CANMET Mining and Mineral Sciences Laboratories

Introduction to Metal Leaching and Acid Rock Drainage (Drainage from Sulphidic Rock)

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Canmet MINING

Jan 22, 2020

Canada

Administration

- Welcome!
- Fire exits and washrooms
- Cell Phones
- Reference material
- Please ask questions no matter how simple
- Comments that illustrate, refine or provide a different point of view are also welcome

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Price & Errington (1997) BC MEM ML/ARD Guidelines

Price (1997) BC MEM Guidelines and Recommended Methods for Prediction

Price et al. Glossary of Terms Used in MLARD Work

Price 2009. MEND Prediction Manual of Drainage Chemistry from Sulphidic Geologic Materials

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Course Outline

four sessions each consisting of 60 min lecture and 30 min exercise and discussion

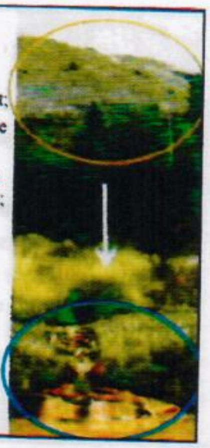
8:30-10:00	Overview of Properties and Processes
10:00-10:20	Break
10:20-12:00	Prediction and Water Covers
12:00-1:00	Lunch
1:00-2:30	Dry Covers, Treatment, Modify Storage and Material Composition
2:30-2:50	Break
2:50-4:30	Regulation, Challenges and Solutions

The objective is to increase understanding of metal leaching and acid rock drainage (ML/ARD). The information includes:

- what are ML/ARD and why is it important;
- contributing factors and underlying science and vocabulary;
- tools, procedures, design and maintenance requirements for prediction and mitigation; and
- challenges and resulting solutions

This knowledge can be used to:

- work more effectively and constructively;
- review plans, programs and results;
- ask the right questions at the right time; and
- help staff that do ML/ARD related work.



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Overview of Properties and Processes

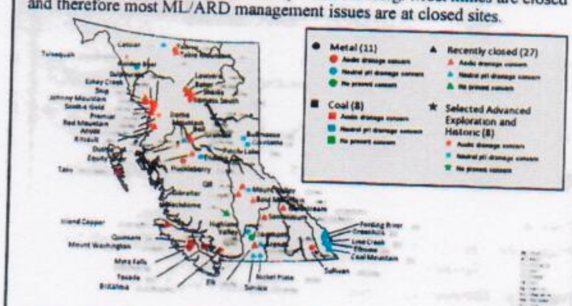
1. Why is this topic important?
2. Properties and processes and how they affect drainage?
3. Activities and materials exposing sulphidic geologic materials

Canada

Why is This Topic Important:

Requirements and challenges for prevention of impacts from sulphidic materials

Ensuring well informed, environmentally sound mining and management of closed mines is important both for jurisdictions with many mines and society in general. Operating mines are the tip of the ice berg. Most mines are closed and therefore most ML/ARD management issues are at closed sites.



OPERATING AND CLOSED MAJOR MINE SITES IN B.C in 2003.

Since this map was produced, BC has added many new mines with acidic or neutral pH concerns

Food production, housing, energy production, health care and transportation all depend on products from mining sulphidic rock. This includes:

- coal and iron for steel in vehicles, machinery, construction etc…
- trace metals such as copper, lead and zinc for engines, wire and electronics
- precious metals such as gold and silver for electronics and safety devices
- coal and uranium for power
- diamonds for cutting and polishing.

Huckleberry Copper Mine

People's need for the products of sulphide mining mean that the question is not whether there will be sulphidic mining but whether society will manage sulphidic mines and mine sites responsibly.

This does not mean acceptance of poor mines and poor mining practices, but rather that society should ensure and enable good mining practices, including successful long-term post-closure mine site management.

As will be discussed, the costs of failure are prohibitively expensive.

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Abandoned Kam Kotia Mine prior to mitigation by Ontario

Why should you care?

Drainage from sulphidic rock may be acidic or contain elevated metals that if not properly managed can have significant negative impacts on the environment.

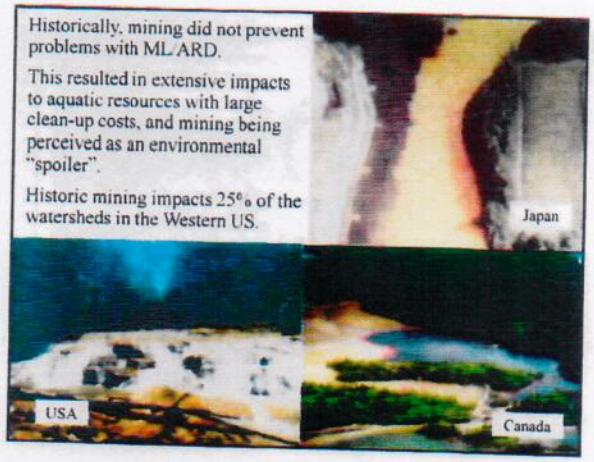
Impacts may persist for hundreds of years.

Although mines themselves have a relatively small foot print, polluted drainage from sulphidic rock has the potential to impact large areas and result in extensive impacts to aquatic resources.

Historically, mining did not prevent problems with ML/ARD.

This resulted in extensive impacts to aquatic resources with large clean-up costs, and mining being perceived as an environmental "spoiler".

Historic mining impacts 25% of the watersheds in the Western US.



Japan

USA

Canada

Faro, Yukon
~$1 billion

Giant, NWT
~$1 billion

When mining companies went bankrupt, the Canadian taxpayer has had to deal with the environmental impacts with remediation costs of up to ~$1 billion each at the Faro and Giant mines.

Britannia, BC
$100 million

Over the last 30 years, contamination of land and water has become an industry, public and regulatory concern and recognition of the large costs and technical challenges has resulted in mines being planned and operated in a manner that better protects the environment.

Mines should now provide detailed plans showing that they understand the site-specific challenges and can and will proactively prevent impacts.

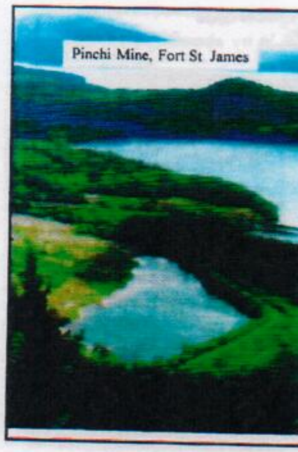
Faro Mine, Yukon

While practices have improved, there remain some major procedural, technical and governance challenges in sustaining environmentally sound mining practices:

- high costs and environmental consequences of failure;
- many contributing processes (large info. requirements) and highly specialized, technical aspects of the work;
- many key properties in flux and difficult to measure;
- mitigation must function over a long-time frame; and
- limited long-term operating experience.

As a result, ML/ARD mitigation can play a major role in determining the economic feasibility, environmental risks and social support for a project.

There are many factors that if not properly handled can damage our/your sensitive resources.



Proactive

One key requirement and challenge is the need to be pro-active.

Mines must provide well-informed mitigation plans that demonstrate how proactively issues will be addressed, contaminant loadings will be reduced and receiving environment objectives achieved.

Impacts are minimized and mitigation measures are far more cost-effective if mitigation needs are incorporated into the initial mine plan.

Long-Term Maintenance

In order to function indefinitely, most mitigation measures require continual, long-term maintenance, monitoring, replacement, repair and a degree of adaptive management.

Where long-term operation and maintenance are required there is no walk-away and mitigation of sulphidic rock is a permanent, ongoing land use.

Success depends on attention to detail and a major challenge in the maintenance of mitigation measures is the lack of appetite and limited attention span of the public and government in dealing with the ongoing details.

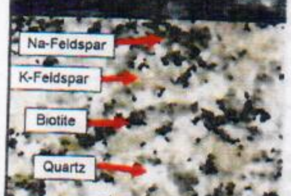
Properties and processes of sulphidic rock and how they affect drainage

Geologic Materials

Geologic material (rock and soil) are typically composed of sand or smaller sized mineral grains.

Minerals have a characteristic, elemental composition, distribution and structure.

Sulphide minerals contain a sulphide (S^{1-} or S^{2-}) with a metal or metalloid (e.g., Fe, Pb, As).



Sulphide Minerals

There are many types of sulphide minerals. The most common are Fe sulphides, especially pyrite (FeS_2).

Trace elements may be a small constituent in Fe sulphides or form a completely different mineral - Arsenopyrite ($FeAsS$), Chalcopyrite ($CuFeS_2$), Sphalerite [$(Zn,Fe)S$], Tetrahedrite $(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$

Most sulphide minerals are relatively insoluble, which is one reason why oxidation is so important.

Weathering

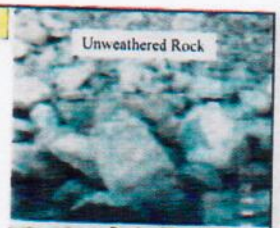
Bedrock buried within the earth is physically and chemically stable.

By creating walls and particles mining exposes rock surfaces to atmospheric phenomenon, such as air, water, freeze-thaw, wet-dry, biological activity and changes in temperature and pressure.

Rock exposed to atmospheric conditions is no longer stable and starts to physically and chemically change.

Alteration resulting from exposure to atmospheric conditions occurs at the surface and is called weathering.

There are a many different types of weathering reactions.



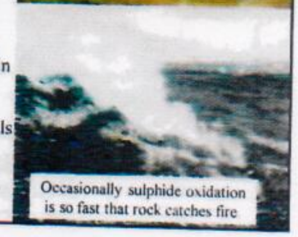
Fast Oxidation and Dissolution

All bedrock exposed to air and water is reactive, but reaction rates for most rock is very slow, and changes usually take thousands of years.

Rates of oxidation and dissolution of sulphide minerals and sulphidic rock exposed to air and water are relatively fast.

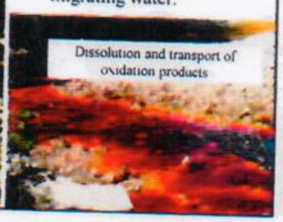
Fast rates of oxidation and dissolution are why drainage from exposed sulphidic rock may contain high concentrations of sulphate, metals and acid.

Drainage containing elevated metals and acid from sulphidic rock is often referred to as metal leaching and acid rock drainage (ML/ARD).



The three weathering processes primarily responsible for the problems with drainage from sulphidic rock are:

- oxidation of sulphide minerals (loss of electrons or rusting) and then
- dissolution and transport of oxidation products by migrating water.



Sulphide Oxidation

Sulphide minerals consist of sulphide (S^{1-} or S^{2-}) combined with metals (e.g., Pb) or metalloids (e.g., As).

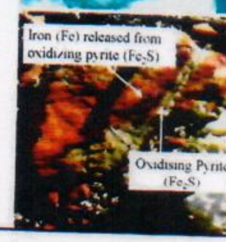
Oxidation transforms sulphide-sulphur (FeS_2-S) into sulphate (SO_4-S) and breaks the bond between the sulphur and metal ions (e.g., Fe or Zn).

Oxidation is a critical part of the process because it can transform relatively insoluble components of sulphide minerals into chemical species that more easily dissolve.

Oxidation of sphalerite (ZnS) releases zinc (Zn):

$ZnS + 2O_2(aq) \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq)$

Note: (aq) indicates chemical species are dissolved.



Sulphide Oxidation Products

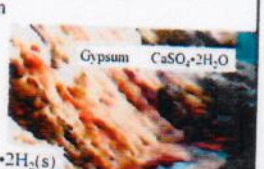
Dissolved aqueous species (aq) may be:

- free ions (Fe^{3+}, Zn^{2+} and SO_4^{2-}) or
- aqueous complexes of metals (Fe^{3+}, Zn^{2+} or Mo^{6+}) with anions (OH^-, CO_3^{2-}, HCO_3^- and CH_3) such as $FeOH^{2+}$, $ZnCO_3^0$ or MoO_4^{2-}.

$FeS_2(s) + 15/4O_2 + 1/2H_2O \rightarrow Fe^{3+}(aq) + 2SO_4^{2-}(aq) + H^+(aq)$

Dissolved species can be removed from water by precipitation or adsorption.

Dissolved species (Ca^{2+} and SO_4^{2-}) precipitate when their concentration exceeds a mineral solubility product (e.g., Ksp $CaSO_4 \cdot 2H_2O$).



$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O \rightarrow CaSO_4 \cdot 2H_2(s)$

Dissolution is important because it allows chemical species to be transported by surface and ground water.

Transportation brings contaminants of concern (e.g., Cu) in contact with sensitive receptors (e.g., vegetation, fish).

Environmental impacts depend on:

- amount of contaminants in the drainage and
- sensitivity of the flora and fauna in the receiving environment.

Sensitivity varies with the species and the contaminant.

Solubility Limits

Maximum "equilibrium" dissolved concentrations

Increasing Concentration of Dissolved Species (mg/L)

$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O(s)$

With increase in mass and/or time, sulphide oxidation increases the concentration of dissolved chemical species.

Often maximum "equilibrium" dissolved concentrations (e.g., solubility limits) are reached and precipitation and adsorption prevent a further rise in concentration.

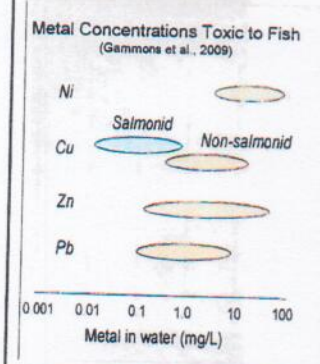
Rates of dissolution and precipitation, and maximum dissolved concentrations depend on the physical and chemical properties of minerals and the drainage and will change if the drainage chemistry changes.

Increasing Rock Weight or Volume, Solid Liquid Ratio, Reaction Rate or Time

Dissolved oxidation products reach solubility limits and precipitate in-situ or downstream.

Knowledge of site-specific, maximum dissolved metal concentrations and conditions that lead to mineral precipitation are very valuable when predicting drainage chemistry and possible environmental impacts.

Metal Leaching



The term 'metal leaching (ML)' is used because high concentrations of dissolved major metals (Fe and Al) and especially trace metals (e.g., Pb, Ni, Cu and Zn) are the most common environmental problem resulting from sulphidic rock.

Environmental impacts may also occur due to high concentrations of metalloids (arsenic and antimony) and non-metals (selenium and sulphate).

Note, just as all rock is reactive but most react slowly, all rock releases metals but usually at a much slower rate than sulphidic rock.

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Toxicity

Some of the elements, such as copper, zinc and selenium, in sulphide minerals are nutrients and essential for healthy growth.

Natural water bodies already contain all the metals and other elements released by sulphide oxidation.

Harmful effects from ML/ARD primarily result from dissolved concentrations (e.g., mg/L) of existing elements becoming too high.

Speciation of dissolved elements may play a role. Complex formation with OH^-, CO_3^{2-}, HCO_3^- and CH_3 can reduced metal toxicity (e.g., ,). An exception is methylated mercury ( ).

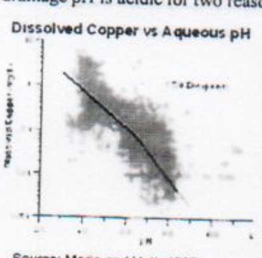
Change in oxidation state may also alter toxicity (e.g., more toxic than As^{5+})

Acidic Rock Drainage (ARD)

In addition to metals, sulphide oxidation produces acid and can result in drainage with an acidic pH.

Pyrite: $FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$

Environmental impacts are greater and more common when the drainage pH is acidic for two reasons.



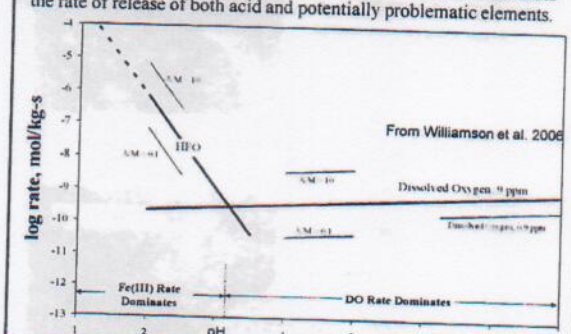
Source: Morin and Hutt, 1997

First, an acidic pH increases the solubility and the maximum "equilibrium" dissolved concentrations of most metals.

Increased metal solubility is illustrated by the increased copper concentrations as the pH decreases at Island Copper.

An exception is the metal molybdenum whose solubility decreases at an acidic pH.

The second reason environmental impacts are more common when the drainage pH is acidic is because the rate of sulphide oxidation increases below pH 3.5. An increase in the rate of sulphide oxidation increases the rate of release of both acid and potentially problematic elements.

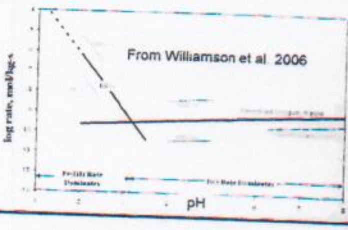


Sulphide oxidation occurs in a film of water on the mineral surface and therefore sulphide oxidizing agent must be dissolved.

The primary oxidizing agents are dissolved oxygen (O_2) and iron (III - Fe^{3+}).

Above pH 3.5, the solubility and therefore the concentration of dissolved Fe(III) is low and the primary oxidizing agent is oxygen.

Below pH 3.5, dissolved Fe(III) concentrations are generally much higher than dissolved O_2 and rates of sulphide oxidation are much higher than at higher pH.



Sulphide oxidation below pH 3.5

Role of Bacteria

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 4H^+$$

abiotic slow, bacteria fast + O_2 ($Fe^{2+} \rightarrow Fe^{3+}$) + FeS_2 abiotic fast ($Fe^{3+} \rightarrow Fe^{2+}$)

Sulphide oxidation by oxygen and Fe(III) occurs at a similar rate either abiotically or biotically.

The rate of abiotic oxidation of iron(II) to (III) is relatively slow and the mechanism by which bacteria increase the rate of sulphide oxidation is by increasing the rate of regeneration of Fe(III) from Fe(II). By increasing the resupply of Fe(III), iron oxidizing bacteria (e.g., Acidithiobacillus ferrooxidans) can accelerate sulphide oxidation by many orders of magnitude relative to abiotic rates.

Microbial activity does not accelerate sulphide oxidation at near-neutral or basic pH because Fe (III) is not soluble and therefore not an oxidizing agent.

Neutralization of ARD

Not all oxidizing sulphidic rock is acidic.

Drainage pH depends on the relative reaction rates of:

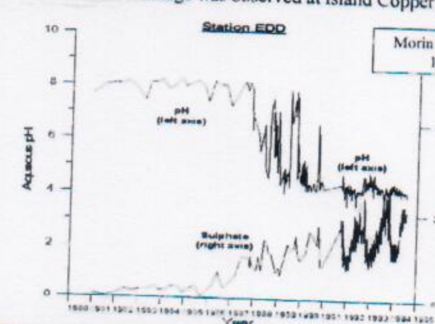
- acid generation by sulphur minerals and
- neutralization by other minerals (NP).

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$$

Acidic drainage will only result if the reaction rate of neutralizing minerals is too slow or neutralizing minerals are exhausted.

Calcium and magnesium carbonate minerals, such as calcite ($CaCO_3$), provide fast neutralization capable of matching the fastest rates of acid generation and are the primary source of neutralization.

It may take 10s to 100s of years before the depletion of neutralizing minerals results in acidic drainage. An absence of acidic drainage up to now does not prove it will not occur in the future. It took more than 15 years before acidic drainage was observed at Island Copper (see below).



Neutral and Basic pH Drainage may be a Concern

Dissolved trace element concentrations in drainage from sulphidic rock are usually lower at near-neutral or basic pH than acidic pH, but may still exceed receiving environmental guidelines (Stantec, 2004).

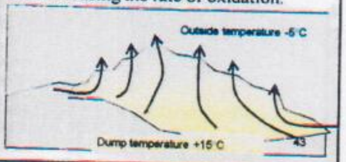
Element	pH	Example of Dissolved Concentration (mg/L)	Most Restrictive Receiving Environment Guideline (mg/L)
Antimony	8.5	0.9	0.006
Arsenic	8.0	0.3	0.005
Cadmium	6.5	0.07	0.000017
Cobalt	8.0	1.1	0.0009
Copper	7.3	0.06	0.002
Manganese	8.1	33.5	0.05
Molybdenum	8.3	29	0.073
Nickel	8.1	3.8	0.025
Selenium	7.5	1.6	0.001
Zinc	8.1	14.4	0.03

Two of the most costly mitigation programs for sulphidic drainage at British Columbia mines are the treatment of near-neutral pH drainage: elevated molybdenum (Mo) at Brenda Mine near Peachland and arsenic (As) at Nickel Plate Mine near Hedley.

Sulphide oxidation produces heat (exothermic)

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ + heat$$

In addition to releasing chemical species, sulphide oxidation also produces heat (exothermic). Heat generated by sulphide oxidation may increase temperatures above 60°C and may result in tailings or waste rock catching fire. Warm air within sulphidic waste rises pulling in new air and increasing the rate of oxidation.



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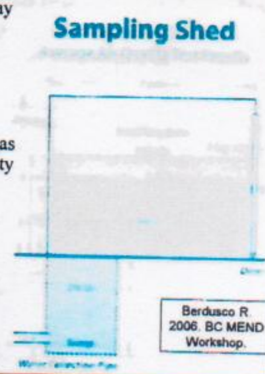
Act Safely - Gas Composition

Changes also happen to the pore gas:

- sulphide oxidation lowers oxygen levels and at high temperatures may emit sulphur dioxide (SO_2),
- carbonate dissolution increases carbon dioxide levels and
- sulphate reduction may emit hydrogen sulphide (H_2S).

Changes to the composition of pore gas may be a health concern and air quality should be checked before entering confined locations or depressions.



Berdusco R. 2006. BC MEND Workshop.

Sulphide Geologic Materials

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Natural Exposure

Many activities expose sulphidic geologic materials to oxidation and leaching, not only mining.

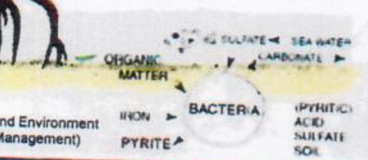
Natural sulphidic outcrops and talus produce elevated metal leaching and acidic drainage, but contaminant release is typically limited by the shallow depth and the slow rate of rock exposure.

High background concentrations of contaminants due to natural sulphidic outcrops and talus reduce the diluting, absorptive and attenuating capacity of the receiving environment and increase the cumulative effects of anthropogenic sources.

Sulphidic Marine Sediments

Marine sediments often contain pyrite and when drained for agriculture or construction may produce acidic drainage.

Pyrite oxidation is an issue for farmers in Delta and was an issue for construction on marine soils at the Sydney Olympic Park.



(from Queensland Environment and Resource Management)

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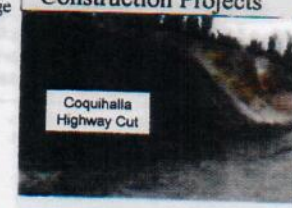
Construction Projects

Construction projects expose large masses of rock to air and water.

Although most rock is not a concern, there are numerous examples where the rock is sulphidic and excavation and placement of materials in construction projects created environmental problems.

The adjacent pictures shows a section on the Coquihalla Connector highway in British Columbia where the cut and fill of sulphidic rock resulted in exposure of sulphidic rock and the discharge of acidic drainage into a stream upstream of a provincial trout hatchery.



Mining

Sulphidic rock drainage is an important issue for mining because:

- mines rapidly excavate many billions of tonnes of rock
- rock at most precious and base metal, coal, diamond and uranium and some iron ore mines contain elevated concentrations of sulphide minerals.

Air and water penetrate fractured bedrock near the surface and the depth of surface weathering may be quite deep, especially in old landscapes in the tropics.

In Canada, glaciation has often removed most of the soft weathered rock.

Consequently, prior to mining most bedrock is initially unweathered and weathering starts when mining exposes walls and breaks bedrock into particles exposing rock surfaces.

Mines with notable oxidation prior to mining include Bell, Kemess South and North, Red Chris and KSM.

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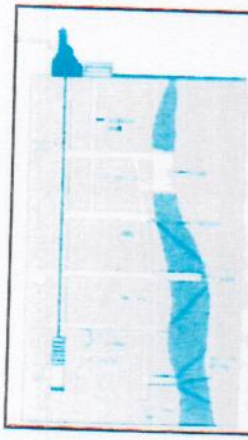


Mines have different shapes and sizes.

One major distinction is whether mines are open pits or underground.

Underground mines may make result in subsidence of the overlying ground.

Open pits extract more ore, but create far more waste rock.

Bedrock is most commonly drilled and blasted, using sufficient explosives to break bedrock into small enough sized particles for removal.

Removal is usually by trucks.

Ore versus Waste Rock

Rock containing the economic commodity is called ore.

Rock that has no economic value, and is excavated to access ore, is called waste rock.

For cost reasons, waste rock is usually placed close to and downhill of mine workings.

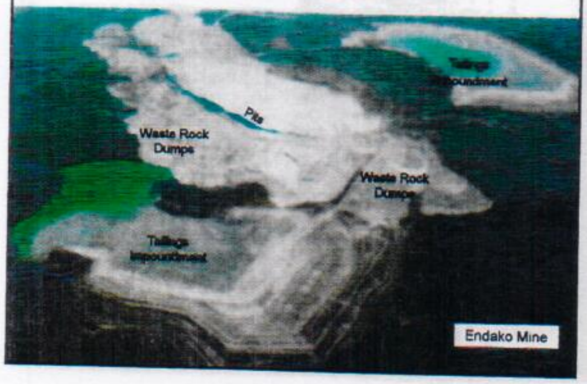
The processing of ore starts with reduction of the blasted rock to small stone and then sand/silt-size.

After the economic product is removed, the remainder is usually sand/silt-sized particles in a slurry.

The tailings slurry may be stored behind a dam in an impoundment.

Tailings may be reworked for use as backfill or dried and stacked.

The largest components at most mines are the mine workings and the tailings and waste rock.



The type of mine will play a role in determining size and type of mine components.

Mines require large volumes of material to construct roads, dams and structural backfill, and often use waste rock or tailings.

Construction material may also come from outside the mine, but even rock quarried some distance away may be sulphidic and a geochemical assessment is required to determine if it is suitable for construction.

Phases of the Mine Life

Mine sites pass through a sequence of phases – exploration, proposal/construction, operation and closure. Environmental impacts from ML/ARD may occur during any phase.