscoe Postle Associates (SWRPA) Inc., January 8, 2009
- USEPA 2004. EPA/Abandoned Mine Lands/Technical Resources
- USEPA 2007. Aquatic Life Ambient Freshwater Quality Criteria – Copper, 2007 Revision. Washington, DC.
- USEPA 2010. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses, Charles E. Stephen, Donald I. Mount, David J. Hansen, John R. Gentile, Gary A. Chapman, and William A. Brungs, PB85-227049 EPA Office of Research and Development, 1985, with rev. 2010.
- USEPA 2014. An Assessment of Potential Mining Impacts on Salmon Ecosystems of Bristol Bay, Alaska. U.S. Environmental Protection Agency, Washington, DC, 910-R-14-001A, January 2014
- USGS 2008. Porphyry Copper Deposits of the World: Database and Grade and Tonnage Models, 2008. Open File Report 2008-1155, Singer, D. A., V. I. Berger, and B. C. Moring, U.S. Geological Survey.
- USGS 2012. Magmatic Ore Deposits in Layered Intrusions—Descriptive Model for Reef-Type PGE and Contact-Type Cu-Ni-PGE Deposits, Michael L. Zientek, USGS Open-File Report 2012–1010
- Wang, N., et al. 2009. "Evaluation of acute copper toxicity to juvenile freshwater mussels (fatmucket, *Lampsilis siliquoidea*, in natural and reconstituted waters." *Environmental Toxicology and Chemistry* 28(11): 2367-2377.