Geological Controls on Pit Lake Chemistry: Implications for the assessment of Water Quality in Inactive Open Pits

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ABSTRACT

Open pitting is a method of mining used to exploit many mineral commodities. In many instances mining occurs below the water table leading to active dewatering of the pit during mining. On suspension of activity, pumping is terminated and as infilling of the pit is not always economic the pit is flooded, forming a pit lake.

Pit Lakes are viewed as a significant environmental issue owing to their visible presence. It is often, erroneously assumed that all pit lakes will be acid and of poor quality. Consequently in many cases extensive water quality modelling is undertaken to determine the chemical characteristics of a pit lake, with only scant geological knowledge of the pit walls. However, the water quality of a mine pit lake is largely predictable from geological knowledge of the ore deposit, the host rocks and mineralogy.

In this paper we present a case study from Nevada of an inactive open pit on which a detailed study was conducted to determine the environmental impacts. This study was greatly enhanced by using geological and geochemical mapping of the pit walls in order to determine controls on pit lake chemistry. The application of the methodologies proposed here will greatly improve future pit lake studies.

INTRODUCTION

Over the last three decades a trend in metal mining has been to move away from traditional underground mining to large scale open pit mining as new metallurgical techniques and economics make lower grade and/or mineralogically complex deposits, financially feasible. The exposure of sulfides and penetration of pitting below the water table has an impact on the hydrological-hydrogeochemical cycles around the pit. Typically in inactive pits a lake is present.

Whilst the effects of these geological processes are an essential part of environmental impact assessment for mining development or closure, very often the evaluation does not consider geological information. A common misconception of pit lakes is that they are always acidic or of poor quality protocol (Miller et al., 1996; Tempel et al., 1997). The assessment of pit lake chemistry very often relies on a few analysis of water quality and possibly limited rock characterization followed by extensive modelling of future water quality for the site. This methodology can only provide a part of the full picture site characterization, which could be greatly improved by a good geological understanding of the pit wall that can be used to refine the overall assessment. In this paper we aim to summarise the main geological controls on pit lake chemistry, define a methodology for assessment and then using a case study demonstrate how this has been used.

GEOLOGICAL CONTROLS

Structural control on local hydrology

Many ore deposits demonstrate strong structural control on the ore zones. Fractures are not only important in controlling the extent of mineralization and wallrock alteration but also an important component affecting modern groundwater flow. The interaction between water and minerals along permeable fractures will lead to a modification of water quality. Additionally where these fractures present an impermeable barrier, such as in the case of a clay filled fault gouge then this prevents water from reacting with a host rock.

Geochemical control on potential pit lake chemistry

Mineral-water reactions have been shown by several published studies to have a strong control on water chemistry in closed basins, such as a mine pit lake (Davis and Ashenberg, 1989; Huang and Tahija, 1990; Friese, 1996; Murphy, 1997; Robins *et al.*, 1997; Tempel et al., 1997). The primary environmental concern related to mineral buffering of pit lake chemistry is the oxidation of sulfides resulting in the formation acidic metal-sulfate-rich waters. These waters will emanate as small seeps in an open pit.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

Essentially acid generating minerals can be primary minerals, chiefly sulfides of the type, MS_2 or secondary sulfate minerals. The most common cause of acid generation is the oxidation of FeS_2. Pyrite and/or marcasite generate the acidity of the mine waters, through the release of H^+ and simultaneously supply large quantities of Fe and sulfate by a reaction such as:

$$FeS_2 + 32O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Where alkalinity-acidity is balanced, acid generation and neutralisation is localised. Where this does not occur or where acid generation exceeds the acid neutralising capacity of the mineral lode an acidic discharge will be emitted, in some cases even leading to super-saturation of H^+ such as recorded for Iron Mountain drainage (Alpers and Nordstrom, 1991). The relative reactivity of sulfide minerals is influenced by mineralogical controls with coarser euhedral crystals being less reactive than fine grained amorphous grains. Additionally massive sulfides will tend to react faster than isolated sulfide crystals due to delocalisation of electrons to adjacent sulfide grains (Sivenas and Beal, 1982; Thornber, 1983,1992). These act like "self-corrosion" allowing oxidation even in anaerobic environments. Where sulfides are disseminated gangue minerals essentially insulate them from other sulfides (or conductors). Oxidation of these minerals requires the migration of oxygen in water to reach the face of the sulfide grain.

On weathering, sulfides can release all acid potential 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 which are stable only in oxidizing acidic pH environments, for example the formation of jarosite:

$$3FeS_2 + 10O_2 + 10H_2O + K^+ = KFe^{3+}{}_3(SO_4)_2.(OH)_6 + 4SO_4{}^{2-} + 9H^+$$

For each mole of pyrite oxidized, only a third of the available sulfate and hydrogen is released. The rest is stored as unhydrolyzed, partly oxidized iron mineral. Acidity from these minerals is generated by the hydrolysis of ferrous iron to ferric ion and subsequently to ferric hydroxide and is often termed "mineral acidity". Typically this happens through a reaction such as:

$$Fe^{2+} + 2O_2 + H^+ = Fe^{3+} + 2H_2O$$

Followed by ferrolysis:

$$Fe^{3+} + 2H_2O + O^{2-} = Fe(OH)_3 + H^+$$

As the water table rises or as recharge percolates through the unsaturated rock, dissolution of these minerals will take place and will adversely affect water quality. This phenomenon has been observed as acid generation exceeds acid consumption.

Acid-neutralisation reactions result from mineral buffering of H^+ in drainage. This buffering is frequently accompanied by the precipitation of metal-hydroxides, hydroxy-sulfates and oxyhydroxide minerals. These reactions can reduce the rate of acid generation by forming an inhibitory surface coating to the reactive sulfides. The major buffering minerals for ARD are shown in the appendix.

The major mineral phase which consumes acidity is calcite by the reaction:

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4.\,2H_2O + CO_2$$

Carbonate minerals have a varying degree of acid neutralisation. In the case of siderite and to a lesser extent ankerite the reason for the limited neutralising capacity is that ferrous iron in these minerals are an additional source of acidity due to the strong hydrolysis of ferrous iron in solution .

The order of carbonate neutralising capacity is dolomite>calcite>ankerite>siderite. This order of reactivity is partly controlled by equilibrium mass-action constraints and partly by kinetic limitations. Generally the rate of dissolution is sufficient to maintain water pH in the range 6.5-7.5. For dolomite dissolution is slower and for ankerite and siderite disequilibrium is common.

If all available calcite is removed then pH will decrease to a dolomite buffer range of pH 6-7. When dolomite is depleted pH will fall to the siderite buffer regime of pH 4.8-6.3. In the carbonate buffer zones the precipitation of metal hydroxides are promoted with dissolved Fe derived from sulfides, Mn and Al from wallrock oxides and silicates. As acid generation continues and carbonate minerals are depleted, pH will fall until the hydroxide buffer zones are reached, for $Al(OH)_3$ this is the pH range 4-4.3 and for $Fe(OH)_3$ the pH range 2-4. Under very low pH conditions, the dissolution of aluminosilicates can be an important acid neutralization mechanism. Dissolution is slow and also involves dissolution of secondary minerals. Some calc-silicates, such as wollastonite, have the potential to provide significant buffering.

Thus three essential mechanisms are operative, primary and secondary acid generation and alkaline generation or acid buffering (Bowell et al., 1996). The relative association, concentration and reactivity of the minerals involved will influence water chemistry.

METHODOLOGIES FOR GEOLOGICAL ASSESSMENT

Field Mapping

Given the importance of geological controls on pit lake chemistry (as described above) the geological mapping of pit walls can be viewed as being essential in evaluating pit environmental geology.

Important criteria required for this includes the following:

- Location of main host rock and ore-bearing zones

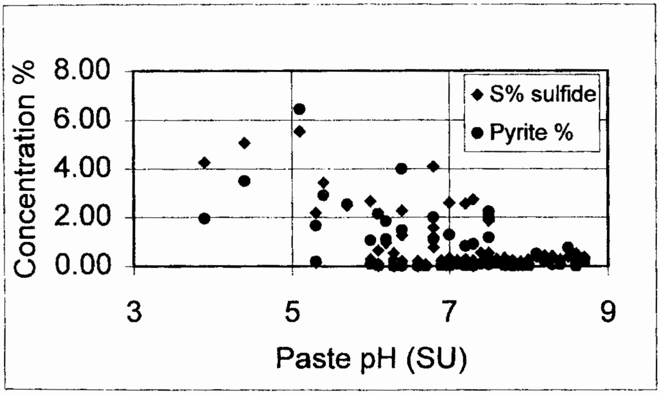
- Location of major fractures and their potential role as either water flow paths or flow barriers; providing a refinement of any conceptual model constructed to evaluate the pit environmental geology.
- Identification of major acid producing and acid consuming minerals in the host rocks and ore zone.

Field Analysis

This visual estimate can be supported by field analysis including assessment of reactivity, *via* paste pH/TDS and total acidity, *via* field Acid Concentration Potential (SRK, 1989; 1998). Essentially the lower paste pH the more reactive the acid salts, typically acid volatile sulfate salts, in the material.

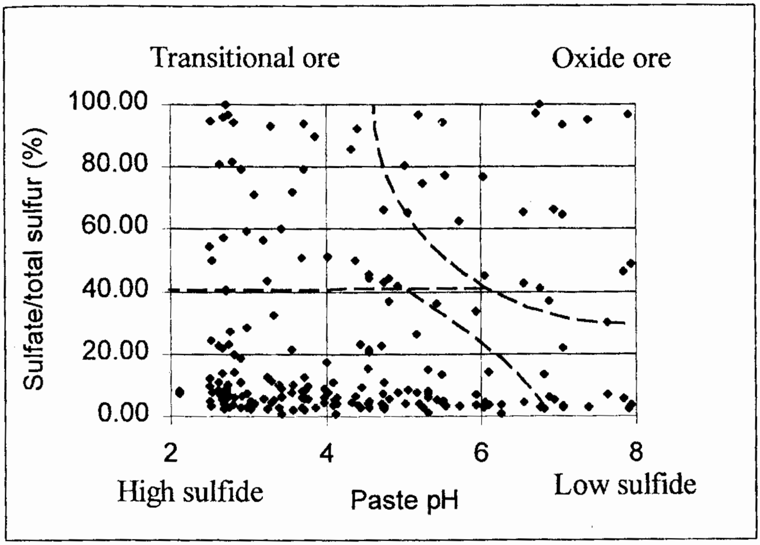
Acid Concentration Potential from field results is also shown for the same samples. As can be observed this shows a negative correlation with paste pH and a stronger correlation with sulfide sulfur (Figure 1).

Figure 1: Correlation between sulfide S, pyrite and field paste pH, data from several mineral deposits



The discrepancy in some samples can be explained by the sulfur chemistry of the samples. Where sulfur chemistry is dominated by sulfide then for disseminated sulfides, oxidation is sluggish and despite high potential for acid generation, paste pH is not particularly acidic(Figure 2). Where sulfides are more massive (and therefore can "self-corrode") or sulfate sulfur forms a higher portion of the sulfur assay then paste pH is typically acidic. This assessment then provides an objective basis from which laboratory samples can be selected for testwork and refines many of the assumptions used in geochemical and hydrogeological modelling of a pit lake.

Figure 2: Sulfate/Total Sulfur (%) versus paste pH. Data from several different deposits



CASE STUDY : SUMMER CAMP PIT, GETCHELL MINE, NEVADA

The Getchell mine,in northwestern Nevada has been mined over several intervals since 1934 and the recent operations have been active since the mid-1980's. Mining has primarily focused on near surface oxide and sulfide ores which have been exploited *via* open pits. The Summer Camp Pit (SCP) deposit was found by exploration drilling in 1989 and mining was initiated in October 1990. Mining of the economic ore in the pit was completed by October 1991. Dewatering was carried out during operations. The pumps were switched off in October 1991. Soon after this the pit sump turned acidic. Water quality recovered in terms of pH and arsenic in 1993 when dewatering of the Getchell Main Pit (2 miles to the north) and subsequently in 1995 the Getchell Main underground mine began supplying a large volume of alkaline water (Figure 3). The pit currently serves as water storage for seasonal excess of mine water and acts as a settlement basin for the turbid waters produced by the Getchell Main underground mine. However this water has also contributed appreciable levels of arsenic, sulfate and Total Dissolved Solids (TDS)

Environmental Geology of the Pit

Geology in the SCP is dominated by andalusite and pyrite bearing hornfels, marble and a series of breccias and veins (Figure 4). The gold mineralization on Summer Camp pit is typical of sediment-hosted disseminated gold deposits or Carlin-type deposits (Berger, 1989; Berentsen et al., 1996).
The ore appears to have comprised a number of discrete "higher grade" zones (breccias or jasperoids) linked by lower grade zones in hydrothermally altered wallrock. Throughout the

lithologies exposed in the upper 8-10 m of the pit sulfides have been partly or completely oxidized with mineralized units in the pit resembling gossans with intense iron staining and well developed boxwork textures after sulfide minerals. Elsewhere in the pit E-W trending faults are infilled by barren breccias and fault clay gouge which from the experience of exploration geologists, involved in the drilling work, appear to act as an aquitard . The breccias and veins contain mainly of quartz, carbonates, sericite, carbon with up to 20% sulfides comprising pyrite, realgar, orpiment, sphalerite, chalcopyrite, electrum and secondary pararealgar, goethite, jarosite and Fe-Ca-Zn-Cu arsenate, carbonate and sulfate minerals (Bowell, 1997). The disseminated mineralization is characterised by pyrite, pararealgar, stibnite and orpiment dispersed in the rock matrices and associated with amorphous carbon, calcite, ankerite-dolomite, sericite, clays and cut by fine quartz veinlets.

The mineralogy described above of the various geological units in the SCP area can be used to infer potential for acid generation/neutralization in the lithologies.

For acid generation the most significant mineral is pyrite particularly fine grained framboidal pyrite followed by chalcopyrite and arsenopyrite. Other sulfides have a lower ARD potential with realgar actually showing little effect on water pH (Thornber, 1992). Some secondary minerals will also contribute acidity, principally the iron and copper sulfates. The principal acid consuming minerals are calcite and ankerite-dolomite. Siderite and to a lesser extent ankerite although net acid consumers will also generate some acidity from the ferrous to ferric conversion.

Consequently all the mineralized units and the pyritic hornfels, particularly the black carbonaceous units, can be considered as being acid generating units. In neutralising ARD high alkalinity from carbonate dissolution is required so the marble and to a lesser extent the carbonate-bearing hornfels units are useful acid consumers. The microgranite rocks in the north of the pit are possibly weak acid generators, due to the presence of pyrite. The superficial materials are likely to be inert with respect to ARD. Additionally the mineralogy has an important role in considering the geochemical availability of deleterious elements in the ore material. The principal deleterious elements will be the chalcophile elements such as arsenic, copper, antimony and zinc which are concentrated in the mineralized units and to a much lesser extent the hornfels. Additionally acidic waters have the potential to mobilise aluminium from alumino-silicates in the wallrocks which would be dissolved in response to mineral buffering.

Environmental Geochemical Assessment of the Pit

In order to select samples for laboratory analysis field analysis of paste Fe, Sulfate, TDS, field ABA and pH were undertaken. The summary of these results is shown in Table 1 and the sampling points on Figure 4.

Whilst undertaking geological mapping field data for paste and aquatic pH, TDS, Fe, and sulfate were collected. Paste pH and Electrical Conductivity were measured using Hanna field meters, Fe, and sulfate were measured using a Cole Parmer spectrophotometer. Total Dissolved Solids were calculated using the conversion method of Hem (1985). Paste concentrations are generally lower than laboratory concentrations as this test reflects the highly reactive component but is a good guide to the relative reactivity of the lithologies.

The data demonstrates that the pyritic-black hornfels and ore zones are the significant contributors of low pH, high TDS, Fe-sulfate leachate into the pit lake. From this screening appropriate samples to reflect the full range of leachate characteristics can be selected and subjected to laboratory testwork. The strong control by secondary sulfate salts in this case study meant that many of the field ABA results were in close agreement with laboratory results where sulfate sulfur was a significant component of the sulfur chemistry.

Table 1: Summary of field chemistry and laboratory results

Parameter	Field result (mean+2SD)	Laboratory result (mean)
pH	5.12±1.8	5.21±1.4
TDS, mg/l	927±213	898±196
Fe, mg/l	18.32±9.88	16.72±7.19
Sulfate, mg/l	366±280	250±187

On the basis of the field data a provisional acid potential map (Figure 5) could be drawn up for the site thus refining during fieldwork sample selection for laboratory follow-up testwork and the conceptual model developed as an aid to manage the site.

As can be observed from the diagram acid generating potential is concentrated in the partly oxidized and unoxidized portions of the sulfide-bearing rocks. Sulfide oxidation or dissolution of acid volatile sulfates will only occur if these minerals are exposed to sufficient dissolved oxygen and a catalyst to drive the sulfide oxidation reaction. This is reflected in the field data which demonstrates that at the time of sampling a small exposure of partly oxidized pyrite was exposed on the south west wall of the pit resulting in acid generation. The geological investigations at SCP highlighted the importance of secondary iron sulfates over primary sulfides as being the major control on pit lake pH. If similar detailed environmental geology studies were carried on similar pits the same result may also be found. This has important consequences for the control and mitigation of acid inflow into a pit lake.

CONCLUSIONS

In this paper we have attempted to describe some of the important geological controls on the environmental impacts associated with metal mine open pits. The importance of understanding geological processes that generate and control changes in water quality and quantity in a pit lake are stressed.

A case study, of the Summer Camp Pit in Nevada, is presented as a demonstration of field geological techniques in the Environmental Impact Assessment of an open pit. Such work greatly improves sample selection criteria for more comprehensive laboratory testwork and refines the understanding of impacts at an early stage in a project. By using detailed geological information on the pit host rocks the importance of secondary sources of acid generation was highlighted. This information will be used to control and mitigate acid inflows to SCP.

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REFERENCES

ALPERS, C.A. and NORDSTROM, D.K. (1991) Geochemical evolution of extremely acid mine waters at Iron Mountain, California: Are there any lower limits to pH ? In: *Proceedings Second Int. Conf. Abatement Acidic Drainage,* 2, 321-342. MEND Secretariat, Ottawa, Ontario.

BERENTSEN, E.J., NANNA, R.F., HAZLITT, S.J. and ESTES, L.D.(1996) Discovery and geology of the Turquoise Ridge gold deposit. *Mining Engineer*, October 1996, 31-35.

BERGER, B.R. (1989) Geological relationships at the Getchell mine and vicinity, Humbodlt County, Nevada. *Society of Economic Geologists Fieldtrip Guidebook, Field Conference to Northern Nevada*, 111-135.

BOWELL, R.J (1997) Review of Mineralogy and Water Quality of the Summer Camp Pit System. *SRK Report 710RB034 for Getchell Gold Company.* 305pp.

BOWELL, R.J., FUGE, R., CONNELLY, R.J. and SADLER, P.K.J. (1996) Controls on ochre chemistry and precipitation in coal and metal mine drainage. In: *Minerals, Metals and the Environment II, Prague, September 1996.* I.M.M., London. 291-322.

CRAVOTTA, C.A. III (1994) Secondary iron-sulfate minerals as sources of sulfate and acidity. In: Environmental Geochemistry of Sulfide Oxidation (eds: C.N. Alpers and D.W. Blowes). *Am.Chem. Soc. Sym. Series*, 550. 345-364.

DAVIS, A., and ASHENBERG, D. (1989) The aqueous geochemistry of the Berkerley Pit, Montana, USA. *App. Geochem.,* 4, 23-36.

FRIESE, P. (1996) Acid mine pit lakes. In: Proceedings of the Goldschimdt Conference. San Francisco

HEM, J.D. (1985) Study and Interpretation of the Chemical Characteristics of Natural Waters. *USGS Water Supply Prof. Paper,* 2254, (3rd ed.). 253pp.

HUANG, H-H. and TAHIJA, D., (1990) On the nature of Berkerley Pit Water. *Proceedings Mineral and Hazardous Waste Processing Symposium.* Butte Montana 10/01/90.

MILLER, G., LYONS, W.B., and DAVIS, A. (1996) Understanding the water quality of pit lakes. *Environ. Sci. & Tech.*, 30, 118-123A.

MURPHY, W.M. (1997) Are pit lakes susceptible to limnic eruptions ? *Tailings and Mine Waste 97.* 543-548. Balkema, Rotterdam

ROBINS, R.G. et al.(1997) Chemical, physical and biological interaction at the Berkerley Pit, Butte, Montana. *Tailings and Mine Waste□97.* 529-541. Balkema, Rotterdam.

SIVENAS, P and BEALS, F W. Natural geobatteries associated with sulphide ore deposits. *J Geochem. Explor.*, 17, 1982, 123-143.

SRK, (1989) *Draft ARD Technical Guide*, 1. BC AMD Task Force.

SRK (1998) *Protocols for ARD Assessment*. SRK(UK) Ltd

TEMPEL, R.N and BENNETT, J PRICE, J. G., LECHLER, P, SHEVENELL, L. and PASTERNAK, K.,BARTA, J., and BOWELL, R.J. 1997 Geochemical Modeling of natural waters at Getchell mine, Humboldt County, NEVADA. *Proceedings of "Living with a Closed Basin" Nevada Water Association Annual Meeting, Elko October 1997*

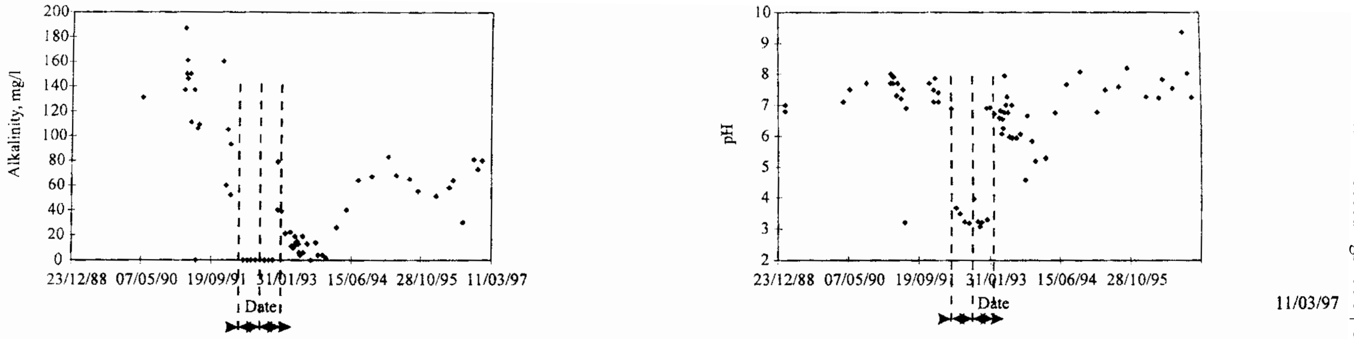
THORNBER, M.R. Mineralogical and electrochemical stability of the nickel-iron sulphides pentlandite and violarite. *J. Appl. Electrochem.*, 13, 1983 253-267.

THORNBER, M.R, (1992) Chemical processes during weathering. In: *Handbook of Exploration Geochemistry, vol 4: Regolith Exploration Geochemistry in Tropical Terrains* (eds: C R M Butt and H Zeigers), 65-99. Elsevier.

Appendix: Summary of Common Primary and Secondary Acid Generating and Neutralizing minerals

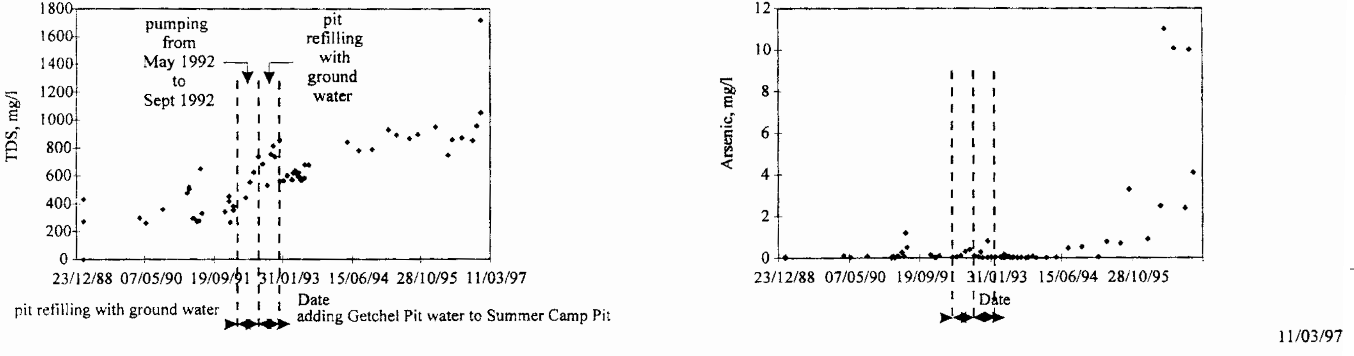
Mineral	Formula	Present in SCP
***Common Primary Acid Generators*[1]**		
pyrite-marcasite	FeS_2	Yes
pyrrhotite	$Fe_{1-x}S$	Yes
chalcopyrite	$CuFeS_2$	Yes
arsenopyrite	$FeAsS$	Yes
pentlandite	$(Fe,Ni)_9S_8$	
molybdenite	MoS_2	Yes
enargite	Cu_5AsS_4	
tennantite	$Cu_{10}(Cu,Fe^{2+},Zn,Hg\ Ag)_2(As,Sb)_4S_{13}$	Yes
orpiment	As_2S_3	Yes
stibnite	Sb_2S_3	Yes
Primary Acid Consumers		
calcite	$CaCO_3$	Yes
anikerite-dolomite (zoned)	$Ca,Fe(CO_3)_2$ -$Ca,Mg(CO_3)_2$	Yes
siderite	$FeCO_3$	
muscovite-biotite	$(K,Ca,Mg,Na)(Mg,Fe^{2+},Al)Al_2Si_{2\text{-}3}O_{10}(OH)_2$	Yes
K-Na feldspar	$(K,Na)AlSi_3O_8$	Yes
Ca-Na feldspar	$(Ca,Na)Al(Al,Si)Si_2O_8$	Yes
scheelite	$CaWO_4$	Yes
apatite	$Ca_5(PO_4)_3F$	Yes
fluorite	CaF_2	Yes
realgar	AsS	Yes
***Secondary Acid Generators/Source of Delerterious elements*[1]**		
scorodite	$FeAsO_4.2H_2O$	Yes
pharmacolite	$CaHAsO_4.2H_2O$	Yes
weilite	$CaHAsO_4$	Yes
legrandite	$Zn_{14}(AsO_4)_9OH.12H_2O$	Yes
austinite	$CaZnAsO_4OH$	Yes
cornwallite	$Cu_5(AsO_4)_2.12H_2O$	Yes
goethite	$FeOOH$	Yes
pyrolusite	MnO_2	Yes
manganite	$MnOOH$	Yes
pararealgar	AsS	Yes
mirabilite	$Na_2SO_4.10H_2O$	Yes
gypsum	$CaSO_4.2H_2O$	Yes
chalcanthite	$CuSO_4\ .2H_2O$	
langite	$Cu_4(SO_4)(OH)_6\ .2H_2O$	Yes
jarosite	$K\ Fe_3^{3+}(SO_4)_2(OH)_6$	Yes
copiapite	$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2.20H_2O$	Yes
halotrichite	$Fe^{2+}Al_2(SO_4)_4.22H_2O$	Yes
melanterite	$Fe^{2+}SO_4.7H_2O$	Yes
***Secondary Acid Consumers and Adsorbents for delerterious elements*[1,2]**		
azurite	$Cu_3(CO_3)_2(OH)_2$	Yes
malachite	$Cu_2CO_3(OH)_2$	Yes
illite	$KAl_2(Si,Al)_4O_{10}(OH)_2$	Yes
smectite	$(K,Na)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O$	Yes
barite	$BaSO_4$	Yes

[1] Other minerals do exist in the lithologies which have a minor (in terms of volume) impact on acid generation/neutralization ir SCP[2] Some secondary sources can also act as adsorbents or consumers of delerterious elements or buffer pH (such as jarosite anc goethite)



ALKALINITY VARIATION WITH TIME

pH VARIATION WITH TIME



TDS VARIATION WITH TIME

ARSENIC VARIATION WITH TIME

Figure 3: Trends in pit lake chemistry, Summer Camp Pit

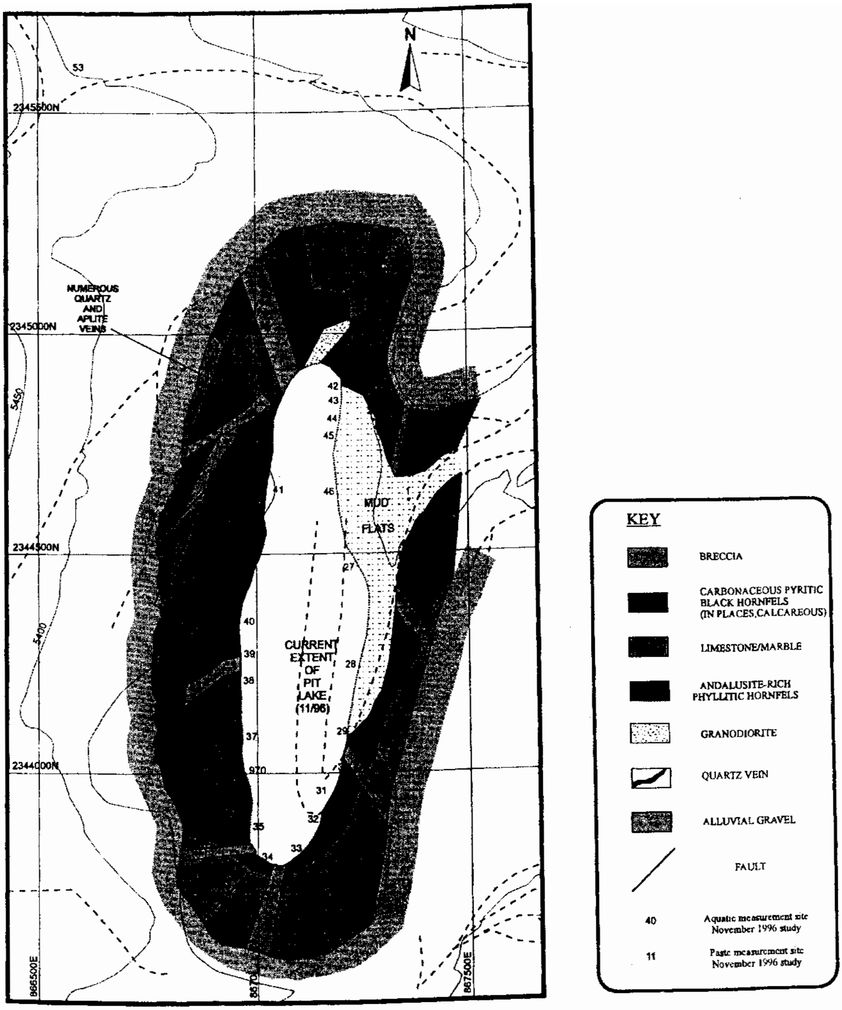


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Figure 4: Simplified geology and sample point map
Summer Camp Pit

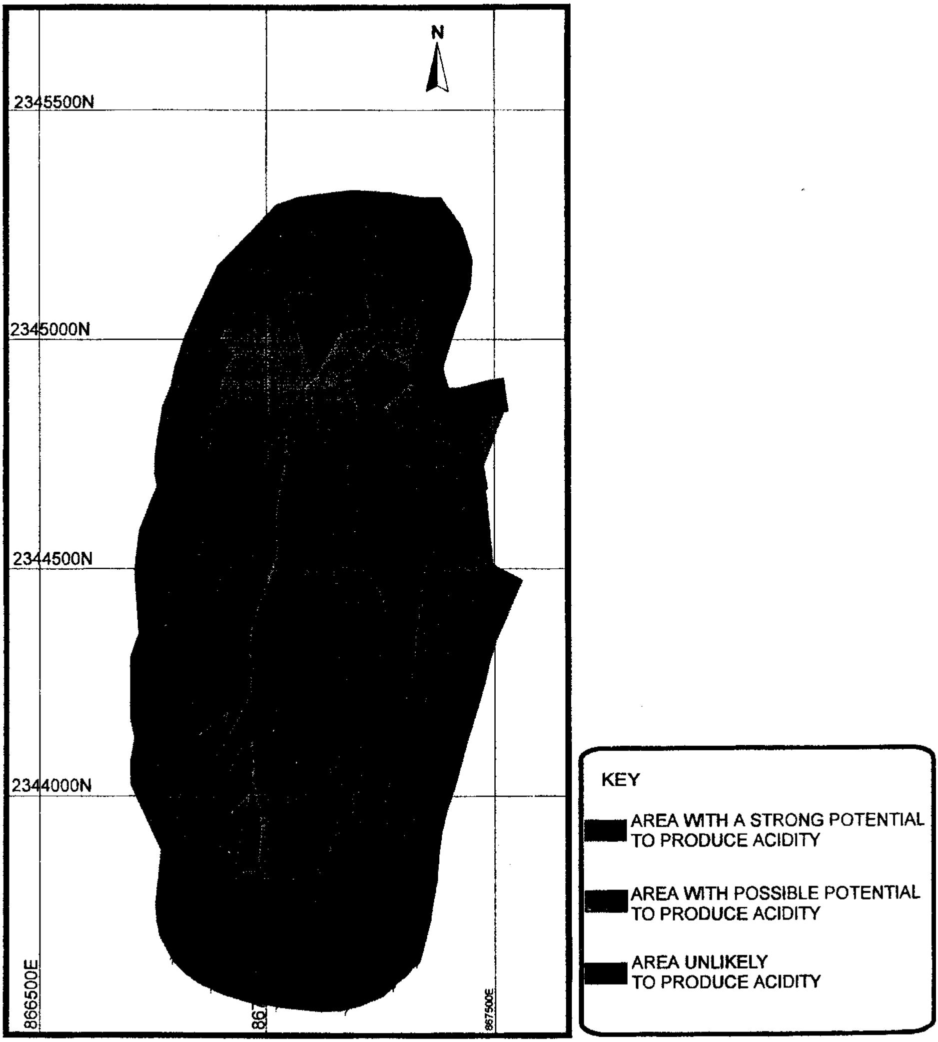

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Figure 5: Schematic classification of Summer Camp Pit geology with respect to Acid Generation Potential