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# Quality of Seepage and Leachate from Mine and Mill Wastes and Control of Its Effects

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Mine and mill wastes, such as waste rock and tailings, are possible sources of road construction material. However, although such materials may be suitable from geotechnical considerations, they may prove to be problematic as they may produce contaminated seepage and leachate. A classification is presented of the types of mine and mill waste. Three important considerations in the use of these mine wastes are (a) the origin and characteristics of the waste rock; (b) the influence of mineral extraction process on leachate quality from tailings (typical problems associated with the various waste types are highlighted); and (c) changes in soil structure due to leachate, e.g., the Na ion, which can accelerate weathering or lead to changes due to ion exchange. Leachate from mine waste can have detrimental effects on the environment due to effluent quality. It can also influence the integrity of engineering structures through chemical attack in many forms. The detrimental effects of leachate from mine waste can be controlled by treatment before placement, treatment during placement, treatment of effluent, and other methods, e.g., the use of detergents to inhibit bacterial activity in the formation of acid drainage.

Mine and mill wastes, such as waste rock and tailings, are possible sources of road construction material. Such materials are available often in abundance and usually exhibit excellent geotechnical characteristics. Furthermore, because these materials are waste products, they are usually economically attractive. However, it is important that the potential chemical problems associated with mine wastes be investigated prior to their use as road building materials. Such problems can usually be solved in time, if they are recognized.

Although many chemical leachate problems can be associated with mine and mill waste, as will be discussed later, acid drainage is by far the most common and potentially serious. Acid drainage is the result of the oxidation of sulfur-rich minerals, most commonly pyrite. Bacteria act as important catalysts in the oxidation process and the development of acid drainage problems.

The purpose of this paper is to present an overview of seepage and leachate problems associated with mine waste and possible ways of limiting their impact. The information is based on our experience and some of the latest literature sources.

## EVALUATING MINE WASTE

### Classification of Mine Waste

Mine waste is defined here as all solid wastes associated with mining activities and smelters as well as the chemical industries where a mineral is used in the manufacturing of chemicals, such as the fertilizer industry.

Mine waste will be classified for this discussion as follows:

1. Overburden material resulting from stripping operations for strip or open pit mining;

2. Waste rock, including rock that contains sub-economic ore grades as well as "country rock" or rock that is not ore-bearing;

3. Tailings, the fine material remaining after crushing, milling, and processing of an ore;

4. Slag, the waste from smelting operations and usually disposed of as a high-temperature-melted material (the resulting waste is therefore very hard and massive unless recrushed); and

5. Other materials, such as calcine from pyrite roasting for the production of sulfuric acid (1) and gypsum tailings resulting from the production of phosphoric acid (2), fall in this category.

Although it is useful to classify mine waste, as done above, it must be emphasized that no unique leachate problems are associated with any type, e.g., all the types of mine waste can produce acid drainage. The usefulness in the classification is to identify the sources of waste and disposal methods, as each type of waste is usually disposed of separately during mining operations, e.g., overburden and waste rock dumps are separated from tailings impoundments and slagheaps.

### Leachate-Producing Capacity of Wastes

There are two major considerations in evaluating the capacity of mine and mill waste to generate contaminated leachates: (a) the origin and characteristics of the waste rock, and (b) the influence of mineral extraction processes, especially the influence of chemicals added.

### Origin and Characteristics of Waste Rock

The origin and characteristics of ore or waste rock determine the sulfide and carbonate contents of the waste and its potential for acid generation; hazardous chemical and radiochemical constituents present in the waste, such as heavy metals; and the potential for mobilization and release of these hazardous materials by way of expected interaction with the environment that will be developed by the use of the waste.

Caruccio and others (3) state: "In terms of a sample's potential to produce acidity (all other parameters being equal) the samples with a predominance of fine grained (framboidal) pyrite generate orders of magnitude more acid than samples having coarse grained pyrite".

An important consideration in the acid-producing capacity of a material is the relative percentage of

both sulfide and calcareous minerals present. Consideration of only sulfur content may give a wrong impression of the potential acid production of a material. The calcareous minerals present may act to neutralize the acid formation. However, the exact physical state and the low solubility of specific carbonate minerals in water may inhibit alkaline production (3).

Caruccio and others (3) conclude: "In general, samples with neutralizing potential (NP) values of more than 15 mg of CaCO<sub>3</sub> equiv. per lg and sulfur contents less than 0.5% can be expected to produce alkaline leachates, whereas samples with NP values of less than 2 mg of CaCO<sub>3</sub> equiv. per lg and sulfur contents greater than 1.5% can be expected to produce acidic leachates."

Heavy metals, e.g., copper, lead, and zinc, present a problem if they are both chemically available and chemically mobile. Physiochemical reactions--adsorption, precipitation, etc.--inhibit mobility at normal pH ( $\pm 7$ ) conditions and metals tend to be mobile only at low pH values; i.e., pH < 5.3. Ideal conditions for such mobilities are the intimate association of sulfides and metals, such as disseminated sulfide type of wall rocks adjacent to ore bodies. When there are sulfide oxides in this type of waste rock, the heavy metals are available for ready mobilization. In most cases the potential to produce acid leachates will also be indicative of a waste's potential to liberate contained hazardous materials to the leachate. This is especially true for heavy metals and radioactive elements such as radium, thorium, and uranium. The solubility of the elements, and therefore their mobility, increase dramatically in acid environments (4,5).

#### Influence of Mineral Extraction Processes

There are very few mineral extraction processes that do not involve the addition of one or more chemicals to the crushed ore. In hydrometallurgical processes dependent on leaching, some kind of leach solution is applied, e.g., cyanide (usually NaCN) for gold and silver, sulfuric acid or sodium carbonate and bicarbonate for uranium, and sulfuric acid for copper. Most minerals are extracted best in an acid solution, but some are extracted in an alkaline environment.

It is important that the particular metallurgical process, as well as the possible leachates that can be expected from such waste, be considered in evaluating the suitability of mine waste for use in construction.

Extraction efficiency is improved in many instances by grinding the ore very finely. In some cases, material is produced that is 80 percent finer than the no. 400 sieve (0.038 mm). In addition to chemical concerns of such materials, the geotechnical characteristics of such fine material are questionable also with respect to their use in earth structures.

Radioactive minerals such as uranium, thorium, and radium are liberated not only through grinding, but also are concentrated during the extraction process. Uranium mill tailings have good geotechnical characteristics (6); however, the radiation hazards associated with such tailings make them unacceptable for use in construction. In Grand Junction, Colorado, uranium tailings were used as backfill around residences and public buildings. This practice led to unacceptable increases of radon gas concentrations within the structures and resulted in a costly remedial action program (7). However, for nonconfined conditions, radon gas buildup would not likely be a health concern. Physical separation from radioactive constituents must be assured in any construction use.

Heap leaching of low-grade ores is becoming common practice (8,9). In such cases, the ore is stacked in a heap (crushed or uncrushed) and leached with a concentrated extractant solution. At the end of the leach cycle, the heaps are usually flushed with water to secure maximum recovery of the extracted product. Mine waste resulting from heap leach operations may produce, therefore, "acceptable" leachates. However, more than surface sampling of such materials is necessary to evaluate them. Some leaching operations may lead also to accelerated weathering and degradation of the rock leached, which influences the geotechnical characteristics of the material.

#### PROBLEMS ASSOCIATED WITH LEACHATES FROM MINE WASTE

Two major implications of the quality of leachates from mine wastes are the (a) impact on the natural environment and (b) impact on engineering structures through chemical attack. These implications are important when mine waste is considered as a possible construction material. However, they become of paramount importance when construction is planned in the vicinity of existing (or future) mine-waste-disposal facilities. Leachates from such facilities can attack not only concrete and steel structures but also can influence the integrity of earth structures, e.g., through the more rapid weathering caused by acid leachates.

This section will consider some of the chemical processes involved in producing these impacts. Such an understanding is important when control techniques for leachates are evaluated.

#### Impact of Leachate on Natural Environment

##### Acid Generation

Acid drainage from sulfide-rich rocks has long been recognized as a problem, and the basic technology and philosophy of acid mine drainage control have not changed in more than 30 years (10). It has been known for about the same period that the bacterium *Thiobacillus ferrooxidans* influences acid formation. There are other bacteria that influence acid formation; however, *T. ferrooxidans* is by far the most important (3,10). This bacterium is unimportant in saturated environments, but it increases acid formation near the land surface where oxygen is readily available. It is intermittently significant; furthermore, in the intermediate zone of aeration where it increases acid production for three to four days from infiltration after each rainfall, after which the rate of such formation diminishes (10).

The major reactions responsible for pyrite oxidation and subsequent acid formation are given in Figure 1 (10). In general terms, these types of reactions apply also to other sulfide minerals, e.g., chalcopyrite, galena, etc., to varying degrees. This additional problem with heavy metal sulfides is the increased availability of the heavy metal itself for transport on acidification. Kleinmann and others (10) give a detailed description of the three stages in this process. The following are important considerations when control techniques are evaluated:

1. It is possible to forestall acidification during stage 1 by adding alkalinity to the reaction system; if alkalinity exceeds acidity, the major downstream effect is an increase in sulfate concentration.
2. Once acidity significantly exceeds alkalinity, it becomes much more difficult to return an acid-producing system to stage 1.
3. Stage 2 is initiated as abiotic oxidation of

Figure 1. Reactions in acid generation from pyrite.

	1. $\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} + \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$
	2. $\text{Fe}^{2+} + \frac{5}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 + \text{Fe}(\text{OH})_3(\text{s}) + 2\text{H}^+$
	3. $\text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}^+ + \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O}$
	4. $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} + 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$
<u>Stage 1</u>	
Mechanism	Reaction 1: proceeds both abiotically and by direct bacterial oxidation
	Reaction 2: proceeds abiotically, slows down as pH falls
Chemistry	pH above approximately 4.5; high sulfate; low iron; little or no acidity
<u>Stage 2</u>	
Mechanism	Reaction 1: proceeds abiotically and by direct bacterial oxidation
	Reaction 2: proceeds at rate determined primarily by activity of <u>T. ferrooxidans</u>
Chemistry	approximate pH range of 2.5-4.5; high sulfate; acidity, and total iron increasing; low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio
<u>Stage 3</u>	
Mechanism	Reaction 3: proceeds at rate totally determined by activity of <u>T. ferrooxidans</u>
	Reaction 4: proceeds at rate primarily determined by rate of reaction 3
Chemistry	pH below approximately 2.5; high sulfate, acidity, total iron and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio

$\text{Fe}^{2+}$  slows and *T. ferrooxidans* takes on its primary role of oxidizing  $\text{Fe}^{2+}$ , thereby allowing reaction 2 to continue producing acidity and ferric hydroxide.

4. It is possible to stabilize pH during stage 2 if the soil permeability is low and when a small amount of pyrite surface area is exposed. Otherwise, the pH decline continues to the third stage, where acid production is most rapid.

5. Stage 2 includes the oxidation of both fibrous and coarse-grained pyrite.

6. Once stage 3 is reached, acid production can be reduced only by slowing reaction 3 (see Figure 1). It is done traditionally by limiting the available oxygen, but the more direct route of inhibiting *T. ferrooxidans* is also possible.

The principal impacts on water/leachate quality from such oxidation will be elevated levels of iron, sulfate, totally dissolved solids, and a lower pH value. Unless the environment in which the leachate is being generated has an inherently high neutralization capacity, iron levels will exceed water quality standards in the majority of cases, as drinking water standards are low (0.3 mg/L). In terms of construction and structures, the higher sulfate levels and low pH value give cause for concern, as both are known to degrade concrete.

Impacts themselves may not be apparent immediately but can be serious over an extended period. For example, oxidation can occur despite apparent neutralization in wastes giving a delayed impact. A recent investigation by one of the authors in New South Wales, Australia, showed that tailings water

from a base metal mine, which was neutralized to pH = 10 with lime at the thickener stage of the process, produced a liquid in the return water reservoir with a pH of  $\pm 3.5$ .

#### Acid Leachate as a Result of Extraction Process

As mentioned above, acids are often used as leach solutions in extraction processes. For example, copper is leached from heaps by using a solution with pH = 0.5, while the effluent has a pH of about 3.5. Uranium ore is typically leached at a pH of 1.2 to 1.5. From the discussion of acid generation, it is clear that if any acid-generating minerals are present, the acid drainage problem will be worsened considerably in this case.

When no acid-generating minerals are present, as is usually the case in the production of uranium through acid leaching of sandstone-related ore, the presence of a neutralizing source, such as calcium carbonate ( $\text{CaCO}_3$ ) as a neutralizing agent, is the most important consideration in controlling the quality of leachate (4).

#### Cyanide

Cyanide ( $\text{NaCN}$ ) is commonly used for the extraction of precious metals as well as in some flotation processes to suppress the influence of pyrite. The wastes contain usually low levels of cyanide in the latter case; however, this is not always true in the former. Although some washing is accomplished after cyanide leaching, the cyanide level in the waste usually exceeds drinking water standards (0.06

Table 1. Various cyanide complexes and their relative stability.

Term	Examples Present in Solutions for Extracting Gold
Free cyanide	CN <sup>-</sup> , HCN
Simple compounds	
Readily soluble	NaCN, KCN, Ca(CN) <sub>2</sub> , Hg(CN) <sub>2</sub>
Relatively insoluble	Zn(CN) <sub>2</sub> , Cd(CN) <sub>2</sub> , CuCN, Ni(CN) <sub>2</sub> , AgCN
Weak complexes	Zn(CN) <sub>2</sub> <sup>2-</sup> , Cd(CN) <sub>3</sub> <sup>-</sup> , Cd(CN) <sub>4</sub> <sup>2-</sup>
Moderately strong complexes	Cu(CN) <sub>2</sub> <sup>-</sup> , Cu(CN) <sub>3</sub> <sup>2-</sup> , Ni(CN) <sub>4</sub> <sup>2-</sup> , Ag(CN) <sub>2</sub> <sup>-</sup>
Strong complexes	Fe(CN) <sub>6</sub> <sup>4-</sup> , Co(CN) <sub>6</sub> <sup>4-</sup>

mg/L). Furthermore, cyanide has been classified as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) of 1976.

Cyanide can be present as free cyanide or in metal composition that has various degrees of stability. These are shown in Table 1 (7).

Free cyanide means the two species, cyanide ion (CN<sup>-</sup>) and hydrocyanic acid (HCN), also known as hydrogen cyanide. The latter is of particular environmental concern, since it is the form of cyanide most toxic to aquatic life, capable of killing fish at concentrations as low as 0.05 mg/L (11). It should be remembered that cyanide is not a cumulative poison for people such as some heavy metals are. Therefore, the toxicity of a system must be determined on total concentration and not prolonged exposure.

The toxicity of the metal-cyanide complexes generally results from their dissociation to produce hydrogen cyanide and not from the stable complexes per se. However, copper and silver cyanide complexes, as such, have been shown to be acutely toxic to fish (11).

Free cyanide concentrations in aqueous systems will be lowered by several natural degradation processes. Cyanide will oxidize in the presence of natural oxygen to cyanate complexes that will then hydrolyze to NH<sub>3</sub> and CO<sub>2</sub>. Cyanide is also given off from the aqueous system by volatilization. Both processes result in a lowering of cyanide concentrations and therefore the toxic properties of a system.

#### Impact of Leachate on Engineering Structures

Acid drainage is a leachate with a major impact on engineering structures. This impact is caused by the low pH of the leachate leading to corrosion of metals and attack on concrete and by high sulfate concentration that also degrades concrete. This process is well understood and will not be discussed further.

Another result of acid formation is where deposits resulting from the bacterial action build up in subsurface drains and finally clog them (12). Typical deposits in drains can consist of iron, manganese, or calcium carbonate. Iron deposits in drains are often called ochre (12). Ochre can be described as a sticky, gelatinous, yellow to reddish mass of ferric hydroxide plus organic material that can clog subsurface drains. Clogging of subsurface drains through ochre is a common occurrence in agricultural drains but can also be a problem in other applications (12).

#### TECHNIQUES TO CONTROL LEACHATE QUALITY FROM MINE WASTE

A useful classification of control techniques for acid drainage problems was proposed by Wewerka and others (13). This classification will be followed here, but in an extended form.

Techniques to control leachate quality from mine waste can be classified as follows: (a) treatment before placement, (b) treatment at and after placement, and (c) treatment of effluent. The techniques involve physical and chemical treatment procedures. Physical treatment may be the simplest in most cases and usually leads to better long-term control of leachates. Both physical and chemical procedures will be discussed here.

#### Treatment Before Placement

The physical preparation of mine waste will influence its acid-generating potential. Pyrite-rich overburden and waste rock should be blasted into large fragments to expose the smallest practicable surface areas. Calcareous material, on the other hand, should be blasted into smaller fragments to increase the area of its reactive surface (14). Such preparation is especially important where these materials will be used together.

Cyanide-rich mine waste can be spread out to allow oxidation and volatilization of the cyanide, as discussed above. Such wastes can also be washed with water to reduce the cyanide content. These two methods must be used with care to prevent acid generation when the waste is pyrite-rich.

Wewerka and others (9) propose the use of calcining as a pretreatment of acid-generating waste. Although they had considerable success with this method, incomplete calcining can lead to a false sense of security.

Calcining consists of oxidation of the sulfur at high temperatures to produce an inert slag. This is the same process used in the production of sulfuric acid from sulfide-rich ores. Smith and Middleton (1) describe environmental problems associated with such waste. The "inert" slag is indeed a good geo-technical material but causes acid generation if incomplete calcining takes place. Calcines are known to have residual pyrite contents of up to 5 percent sulfur. Similar problems can therefore be experienced after calcining.

#### Treatment At and After Placement

One treatment that is meeting with success is the co-placement of acid-generating waste with alkaline agents (13,14). Either natural alkaline agents such as calcareous rock materials can be used, or specially produced materials such as powdered lime can be mixed in with the acid-producing material. One uncertainty in such co-disposal is the long-term effectiveness to reduce acid generation.

Acid generation is dependent on the availability of water and oxygen, as shown above. Both these factors can be controlled through proper design of the proposed earth structure. Acid-generating mine waste can be encapsulated, therefore, in inert soil or rock materials (1,14). Such cover material should have low permeability to limit the infiltration of water. The cover must be shaped such that no ponding of water is allowed, but the run-off rate must be controlled to reduce erosion potential. Erosion resistance of the cover is important to ensure long-term protection.

Acid-generating materials should not be used as fill at levels much higher than the natural ground level in areas where the groundwater level is high or where ponding can take place. In such cases, wetting and drying can occur that would lead to acid generation.

Groundwater flow should be cut off with subsurface drainage if it becomes a problem in acid generation.

Anionic detergents can be used to inhibit the

bacterium *T. ferrooxidans* economically. Such detergents are readily available in biodegradable forms and are environmentally safe at low concentrations. Concentrations above 10 parts per million (ppm) slow acid production while concentrations of at least 25 ppm reduce acidity levels completely by killing the bacteria. Rubber formulations are used with the detergent to obtain controlled release of it for extended periods of time (5).

Thus far, anionic detergents have been used with rubber formulations as sprays for acid-generating waste dumps. An extension of this method is obviously to inject such detergents into an acid-generating mass, almost as a grout. It would be most economical if the level of application can be selected such that *T. ferrooxidans* is killed and then to follow it up with lime injection to prevent further acid generation.

#### Treatment of Effluent

Treatment of acid drainage effluent can be done economically by alkaline neutralization (13). It is necessary to have a catchment basin for such effluent in order to ensure proper treatment and retention time prior to discharge.

Cyanide leachate can be treated by intercepting it in a catchment basin and then to allow oxidation of the cyanide. A positive cutoff should be provided between the cyanide leachate and the groundwater table. A clay liner will result in retardation of the cyanide in leachates, as discussed above. Such a liner is preferred, therefore, to a synthetic liner, which will not provide retardation capacity.

It must be emphasized that treatment of effluent is not to be considered as a long-term solution. Such treatment is usually labor intensive and therefore uneconomical. The source of the leachate must be eliminated. The methods discussed above under treatment at and after placement must therefore be considered.

#### SUMMARY AND CONCLUSIONS

The geotechnical characteristics of mine waste material are usually such that these materials can be used for road construction. However, the chemical characteristics of such wastes should be understood before they are used in construction. The problem of acid leachate is by far the most important problem; however, chemicals resulting from process considerations must also be considered. These include cyanide and heavy metals.

Leachates can have an influence on the natural environmental quality, but they can also influence the integrity of engineering structures through corrosion, chemical attack of concrete, and clogging of drains.

Leachate quality can be controlled through treatment before placement, treatment at and after placement, and treatment of the effluent. The first two are the most effective ways of controlling the problem.

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