

Geochemical Evaluation of Mining Environmental Assessment

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The Association of Exploration Geochemists is currently in a state of change with an acceptance of a growing membership in fields related to exploration geochemistry, principally analytical and environmental geochemistry. The former will be reviewed in a future explore but in this article the assessment of environmental impact from mining projects is reviewed and a case made for the importance of geochemical skills possessed by exploration geochemists.

Far from environmental geochemistry being unrelated to exploration geochemistry, it is argued that, at least in



Figure 2: Acid Pond at the base of a waste rock dump, Bisbee, Arizona.

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respect of mining environmental assessment, it has essentially the same goal (if for different purposes): that of determining anomalous concentrations of chemical elements in natural materials (e.g. Figure 1). In addition, an important objective is to identify the pathways, mechanisms and controls on the processes that facilitate this element transfer.

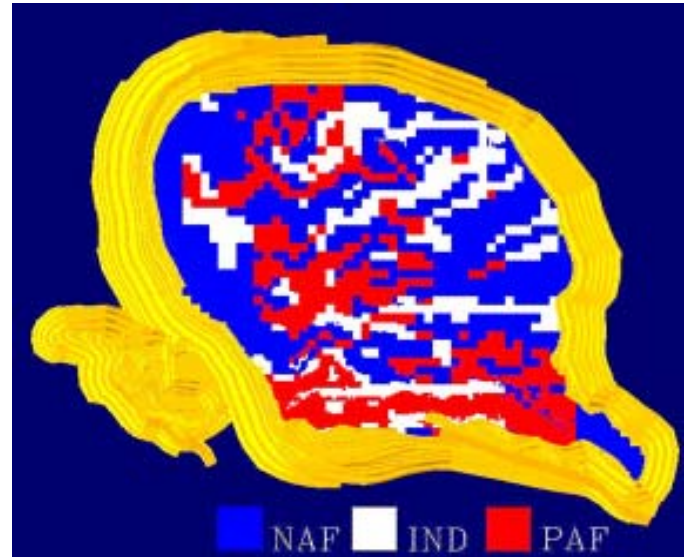


Figure 1: Geochemical mapping showing distribution of acid generating (PAF), neutralizing (NAF) and indifferent or unable to establish behaviour (IND) rock types in a pit. Gold deposit in Tanzania.

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An essential component in the evaluation of a mineral deposit or a mine development project is the consideration of environmental impact, particularly the leaching of deleterious elements such as arsenic and many of the transition metals or of Acid Rock Drainage (ARD) generation. A major part of this assessment is the potential for the materials within the mineral deposit to degrade land or water. With metal and coal mining, the principal concerns are for metal leaching and generation of acid mine drainage.

Metal leaching and generation of acidic drainage from a mineral deposit is a naturally occurring process (Nordstrom, 1982). This can cause a negative impact on the receiving environment (Figure 2 - page 1). The cost of treating problematic elements such as metals or of treating ARD can be high. But, if the major source(s) can be identified, then selective treatment may be more effective than the treatment of a much larger quantity of non-problematic material with which it is arbitrarily classified.

Typically the approach taken historically was to wait until an impact occurred and then design remediation (engineering task, Figure 3). Often this was costly and inappropriate technology was applied so environmental impact were not completely mitigated. A more recent approach has been to acquire estimates of reactivity from laboratory testwork and use this as input components to

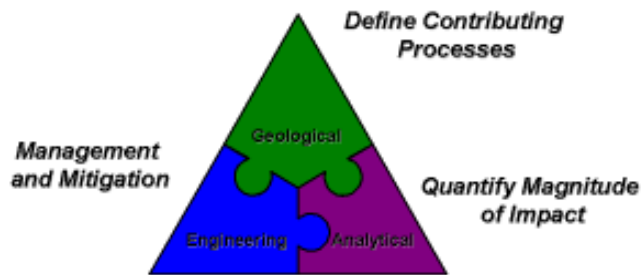


Figure 3: Three-phase approach in evaluating ARD

predictive modeling. Whilst this approach is effective in gaining predictions, very often the predictions do not match reality and unnecessary costs are incurred by the project both in the prediction and then based on this through any work undertaken or regulatory bond applied. Rarely is the third segment of the process (Figure 3) applied, which is to provide a detailed environmental geologic assessment at an early stage in the mineral property development.

The processes that govern generation of acidic leachate and mobilisation of metals (grouped collectively as Acid Rock Drainage or ARD in this paper) can be characterized and classed (SRK, 1989; Nordstrom and Alpers, 1999a). Equally, despite individual peculiarities, mineral deposits can also be classified according to mineralogic and geologic characteristics. Logically it follows that ARD characteristics can also be classed according to geologic rock type (Ficklin et al., 1992; Plumlee, 1994; du Bray, 1995; Howell et al., 2000). In terms of water parameters, different metal mineral deposits can be observed to show striking differences in terms of metal (Figure 4) and anion (Figure 5) chemistry.

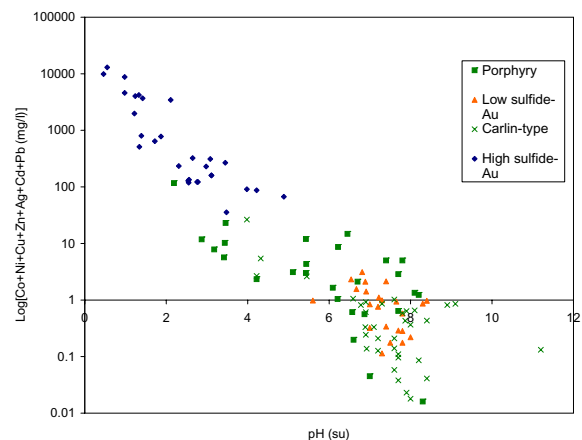


Figure 4: Flicklin diagram for different metal mines

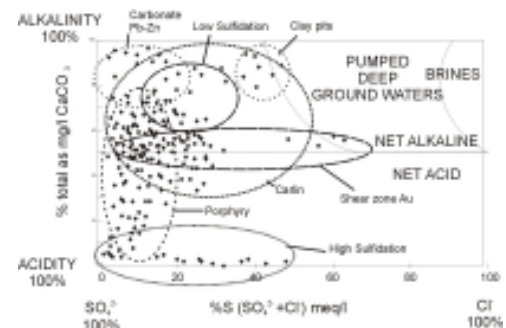


Figure 5: Younger diagram for different metal mines

The geology of a mineral deposit exerts a fundamental control on interaction with the environment. Other important controls such as geochemical and biologically mediated processes, hydrogeology, hydrology, climate, topography, mining and mineral processing methods generally modify the environmental effects inferred by the geology.

In the assessment of the acid generating potential of rock or ore types, two key factors need to be determined:

- The presence of acid generating phases
- The presence of acid consuming phases

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Acid Generation

Primary acid generating minerals are sulfides of the type, MS_2 , the most common being FeS_2 . The mechanisms of sulfide oxidation involve the transfer of electrons and for most sulfides essentially involve electrochemical “corrosion” (Thornber, 1983, 1992). Sulfides are “geo-batteries” with the emphasis on “self-corrosion” by sulfide ores. These electrochemical reactions are a combination of a reduction reaction at a cathode, on the more noble phase and an oxidation reaction at the anode on the more reactive phase.

Additionally hydrogen ions are released in the process of metal hydrolysis and this is most pronounced when the cation is iron due to the further oxidation of Fe^{2+} to Fe^{3+} and hydrolysis to form $Fe(OH)_3$ (Table 1). It should be noted that not all sulfides on oxidation generate acidity (Thornber, 1992). Indeed sulfides of the type M_2S such as chalcocite actually consume H^+ on oxidation.

The rate of sulfide oxidation can be controlled by the



Figure 6: Extensive oxidation of a Kuroko style massive sulfide deposit, Parys Mountain, Wales

rate at which oxygen is supplied and reduced at the cathode-solution interface. The separation of the cathodic oxygen-consuming, alkali-producing reaction from the anodic, oxidizing, acid-producing reaction will have a major control on the mineralogy of the resulting assemblage. The greater the distance between cathode and anode; The more extensive the conducting area; and consequently the greater the potential for sulfide oxidation.

Massive sulfide ores and sulfide-rich zones, such as those in high sulfidation epithermal systems are generally good conductors, and hence reflect significant weathering (Figure 6). The exception is with massive sphalerite, which is an insulator (Thornber, 1992). Where sulfides are more dispersed, such as in some gold-quartz vein ores, distance between oxidizing sulfides is greater and conduction is reduced so the extent of oxidation is not so great. Each sulfide grain weathers as an isolated cell and the only influence that one sulfide grain can have on another is via aqueous solution. Access by dissolved oxygen will determine leaching and sulfide composition will influence pH, water chemistry, reaction rate, and secondary mineralogy. Generally, leaching is greatest near the surface.

On weathering, sulfides can release all acid potential



Figure 7: Melanterite stalactites developed in an exploration adit, Pascua-Lama project, Chile-Argentina

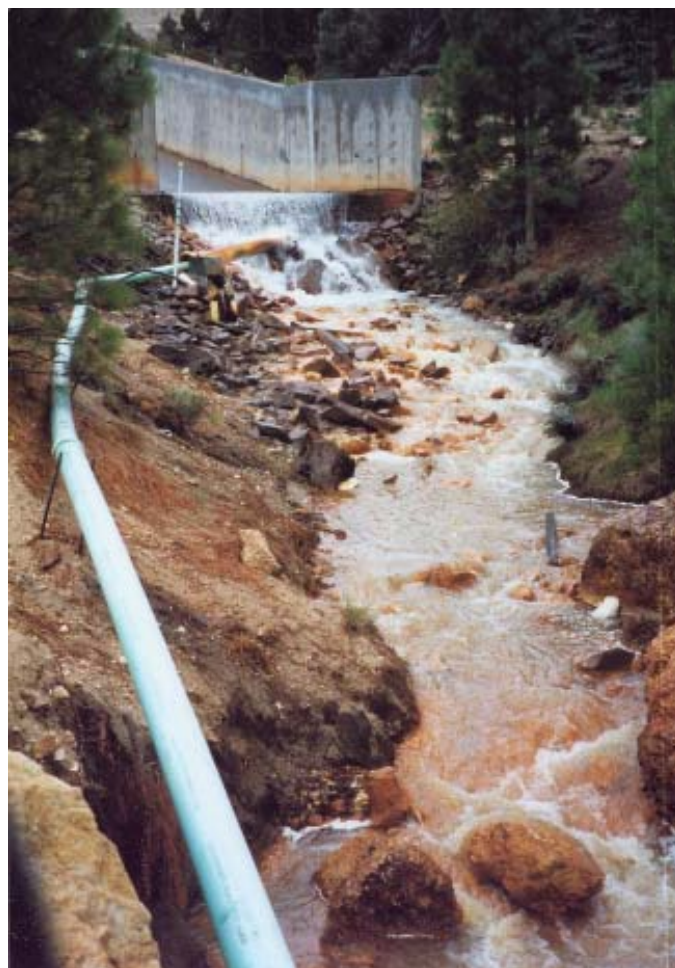


Figure 8: Impact of site ARD impacting fresh storm water, Leviathan mine, California

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producing a range of hydroxides and oxides such as goethite. Alternatively they can release only a portion of the total acidity and store some acidity in secondary salts that are stable only in oxidizing acidic pH environments, such as melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Figure 7). These minerals are highly soluble so can represent an instantaneous source of acidic sulfate-rich water upon dissolution and hydrolysis

Subsequent oxidation of ferrous iron and hydrolysis of ferric iron at $\text{pH} > 2$ provides an additional source of acidity. Hence these minerals are important as both sinks and sources of acidity, sulfate and possibly metal ions on precipitation and rapid release on exposure to moisture (Cravotta, 1994).

Buffering of acid capacity

Acid-neutralization reactions result from mineral buffering of H^+ in drainage. This buffering is frequently accompanied by the precipitation of secondary minerals (Lawrence and Wang, 1997). These reactions can reduce acid generation by forming an inhibitory surface coating on the reactive sulfides. Under acidic conditions, carbonate minerals (e.g, calcite, dolomite and magnesite) readily dissolve and provide bicarbonate alkalinity which results in neutralization of acid and precipitation of metal hydroxides. The major buffering mineral groups and characteristics with respect to ARD are shown in Table 2.

The order of carbonate neutralizing capacity is calcite>dolomite>ankerite>siderite. In the case of siderite and to a lesser extent ankerite the reason for the limited neutralizing capacity is that ferrous iron in these minerals are an additional source of acidity due to the strong hydrolysis of ferrous iron in solution. This order of reactivity is partly controlled by equilibrium mass-action constraints and partly by kinetic limitations (Morse, 1983). Carbonate minerals (especially calcite) have often erroneously been

thought of as the only geologic source of Neutralization Potential (NP). However, carbonates dominate only limestone, dolomite and marble rock types whilst the majority of geologic materials are composed of silicates and hydroxide-oxide minerals.

Silicate weathering as a proton sink has been

Table 1: Oxidation reactions of Iron sulfide and sulfate minerals generating acidity
(from *Bowell et al., 2000 based on compilations by Kleinman and Pacelli, 1991; Thornber, 1992*)

Reaction 1 a) $\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$ b) $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$
Reaction 2 a) $\text{Fe}^{2+} + \text{H}_2\text{O} + \text{O}_2 = \text{Fe}(\text{OH})_3 + 2\text{H}^+$ b) $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 1/2\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
Reaction 3 $\text{Fe}^{2+} + \bullet\text{O}_2 + \text{H}^+ = \text{Fe}^{3+} + \bullet\text{H}_2\text{O}$
Reaction 4 $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$
Stage 1 Reaction 1: proceeds abiotically and by bacterial oxidation (reaction b more common with bacterial oxidation) Reaction 2: proceeds abiotically, slows as pH falls (reaction b more common with bacterial oxidation) pH approximately 4.5 or higher, high sulphate, low Fe, low pH.
Stage 2 Reaction 1: proceeds abiotically and by bacterial oxidation (reaction b more common with bacterial oxidation) Reaction 2: proceeds at rate determined primarily by activity of bacteria such as <i>T. ferrooxidans</i> pH approximately 2.5-4.5, high sulphate, Fe and low pH. Low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.
Stage 3 Reaction 3: proceeds at rate determined by activity of <i>T. ferrooxidans</i> Reaction 4: proceeds at rate determined by rate of reaction 3 pH generally below 2.5, high sulphate, total Fe and low pH. High $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.

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Table 2. Grouping of minerals according to their neutralization potential
(from *Bowell et al., 2000 based on compilations by SRK, 1989; Sverdrup, 1990*).

Group Name	Typical minerals	Buffering pH range ¹ (su)	Approx. NP ² range	Relative reactivity ³
1. Dissolving	Calcite, aragonite, dolomite, magnesite, aragonite, portlandite and brucite	6-11.2	7.8-14.8	1.0
2. Fast weathering	Anorthite, nepheline, olivine, garnet, jadeite, leucite, spodumene, kutnahorite diopside, siderite and wollastonite	5.5-11	2.8-6.2	0.6
3. Intermediate weathering	Epidote, zoisite, enstatite, hyperthene, augite, hedenbergite, hornblende, glaucophane, tremolite, actinolite, anthophyllite, serpentine, chrysotile, talc, chlorite, biotite.	4.8-7.3	1.7-5.8	0.4
4. Slow weathering	Albite, oligoclase, labradorite, vermiculite, montmorillonite, manganite, goethite, gibbsite and kaolinite.	2.4-5.1	0.5-2.9	0.02
5. Very slow weathering	K-feldspar, ferrihydrite and muscovite	2.2-4.1	0.2-0.6	0.01
6. Inert	Quartz, hematite, rutile and zircon	3.3-3.5	<0.01	0.004

¹ buffering pH range evaluated by crushing 5g of pure mineral and mixing with 5ml of distilled water and left to react for 30 minutes. The pH of the distilled water was 3.4 su

² NP range assessed as equivalent buffering potential of 10 g of pure mineral to calcite and titrated with hydrochloric acid. So for example, 10g of portlandite ($\text{Ca}(\text{OH})_2$) was found to have the equivalent capacity to neutralise HCl acid as 14.8g of calcite. Whereas 10g of hornblende was required to buffer HCl acid to a similar pH to only 3.1g of calcite.

³ Calculated from Sverdrup's equation (1990), see below and based on 100% mono-mineral sample

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demonstrated in previous studies (Sverdrup, 1990; Bhatti et al, 1994; Moss and Edmunds, 1992). To assess the buffering capacity of mine wastes, silicate and hydroxide minerals therefore must also be considered. From soil acidification studies, Sverdrup (1990) divided the most common minerals into six groups according to pH dependency of their dissolution rate (Table 2 - previous page).

From the relative weathering rates the mineral groups show, minerals in groups 4-6 will be poor to negligible neutralizing materials due to their sluggish reaction rates. Even the intermediate and fast weathering groups, are not practical neutralizing materials unless they occur in excess of ~10% (Sverdrup, 1990).

Metal leaching and attenuation processes

The primary leaching processes include sulfide oxidation and associated mineral buffering, both of which increase the total dissolved solid load in the resulting water. The accumulation of solutes in solution will lead to saturation with respect to some species. Consequently in response to either saturation or destabilisation as aqueous species, these compounds precipitate as secondary minerals such as arsenates, phosphates, carbonates, sulfates or hydroxides. Additionally some of these solutes can be attenuated through surface adsorption onto mineral surfaces, noticeably iron hydroxides and clays. Metal release and attenuation processes can generally be thought of as occurring continuously in a mine drainage stream and the net effect is what is measured in an environmental assessment (Figure 8).

The process of element binding at the mineral solution interface and like solubility is pH dependent, for example the adsorption of arsenic species by goethite (Bowell, 1994). Many oxide surfaces change from being positive at low pH (thus attracting anions) to negative at high pH (attracting cations). Mine drainage chemistry and particularly the level of heavy metals has been shown to be influenced by adsorption onto precipitated hydrous ferric oxide, or HFO (this may also include minerals like schwertmannite, goethite and jarosite amongst others; Fuge et al., 1994; Bigham, 1994).

An important control on the diversity of the precipitated mineral assemblage is pH. For example, in the oxidation of sulfides at low pH, Fe oxyhydroxides, scorodite and sulfates are formed while at higher pH other salts such as Ca-arsenates, smithsonite and malachite are precipitated. Clay minerals such as smectite ($\text{Na}_3(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) may also be responsible for the concentration of base metals in ochres, particularly in low pH HFO promoting cation adsorption at a lower pH than with Fe-oxyhydroxides (Parfitt, 1978). The formation of smectite clays in secondary mineral zones will be controlled by the geology with propylitic alteration zones more likely to produce complex clay minerals than in Carlin type illite alteration zones.

In order to make this assessment, testwork or modelling programs are conducted to predict the magnitude of impact and to assess future changes. Very often this work is carried out late in a development timetable and can lead to

frustrating and costly delays for the developer. However, the prediction of geochemical impacts from a mineral deposit can be qualitatively determined at an early stage in development and used to execute a more efficient impact assessment. Such processes are well known to exploration geochemists

Summary

In this introduction some of the important geologic controls on the environmental impacts associated with metal mineral deposits have been described. The importance of understanding geologic processes that generate and control environmental impacts is proposed here to be fundamental not just in evaluation but also in future prediction and mitigation of the effects of acid generation and metal leaching.

The processes that generate acidity and leach metals are essentially the reaction between rocks and the environment as the rock mineralogy attempts to define equilibrium with prevailing environmental conditions. Consequently an assessment of ARD can gain considerable benefit from a geologist's knowledge of the geochemical behavior of mineral deposits as well as the changes that can be anticipated over the property with respect to structural changes, groundwater flow and mineralogical variations in the lithologies.

At the reconnaissance stage, the main task is the identification of the major acid-generation or acid-neutralising rock units. This can be achieved by examining the mineralogical content of the known rock types, their competency, petrology and extent of weathering. In highly weathered outcrops, secondary minerals can be identified and natural run-off characterized.

Once a mineralized target has been delineated a more valuable assessment can be acquired with information on mineralogical variations, porosity and structural integrity of relevant lithologies. These data are essential in the rapid assessment of acid-generating/neutralizing potential. Petrology of representative core samples will allow the description of the relationship between various sulfide and gangue minerals to be assessed. Examination of exposed sub-outcrop will reveal the nature and extent of oxidation and chemistry of secondary mineral products if not identified elsewhere. A further task is to delineate likely deleterious trace elements. This information is best collected from whole rock geochemistry acquired during exploration activities.

At the feasibility stage, a comprehensive environmental impact statement for permitting purposes is generally prepared with various detailed monitoring programs and specific studies. Any ARD studies can be significantly enhanced by allowing field geologists an opportunity to be involved in the selection of representative material to reflect the broad range of potential environmental interactions anticipated from exposed underground and pit wall lithologies, waste rock and ore stockpiles.

The geo-environmental understanding of mineral deposits is essential in defining remediation objectives. In many situations, natural drainage is poor and it is inappropriate and in a few cases impossible to remediate a

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site to "pristine conditions" with water quality required to drinking water standards. However, in many states in the USA and in many national government agencies the natural occurrence of ARD has yet to be accepted. The development of valid geo-environmental models provides a challenge to current regulatory requirements. In the future they may support the setting of more realistic closure objectives that account for local geologic variations.

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