The hydrogeochemical dynamics of mine pit lakes

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The hydrogeochemical dynamics of mine pit lakes

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Abstract: On cessation of mining open pits or opencast workings that extend below the water table are likely to fill with water and thus develop a mine pit lake (MPL). This body of water remains as a permanent feature on the mine site and as such becomes a closure issue with respect to water quality and potential to degrade groundwater. Further, it may present a risk to the environment through the development of poor quality water with elevated concentrations of metals, metalloids, sulphate and depressed pH.

The prediction of future pit lake water quality within a MPL is, therefore, essential in considering environmental impact on a closed or abandoned mine facility. The controls on a MPL will vary over time, and will involve chemical, biological and physical processes. Localized and regional-scale processes affect these in turn. Consequently, in order to predict pit lake water quality it is essential to understand the hydrogeological, geochemical and limnological processes that influence water quality.

Open-pit mining has become a common place method for extraction in the mining industry in recent years due to the advancement in mineral processing, which allows the economic utilization of near-surface low-grade high tonnage ores. This is particularly true for gold and copper operations in many parts of the world (Peters 1987).

If mining has occurred below the water table, then on closure and abandonment of these facilities, the pit fills with water producing a mine pit lake (MPL). The length of time needed for the lake to reach full depth will depend on several factors including pit dimensions, rainfall–evaporation budget, groundwater inflow and groundwater regime. By comparison, MPLs tend to show a greater depth to surface area ratio than most natural lakes, with implications for water circulation. Generally, pit lakes are smaller than natural closed lake basins and thus the depth to surface area ratio is usually greater than 1 for a MPL (Table 1).

MPLs can and do exhibit thermal and chemical stratification, and show changes related to seasonal turnover. However, the greater depth to surface ratio limits water circulation and thus a permanent stratified or anaerobic layer remains preserved through the development of a chemoline (Fig. 1). Another major difference is that, for natural lakes, recharge is generally through surface water, whereas, for MPLs, groundwater flow is generally more important (Atkins *et al.* 1997).

In many cases the requirement for predictions of water quality is made during the design and permitting stage, prior to mining. Consequently, the predictions tend to be hypothetical, based on numerical predictive modelling and laboratory assessment of wall-rock behaviour (Pillard *et al.* 1995; Kirk *et al.* 1996; Davis & Eary 1996). It follows that, in some cases, the predictions can be in error due to limitations in the input data available for the model (Kempton *et al.* 1997). Methodologies for the prediction of pit lake chemistry involve construction of a series of linked empirical and physical models to represent the major controlling physio-chemical processes (Bird *et al.* 1994; Miller *et al.* 1996; Havis & Worthington 1997; Kempton *et al.* 1997; Murray 1997; Eary 1998). These processes include groundwater inflow, direct precipitation and pit wall–precipitation contact or run-off water, wall-rock–groundwater interaction, evaporation, and limnological and geochemical processes operating within the MPL itself. The latter includes oxidation–reduction, desorption or adsorption of metals and metalloids with mineral surfaces, precipitation and dissolution, as well as organic processes such as methylation or the activity of sulphate-reducing or sulphide-oxidizing bacteria (Fig. 2). The geochemical enrichment of potentially toxic elements in a MPL can lead to organisms having a harmful level of exposure. For example, within the Berkeley Pit, 342 migratory geese were exposed to a lethal concentration of metals when they used the pit lake on a seasonal migration.

The closure of open-pit mining operations requires careful planning to avoid environmental

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Table 1. *Comparison of hydromorphic properties of pit lakes with those of Natural lakes (After Tempel et al. 1999 with additional data)*

	Surface area (km^2)	Depth (m)	Surface area/depth ratio
Natural lakes			
Lake Superior	82,350	395	208 481
Lake Victoria	69,485	455	152 714
Lake Baikal	30,510	1367	22 319
Pyramid Lake	438	102	4 294
Mine pit lakes			
Berkeley Pit	0.32	259	1.23
Summer Camp Pit	0.113	21.33	5.38
Ruth Pit	0.222	40	5.55
Crone Bane	0.084	17	4.94
Magcobar	0.158	70	2.26

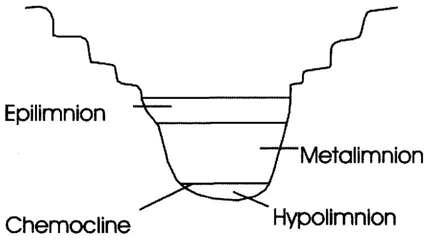


Fig. 1. Schematic representation showing nomenclature used in referring to the zones within a stratified pit lake (after Drever 1988).

impact. Thus, the formation of a MPL can affect both the availability and the quality of water resources in a mining area. Consequently, the assessment of water chemistry is a critical aspect of a open-pit closure programme. This paper presents an invited review of the current status of knowledge regarding the major hydrogeochemical processes that operate within a MPL.

It should be noted that hydrogeological and hydrological processes are also important but are outside the scope of this paper and will not be discussed in detail here. The reader is referred to Fetter (1994), Havis & Worthington (1997), Shevenell & Pasternak (2000) and papers elsewhere in this volume.

Conceptual model

In considering the interaction of a MPL with its environment, the fundamental consideration is what is the relationship of the MPL to the environment. If the MPL acts as a terminal sump,

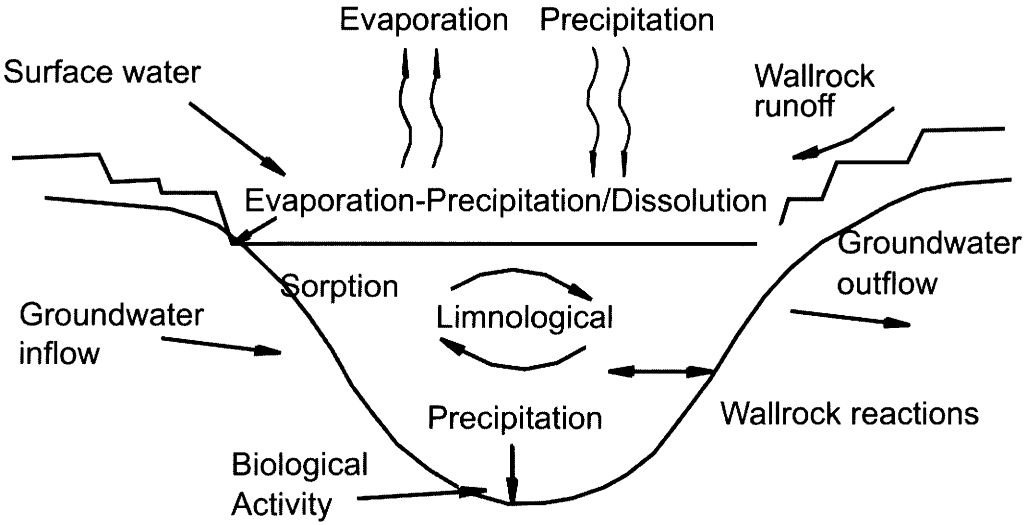


Fig. 2. Schematic representation of the geochemical processes that influence water quality within a mine pit lake.

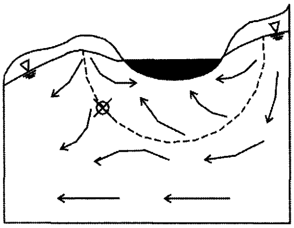
i.e. the lowest hydrological point within a basin, then it acts as an evaporation pan with no net outflow other than evaporation (Fig. 3).

However, if the MPL is not a sump then 'flow-through' can occur within the MPL and it can interact with the surrounding groundwater environment (Robins *et al.* 1997; Davis *et al.* 1998). The Berkeley Pit at Butte, Montana has been one of the most studied MPLs (Davis & Ashenberg 1989; Miller *et al.* 1996; Robins *et al.* 1997). This pit lake is acidic and has high metal and sulphate concentrations (Table 2), and has impacted the immediate groundwater environment along with water draining old underground workings (Robins *et al.* 1997). In the Robinson Mining District, Ely, Nevada, groundwater has been sufficiently influenced by reaction with oxidized sulphide-bearing host rocks both in underground workings and open pits that distinct hydrogeochemical groundwater blocks can be mapped in the district, and groundwater shows a similar chemistry to MPLs (Davis *et al.* 1998).

Mine pit lake chemistry

The chemistry of a MPL is often, erroneously, assumed to be acidic, such as those pit lakes developed at Parys Mountain or Berkeley (Table 2). In many cases MPL chemistry can be circumneutral and have low metal chemistry, such as those as Copper Flat, Yerrington, and Getchell. In some cases, the pH of the pit lake can exceed pH 7, such as at Magcobar mine in Ireland (Table 2).

Terminal Sump



Through - Flow System

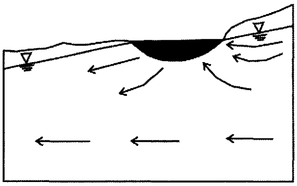


Fig. 3. Hydrogeological scenarios for a mine pit lake interaction with the the groundwater environment.

It should be noted that in this paper the metal and oxyanion concentrations are quoted from filtered samples (at 0.45 μm) rather than total, unless otherwise stated. This is because total metal concentrations will include particulate metals as well and thus the influence of chemical release processes could be overestimated. The 0.45-μm fraction includes all metals mobilized as free ions, chelated species and in a colloidal form.

In high pH environments, high metalloid concentrations can occur (Fig. 4), such as in the North Pit on the Getchell Mine in Nevada, where historically As levels can reach 10 mg l^{-1} (Miller *et al.* 1996). Certainly in these waters evapo-concentration is an important mechanism for enrichment of As and also for Se (Eary 1998). By contrast, low pH environments are characterized by high concentration of dissolved metals as hydrated cations and chelates (Fig. 5) or anions (Fig. 6). The major mineralogical controls on pit lake chemistry, based on predictive thermodynamic modelling for a range of Nevada pit lakes, has recently been published by Eary (1999). These are shown in Table 3 and are supplemented with phases that are important in reducing environments, such as the basal sediments of some pit lakes. Not all of these controls will be relevant to every site, due to local variations in hydrochemistry, but these represent the more common ones.

The chemistry of a MPL may change with time and reflects a dynamic rather than static equilibrium. For example, at the Summer Camp Pit site in Nevada, where water chemistry has changed from acidic to circumneutral (see the case study below).

High sulphide (particularly pyritic) wall-rocks, such as those exposed in the Parys Mountain and Berkeley pits, tend to produce poor water quality (Table 2). Oxidized wall-rocks that contain appreciable carbonate tend to produce better quality pit lakes due to the abundance of reactive buffering in the host rocks, such as at Magcobar in Ireland.

Consequently the chemistry of MPL can vary widely and this can be related to three major groups of controls:

- limnological processes – this relates to the lake's physical processes and how they will influence geochemical reactions;
- geochemical constraints – this is related to the minerals present, the chemistry of reactive water and the environment's physico-chemical status in controlling

Table 2. *Representative analysis of mine pit lakes*

Parameter	Parys Mountain	Crone Bane, Ireland	Magcobar, Ireland	Corta Atalaya, Rio Tinto, Spain	Berkeley Pit, Montana	Ruth Pit, Nevada (1993)	North Pit, Getchell Mine, Nevada (1982)	Cortez Pit, Cortez, Nevada
Ref.	Bowell *et al.* (1996)	Unpublished data	Unpublished data	Unpublished data	Davis & Ashenberg (1989)	Miller *et al.* (1996)	Miller *et al.* (1996)	Miller *et al.* (1996)
pH	2.3	5.77	7	1.6	2.8	3.9	7.67	8.07
TDS, ($mg\,l^{-1}$)	6000	3750	1210	15 000	–	4150	2420	432
Alkalinity ($mg\,l^{-1}$)	0	0	512	0	0	0	–	–
SO_4 ($mg\,l^{-1}$)	5200	2530	563	14 300	5740	2840	1570	90.2
Ca ($mg\,l^{-1}$)	21.6	586	161	379	462	558	530	45.2
Ba ($mg\,l^{-1}$)	<0.001	<0.004	0.071	<0.001	–	0.008	–	0.06
Al ($mg\,l^{-1}$)	108	11	0.6	2400	–	23.7	–	–
As ($mg\,l^{-1}$)	0.77	<0.005	<0.005	22.4	0.05	<0.005	0.38	0.038
Cu ($mg\,l^{-1}$)	69.6	23.4	0.006	245	156	37.1	<0.005	
Fe ($mg\,l^{-1}$)	1300	0.08	5.1	4700	386	6.32	0.16	0.134
Pb ($mg\,l^{-1}$)	<0.001	<0.005	0.032	4.11	–	0.007	<0.005	0.004
Mn, mg/L	4.8	65.2	0.73	344	95	68.6	0.13	0.002
Se ($mg\,l^{-1}$)	0.02	<0.005	<0.001	8.9	–	<0.005	0.003	–
Zn ($mg\,l^{-1}$)	54	29.5	6.3	435	280	32.2	0.02	0.002

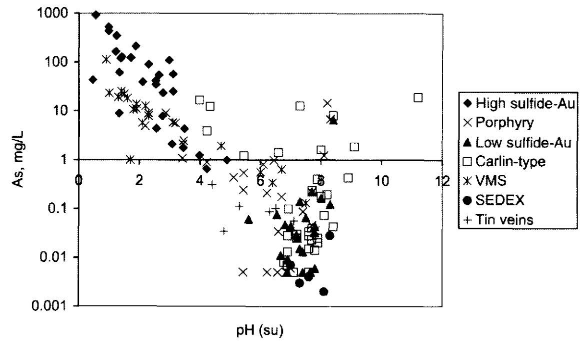


Fig. 4. Variation in arsenic within mine pit lakes as a function of ore deposit type (using the classification of Du Bray 1995) and pH. Data from published and unpublished sources.

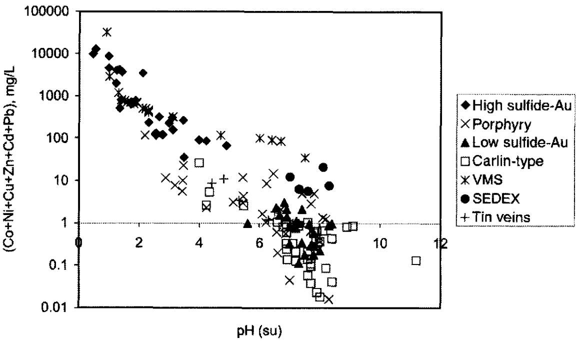


Fig. 5. Flicklin diagram assessing variation in divalent metal cations with pH and ore deposit type (Flicklin *et al.* 1992). Data from published and unpublished sources.

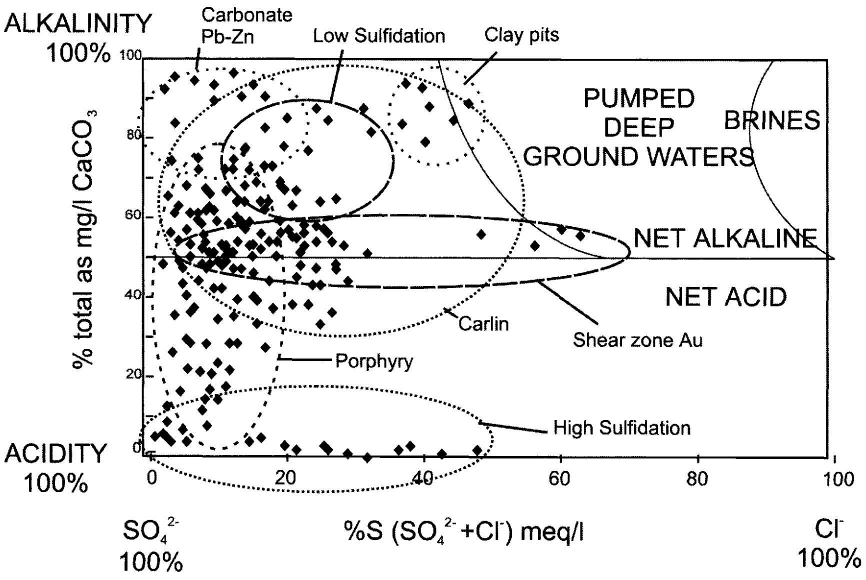


Fig. 6. Younger diagram (Younger 1995) for various pit lake waters. Data from published and unpublished sources.

Table 3. *Geochemical controls on major and important trace components in a mine pit lake system (based on a scheme formulated by Eary 1999). Prediction of mineral phase control based on thermodynamic calculations as well as mineralogy of pit lake sediments*

Component	Acidic (pH <4.5)	Circumneutral (pH 4.5–7.5)	Alkaline (pH >7.5)
Aluminium	Alunite, basaluminute	Gibbsite	Gibbsite
Alkalinity	Not applicable	Calcite	Calcite
Arsenic	Scorodite/adsorption onto HFO	Adsorption onto HFO/Fe-sulphides*	None identified/As- and Fe-sulphides*
Barium	Barite	Barite	Barite/witherite
Cadmium	None identified	Adsorption onto HFO/Zn-sulphides*†	Otavite/Zn-sulphides*
Calcium	Gypsum	Gypsum	Gypsum/calcite
Copper	Chalcanthite/cupromelanterite	Brochantite/covellite/Fe-sulphides*	Malachite/brochantite/covellite*
Fluoride	Fluorite	Fluorite	Fluorite
Iron	Melanterite/halotrichite/Fe-sulphides*	HFO/ferrihydrite/Fe-sulphides*	HFO/ferrihydrite/Fe-sulphides*
Lead	Anglesite/chloropyromorphite	Anglesite/chloropyromorphite/galena*	Cerrusite/chloropyromorphite
Manganese	Manganite/birnessite	$MnHPO_4$	Rhodochrosite
Nickel	Morenosite/Fe-minerals†	Morenosite/Fe-minerals†	Gaspéite/ni-oxides, nickeline
Selenium	Gypsum	Adsorption onto HFO	None identified
Sulphate	Gypsum	Gypsum	Gypsum
Zinc	Zinc melanterite	Hydrozincite/smithsonite/$ZnSiO_3$/Zn-sulphides†*	Zincite/Zn_2SiO_4/Zn-sulphides*

* In reduced environments.
† As a trace element.

the extent to which release and attenuation mechanisms can proceed;

- geological controls – this is related to the characteristics of individual mineral deposits and will influence the extent to which geochemical reactions will occur.

Limnological processes

Pit lakes in temperate climatic zones can develop vertical density stratification that may be seasonal or permanent. The density of water is a function of both its temperature and its salinity or total dissolved solids (TDS) content. Fresh water is densest at a temperature of about 4°C. At a given temperature, water density increases with increasing TDS. As its TDS increases, the temperature of maximum density of water also decreases.

Natural lake processes

Thermally induced seasonal density stratification in mid-latitude lakes of uniform dilute chemistry (uniform low TDS) is due to increases in ambient temperature in the spring and summer. As the air temperature and solar radiation increase, the surface water is heated (Fig. 7). This heating causes the density of the surface layer to decrease. The lake then has a surface layer ('epilimnion') of uniform lower density and higher temperature, and an underlying layer ('hypolimnion') of higher density and lower temperature. A zone called the 'thermocline' or metalimnion, in which the temperature decreases rapidly with depth, separates these layers (Fig. 1). Above the thermocline, the surface water is mixed by wind or surface inflow and is typically in equilibrium with atmospheric oxygen. The epilimnion is typically less than about 10 m deep, because wind-induced mixing in mid-latitude pit lakes seldom reaches beyond this depth. Below the thermocline, oxygen may gradually become depleted by oxidation of dead algae and lake fauna that fall into the hypolimnion from the surface.

At some point in the late autumn or early winter, the surface water temperature drops below that of the underlying water and the surface water density is now greater than that of the underlying water. The surface water sinks until it reaches the level of its new density. Eventually, the entire water column may overturn, depending on the temperature structure of the lower layer and the amount of cooling at the surface. Overturn through the water column could take less than 1 day or occur over several weeks. Overturn causes mixing that replenishes the oxygen throughout the depth of overturn, potentially to the bottom of the lake.

The water behaviour during winter depends on whether ice forms. If ice forms, the water below the ice may gradually lose its oxygen by the same processes that occur in the lower layer in summer. Below the ice, the water may become temperature stratified with 4°C water at the bottom or it could remain well mixed due to heating from the sides and bottom of the pit. Which process occurs depends on the relative temperatures of the air, water, ground and ground thermal conductivity. If no ice forms and the air temperature keeps the surface water in the vicinity of 4°C, the entire lake may remain well mixed and oxygenated throughout the winter.

In spring, the air temperature increases. If ice had formed in the winter it gradually melts and the water temperature increases from the surface downward, as well as from the bottom up. When the surface water temperature reaches 4°C, the lake may again overturn and reoxygenate due to the denser surface water. If no ice had formed and the lake had continuously overturned in the winter, warmer temperatures in the spring would repeat the cycle of thermally induced seasonal density stratification.

Mine pit lake

The seasonal cycle just discussed assumes that the pit lake has essentially no TDS and its density is unaffected by precipitation or evaporation. For example, if spring snowmelt and run-off have a significantly lower TDS than the lake water TDS, the addition could induce stratification near the lake surface, even when no temperature differences exist due to the lower density of the snowmelt. In dry temperate climates that experience positive net evaporation in the summer, evapoconcentration at the lake surface can increase the TDS and thus the density of the surface water. This density increase can potentially offset the density decrease of the surface water due to thermal heating in the summer. In such cases, the lake may overturn in late summer or fall even before the surface water temperature drops below the temperature of the underlying water, as long as the density of the surface water exceeds that of the underlying water.

Long-term (multi-year) or permanent density stratification can occur if a lake has a significant vertical variation in TDS due to large differences in the TDS of various source waters to the lake and/or to processes in the lake that increase the TDS. This in turn affects the density of the deeper water (Fig. 8). For example, if the lake contains enough organic matter to deplete oxygen

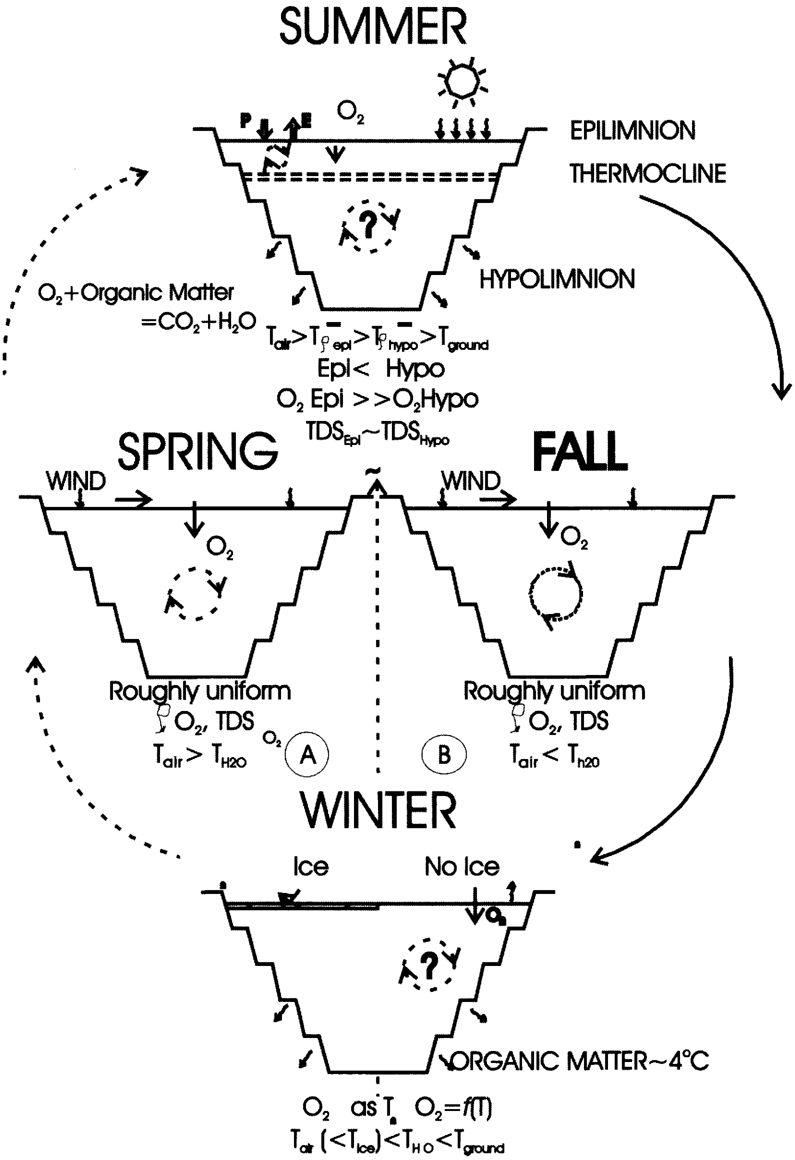


Fig. 7. Thermally induced stratification within a lake (from Parshley *et al.* in prep.).

in the hypolimnion, then during the summer ferric hydroxide that precipitates at the surface will sink, become reduced and dissolve in the basal anoxic water, raising the TDS content and the density of the bottom water.

Typically, a chemically stratified lake has an upper layer of lower TDS water overlying a layer of higher TDS water ('hypolimnion'). A zone called the 'chemocline', in which the TDS increases rapidly with depth, separates the two layers (Table 4). If the bottom layer is sufficiently deep (well below the depth of summer wind mixing), a seasonal middle layer ('metalimnion') may form below the summer thermocline and above the denser hypolimnion. Overturn in the autumn–winter usually occurs throughout the metalimnion, but not the hypolimnion. Thus, once the hypolimnion becomes anoxic, it remains so and will continuously dissolve any ferric hydroxide precipitates falling into it from above. This process further increases the TDS of the hypolimnion and strengthens the density

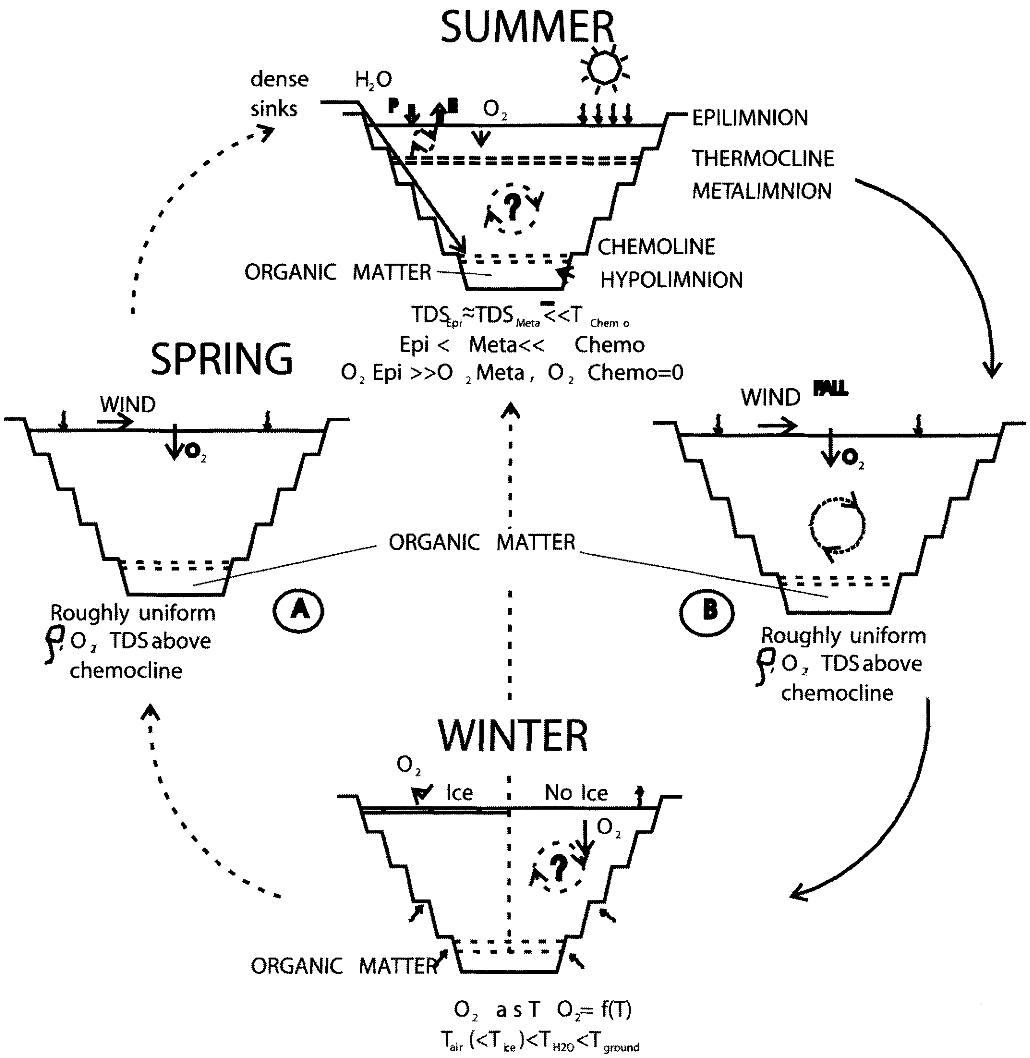


Fig. 8. Chemical and thermally induced stratification (from Parshley *et al.* submitted.).

gradient between it and the overlying layer, perpetuating the stratification. Sulphidization, in the hypolimnion, will lead to natural attenuation of metals and metalloids as well as sulphur (see below).

Few studies reporting MPL site-specific limnological data have been published to date (Gannon *et al.* 1996; Atkins *et al.* 1997; Parshley *et al.* submitted). These studies deal with pit lakes in Nevada in the western USA and display similar trends indicating that turnover occurs in MPLs similar to natural lakes.

Geochemical controls on MPL chemistry

In considering the geochemical processes that influence MPL chemistry (Fig. 9), processes can be viewed in terms of:

- Release processes – those that release elements into the pit lake;
- Attenuation processes – those that remove elements from the hydrosphere either as precipitation or through adsorption;
- Concentration processes – those that lead to accumulation of elements in the MPL.

Table 4. *Examples of stratified pit lakes*

Date	Magobar February 1998	Magobar February 1998	SCP 25 February 1998	SCP 25 February 1998	SCP 13 June 1998	SCP 13 June 1998
Depth, (m)	0	50	0	23	0	20
pH	6.7	6.1	8.01	3.67	8.54	7.5
Eh (mV)			278	−108	256	160
TDS	555	885	714	3490	245	922
Temperature °(C)	7.6	7.9	3.7	6.8	16.4	15.9
Dissolved O_2	1.5	0.15	4.8	1.2	3.9	2.4
Alkalinity	451	753	74	0	154	85
Chloride			46	51	13	59
Sulphate			370	2200	22	420
Na	26	30	33	36	25	34
Mg	52	82	16	46	7.5	19
Ca	142	242	140	400	30	160
Mn	6.2		0.06	1.1	0.21	0.19
Fe (II)			0.14	414	0.1	158
Fe (total)	<0.2	26	0.65	416	1.2	160
Ni	0.078	0.21	0.058	3.2	0.018	0.96
Cu			0.002	0.018	0.013	0.003
Zn	5.8	8	0.01	16	0.03	4
As (III)			0.01	6.6	0.01	15.3
As (total)	<0.005	<0.005	1	7.53	0.025	16
Cd	0.016	0.007	0.002	0.6	0.01	0.006
Pb	0.007	0.004	<0.003	<0.003	<0.001	0.001

* All concentrations in mg l^{-1} unless otherwise stated.

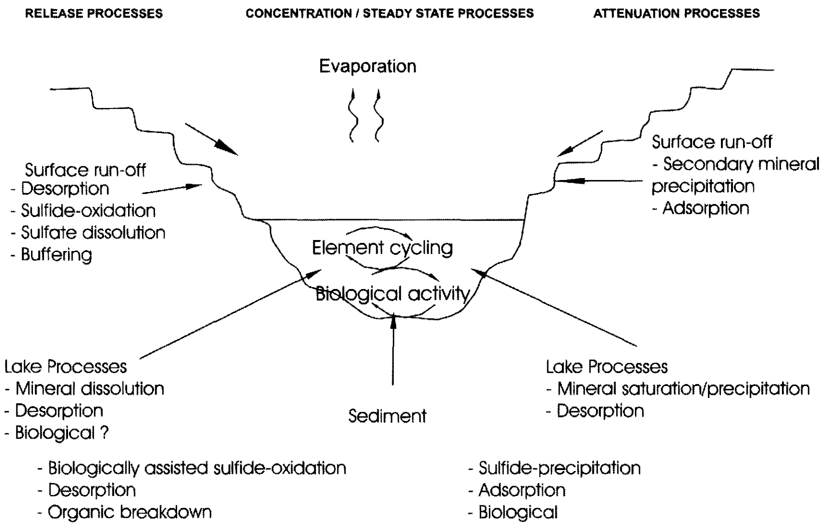


Fig. 9. Relationship between release–attenuation–concentration processes.

Principally these involve sorption onto colloids or evapoconcentration of salt components.

Release processes

This involves mineral–water reactions such as sulphide oxidation, sulphate dissolution or mineral buffering of water chemistry. Within many hard rock pits the most important reactions are those involving sulphide-bearing rocks.

The primary leaching processes for metals include sulphide oxidation and associated mineral buffering, both of which increase the total dissolved solid load in the resulting water. The rates at which such reactions occur are important as they can occur over a time scale of seconds to millions of years (Langmuir 1997). A generalized set of relative half-time reaction rates are shown in Table 5. As can be observed, hydrolysis reaction rates occur at relatively fast rates while mineral dissolution can take much longer. The wide range of precipitation rates reflect

Table 5. *General reaction rates important in mine pit lake systems (based on a compilation by Langmuir 1997)*

Reaction type	Reaction time frame
Solute reactions:	
$H_2CO_3 = H^+ + HCO_3^-$	$C. 10^{-6}$ s
Solute-water reactions:	
$CO_2 + H_2O = H_2CO_3$ (hydration)	$C. 0.1$ s
$Cu^{2+} + 2H_2O = Cu(OH)_2 + 2H^+$ (hydrolysis/complexation)	$C. 10^{-10}$ s
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ (hydrolysis/complexation)	$C. 10^{-6}$ s
$Al_{n+m}(OH)^{+m}_{3n+2m} + m\,H_2O = (n+m)Al(OH)_3(s) + m\,H^1$ (multivalent ion hydrolysis)	h–year
Adsorption/desorption reactions:	
$X(AsO_4^{3-}) + PO_4^{3-} = X(PO_4^{3-}) + AsO_4^{3-}$, where X is the adsorption site	C. s–h
Oxidation-reduction:	
$Fe^{2+} + 0.25O_2 + 2.5H_2O = Fe(OH)_3 + 2H^+$	min–h
Mineral–water equilibria:	
$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$	week–year
Isotopic exchange:	
$^{34}SO_4^{2-} + H^{32}S^- = H^{34}S^- + ^{32}SO_4^{2-}$	Year(s)
Mineral recrystallization:	
$Fe(OH)_3 \cdot n\,H_2O = \alpha\text{-}FeO \cdot OH$ (goethite) $+ (n+1)H_2O$	Year(s)

the variation between precipitation of amorphous solids that can occur in a matter of minutes to formation of crystals that occurs on a geological time scale.

When sulphides are exposed to oxygen and water in the presence of a catalyst they undergo oxidation. The reaction leads to release of metals/metalloids, sulphate and possibly protons, or saturation to form secondary minerals (Thornber 1975, 1992; Nickel & Daniels 1985; Alpers *et al.* 1994; Miller *et al.* 1996; Nordstrom & Alpers 1999*a*; Bowell *et al.* 2000). Essentially, the determination of the resulting water chemistry in most hard rock scenarios will depend on:

- the concentration and presence of acid-generating phases;
- the concentration and presence of acid-consuming phases.

Sulphide–water reactions can produce acid pH water, most noticeably in the case of MS_2 (where M is a metal cation, eg Cu, Mo) and/or with iron-bearing sulphides (Thornber 1992). The mechanisms of sulphide oxidation involve the transfer of electrons because most sulphide minerals are electrical conductors in the semi-conductor–metallic range (Thornber 1983, 1992). The rate of sulphide oxidation can be controlled by the 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, then the more extensive the conducting area. Consequently, this leads to greater potential for sulphide oxidation. Anodic reactions can occur deep within cracks, fissures and along grain boundaries where solutions can penetrate without the necessity for dissolved oxygen (Thornber 1975, 1992). The oxidation of pyrite by ferric iron, can be given as:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \quad (1)$$

This is a first-order reaction with a rate given as $1 \times 10^{-4}\,s^{-1}$ (McKibben & Barnes 1986; Moses *et al.* 1987). With oxygen as the oxidizing agent the rate can be considerably faster by orders of magnitude (Karamenko 1969; Langmuir 1997).

However, it should be noted that not all sulphides on oxidation generate acidity (Thornber 1992; Jennings *et al.* 2000). Indeed, sulphides of the type M_2S such as chalcocite actually consume H^+ on oxidation. To reflect this the oxidation of chalcocite can be written as:

$$2Cu_2S + 6H_2O + 5O_2 = 4Cu^{2+} + 2SO_4^{2-} + 4H^+ + 8OH^- \quad (2)$$

Dissolution or oxidation of pyrite initially produces Fe^{2+} that is almost instantly oxidized to Fe^{3+}, which is either precipitated as an oxyhydroxide or reduced by pyrite generating more Fe^{2+} and increased acidity.

On weathering, sulphides can release all acid potential precipitating secondary minerals (Williams 1990; Nordstrom & Alpers 1999*a*, *b*). 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 melanterite:

$$FeS_2 + \frac{7}{2}O_2 + 8H_2O = Fe^{2+}SO_4{\cdot}7H_2O + SO_4^{2-} + 2H^+. \quad (3)$$

For each mole of pyrite oxidized, only a portion of the available hydrogen is released. The rest is stored as partly oxidized metal sulphate minerals. These minerals are highly soluble so can represent an instantaneous source of acidic, metal sulphate-rich water upon dissolution and hydrolysis, for example the dissolution of melanterite:

$$4Fe^{2+}SO_4{\cdot}7H_2O + O_2 = 4FeO{\cdot}OH + 4SO_4^{2-} + 8H^+ + 22H_2O. \quad (4)$$

Oxidation of ferrous iron and hydrolysis of ferric iron at $pH > 2$ provide the additional source of acidity through the reactions:

$$4Fe^{2+} + 10H_2O + O_2 = 4Fe(OH)_3 + 8H^+. \quad (5)$$

The ability of these minerals to react with water will depend on solubility. Hence, these minerals are important as both sinks and sources of acidity, sulphate and, possibly, metal ions on precipitation and rapid release on exposure to moisture (Nordstrom 1982; Fillipek *et al.* 1988; Cravotta 1994).

Acid-neutralization reactions result from mineral buffering of H^+ in drainage. This buffering is frequently accompanied by the precipitation of secondary minerals (Kwong & Ferguson 1997; Lawrence & Wang 1997; Nordstrom & Alpers

1999*a*). These reactions can reduce acid generation by forming an inhibitory surface coating on the reactive sulphides. Under acidic conditions, carbonate minerals (e.g. calcite, dolomite and magnesite) readily dissolve and provide bicarbonate alkalinity that results in neutralization of acid and precipitation of metal hydroxides. 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 is 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 geological source of neutralization potential (NP). However, carbonates dominate only limestone, dolomite and marble rock types, whilst the majority of geological materials are composed of silicates and hydroxide–oxide minerals.

Silicate weathering as a proton sink has been demonstrated in previous studies (Sverdrup 1990; Bhatti *et al.* 1994; Moss & Edmunds 1992; Kwong & Ferguson 1997). 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 6). From the relative weathering rates of the mineral groups shown (Table 6), minerals in the poor–negligible neutralizing categories are unlikely to react due to their sluggish reaction rates. Even for minerals in the intermediate and fast mineral weathering groups, they will not be practical neutralizing materials unless they occur in excess of approximately 10% (Sverdrup 1990).

Attenuation processes

The accumulation of solutes in solution will lead to saturation with respect to some species. Consequently, in response to either saturation or destabilization as aqueous species, these compounds precipitate as secondary minerals such as arsenates, phosphates, carbonates, sulphates or hydroxides. An important control on the diversity of the precipitated mineral assemblage is pH. At low pH, oxyhydroxides and sulphates are commonly the main precipitates, while at higher pH other salts such as carbonates and hydroxides become more abundant; for example in the case of copper (Fig. 10).

Some solutes can be attenuated through adsorption onto mineral surfaces, noticeably iron hydroxides and clays. This is the process of element binding at the mineral–solution interface and, like solubility, is pH-dependent (Sigg & Stumm 1980; Stumm 1992; Deng & Stumm 1994; Dzombadt & Morel 1990). Many oxide surfaces change from being positive at low pH (thus attracting anions) to negative at high pH (attracting cations).

Pit lake chemistry, and particularly the level of As and 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; Scott 1987; Fuge *et al.* 1994; Bigham 1994; Bowell *et al.* 1996). It should, however, be noted that in many acidic environments, flushing or dissolution of these HFO can lead to high As concentrations in solution, as well as competition from complexing ions mobilizing As-oxyanions.

As described above, as water pH increases above 3, hydrous ferric oxides precipitate that may ultimately crystallize to form goethite or a similar ferric hydroxide (Bigham 1994). As pH increases, ferric hydroxide solubility decreases with a minimum being around pH 6–7. At low pH, precipitated HFO tends to scavenge negatively charged oxyanions, as the surface of the HFO is positively charged in the Helmholtz layer (Deng & Stumm 1994). In low pH environments these HFO particles are usually colloidal sized and have a high reactivity proportional to surface area (Fig. 11). As the pH increases and colloid particles aggregate as Fe–OH bonds become longer and more rigid, due to the excess of hydroxyl molecules, the surface pH of the particles changes, and becomes, negative. In the case of goethite this occurs at a pH of between 6 and 9 (Parfait 1978; Hiemstra & van Riemsdijk 1996). The point at which this occurs is termed the point of zero charge (Stumm 1990). As pH increases the surface of the HFO particles attracts metallic cations and releases oxyanions (Fig. 11). In circumneutral–alkaline oxic environments, As and Se form species such as $H_nAsO_4^{-(3-n)}$ and $H_nSeO_4^{-(2-n)}$ respectively (Bowell 1994). These molecules do form sparingly soluble solids and, as they are not strongly adsorbed, their dissolved concentrations can increase in the pit lake from continued release and evaporation.

Attenuation of metals also occurs through sulphidization in the hypolimnion. Mineralogical analysis of pit lake sediments at Summer Camp Pit, Nevada (see case study below) has identified authigenic sulphides not observed in bedrock geology, including mackinawite ($[Fe, Ni,Co,Zn]_9S_8$)

Table 6. *Grouping of minerals according to their neutralization potential (Sverdrup 1990)*

Group name	Typical minerals	Buffering pH range*	Approx. NP range*	Relative reactivity[‡]
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	2.8–0.6.2	0.6
3. Intermediate weathering	Epidote, zoiste, 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

* Buffering pH range evaluated by crushing 5 g of pure mineral and mixing with 5 ml of distilled water and left to react for 30 min. The pH of the distilled water was 3.4.

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

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

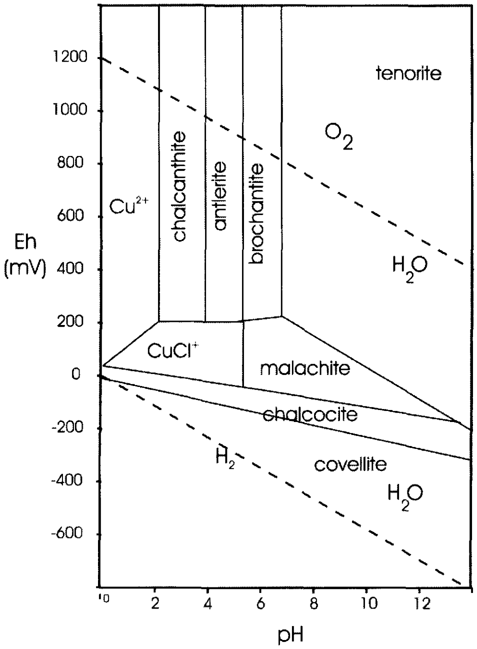


Fig. 10. Simplified Eh–pH diagram for the system Cu–S–Cl–O–H at 298K showing the dominance fields of copper minerals.

and greigite ($Fe^{2+}Fe_2^{3+}S_4$). Similar processes have been observed in deep-sea anoxic sediments (Morse 1994) and natural wetlands (Kwong & Van Stempvoort 1994; Rees 1998).

Concentration processes

In dry environments, where evaporation exceeds precipitation, the latter can exert an important control on water chemistry. The influence of evapoconcentration on brines is well understood (Garrels & Mackenzie 1967; Eugster & Hardie 1978; Drever 1988). As binary salts are precipitated the result is that further evaporation will result in an increase in the relative dissolved concentration of the ion or molecule present in greater concentration. This concept of 'chemical divides' has become the basis of understanding the influence of evaporation on natural lake chemistry in a closed basin (Eugster & Hardie 1978). If a MPL is a terminal sink then evapoconcentration can be predicted to occur over time. On the basis of this approach, Eary (1998) assessed the influence on MPL. As most pit lakes are circumneutral to alkaline, water chemistry is generally dominated by carbonate alkalinity and can evaporate until $CaCO_3$ becomes saturated and calcite is precipitated. Generally, this is the first chemical divide observed in the development of lake chemistry at equilibrium with atmospheric CO_2 (Drever 1988). This can be expressed as:

$$Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O. \quad (6)$$

Consequently, the concentrations of Ca and bicarbonate (and thus pH) will be controlled by calcite precipitation and evapoconcentration. Where the pit lake initially has $2m_{Ca} < m_{alkalinity}$ (here alkalinity is the sum of $m_{HCO_3} + m_{CO_3}$) then with continued evaporation, calcite will precipitate (Eary 1998). When Ca concentration in minimal then calcite precipitation will reduce to such a small amount that carbonate–bicarbonate molecules will concentrate in solution and exsolve CO_2 with further evaporation. This will increase water pH and the resulting highly saline alkaline fluid will have a chemistry of $Na–K–HCO_3–CO_3 \pm Cl \pm SO_4$. Such conditions are observed in several natural lakes such as Pyramid Lake, Nevada (Drever 1988). Where pit lake chemistry shows $2m_{Ca} > m_{alkalinity}$, then evapoconcentration increases until all available carbonate is removed by calcite precipitation and Ca concentrations increase with evaporation. The next 'chemical divide', which in the case of most MPL is that of gypsum, will be the next control on pit lake chemistry, by a reaction such as:

$$CaCO_3 + SO_4^{2-} + H^+ + 2H_2O$$
$$= CaSO_4{\cdot}2H_2O + HCO_3^-. \quad (7)$$

This is the probably the most important control for MPL water quality (Fig. 12). For most MPL in Nevada, Eary (1998) predicted that equilibrium chemistry would be of the type circumneutral $Ca–Na–SO_4–Cl$ chemistry. On the basis of this, Eary (1998) demonstrated that two differing evapoconcentration paths would be followed by oxyanions dependent on the major chemical controls in the pit lake. Where $2m_{Ca} < m_{alkalinity}$ then a $Na–HCO_3–CO_3 \pm Cl \pm SO_4$ type chemistry will result and pH can evolve to highly alkaline conditions ($pH > 9$). In this environment oxyanions are not adsorbed and can accumulate over time. By contrast, where $2m_{Ca} > m_{alkalinity}$ then pH is buffered to be circumneutral and oxyanions are strongly adsorbed and thus are not accumulated in the pit lake. In this scenario, pit lake chemistry evolves over time to become circumneutral $Ca–Na–SO_4–Cl$. On the basis of most case studies, the latter case will be the more common. In very acidic pit lakes the major control will relate to

Table 7. *Hydrogeochemistry of Summer Camp Pit (depth, 0–10 ft)*

Parameter*	15/05/90	18/03/91	03/04/91	24/04/91	31/05/91	26/06/91	05/12/91	04/02/92	04/05/92	04/06/92	27/07/92	03/08/92	06/10/92	03/11/92	02/12/92	06/01/93	17/05/93	05/10/93	08/12/94	02/05/95	01/03/96	14/05/96	11/06/96	01/10/96	01/12/96	03/01/97
pH	7.7	7.7	7.3	7.2	3.2	7.2	7.86	7.1	3.67	3.48	3.22	3.18	3.96	3.08	3.29	6.92	7	5.97	8.06	7.58	7.23	7.82	7.53	9.36	8.02	6.93
TDS (mg l^{-1})	265.5	295	295	271	649	342	265	384	555	625	738	680	531	814	856	566	620	590	789	867	747	858	870	851	955	1717
Alk. (mg l^{-1})	149	155	187	111	0	109	160	93	0	0	0	0	0	0	0	79	14	6	64	68	51	58	64	30	81	80
Sulphate (mg l^{-1})	37	97	nd	Nd	nd	Nd	nd	nd	196	209	588	560	317	572	522	386	360	488	400	450	430	490	430	430	510	1000
Fe (mg l^{-1})	nd	nd	nd	Nd	nd	Nd	nd	nd	3.9	5.6	14	17.2	4.7	47	49.3	0.56	0.74	1.5	0.15	0.48	0.31	0.4	0.13	0.12	0.52	0.37
As (mg l^{-1})	0.021	0.053	0.074	0.27	1.2	0.15	0.023	0.086	0.044	0.11	0.32	0.41	0.12	0.29	0.81	0.04	0.07	0.019	0.53	0.7	2.5	11	10.1	2.4	10	1.4
Cu (mg l^{-1})	<0.02	<0.02	0.03	0.03	1.06	0.06	< 0.02	0.03	0.35	0.47	0.49	0.51	0.29	0.71	0.74	0.05	0.05	0.22	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Zn (mg l^{-1})	<0.01	0.32	0.69	0.76	6.4	1.06	0.01	5.2	11.6	10.8	13	13.7	18.2	26.8	21.2	7.35	5.1	5.5	< 0.02	1.7	1.4	< 0.02	< 0.02	< 0.02	1.5	0.11
Ca (mg l^{-1})	52.4	nd	nd	Nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	99	nd	Nd	164	360	190	180	nd	nd	nd
Mn (mg l^{-1})	nd	nd	nd	Nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.04	nd	Nd	nd	3.7	0.09	0.05	nd	nd	nd

* Alk., alkalinity; nd, not determined; TDS, total dissolved solids.

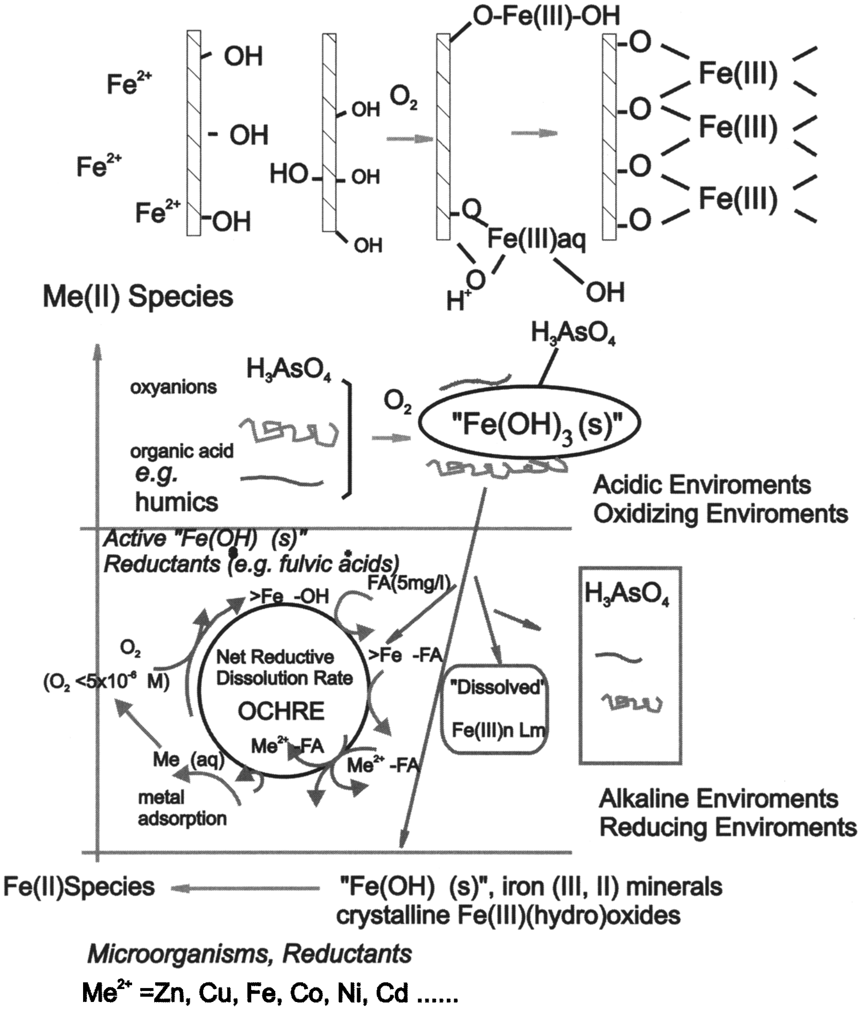


Fig. 11. Schematic diagram showing implications of hydrous ferric oxide chemistry on solute transport at different pH (from Deng & Stumm 1994).

sulphuric acid equilibrium. In the latter, the main controlling salts will be iron sulphates such as melanterite or gypsum. In either case, but particularly in the former, evapoconcentration can produce highly saline, highly acidic metal-rich brines (Nordstrom & Alpers 1999*b*).

Steady-state cycling

Within an established MPL, release and attenuation processes will reach a steady state or equilibrium at some stage. This steady state may be imbalanced by seasonal effects or by evapoconcentration processes. The speciation and distribution of elements within the pit lake may change greatly. Over time, if a lake deepens, then the effects of seasonal turnover will become less as turnover effects do not extend as deep into the lake and, consequently, a permanent hypolimnion becomes established.

Geological controls

Another factor influencing the formation and characteristics of secondary minerals is the deposit geology in which they form. As the major geochemical reactions in a 'sulphide rock' mine are related to acid generation and acid neutralization, so these in turn are related to the abundance of primary sources of these processes, namely sulphides, particularly pyrite, and buffering minerals, dominantly calcite. Over the last

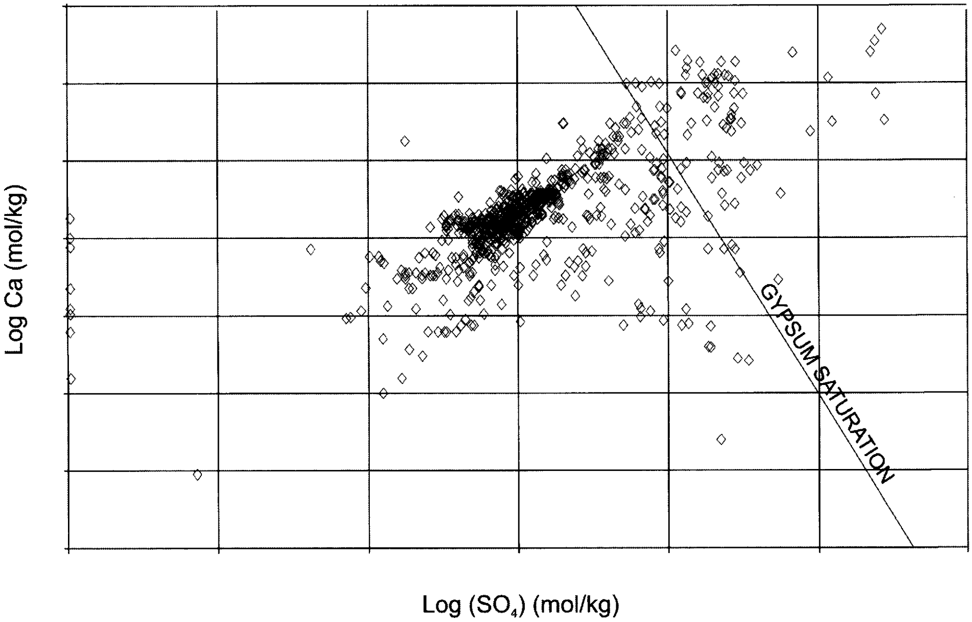


Fig. 12. Relationship between Ca and sulphate in mass-balanced mine pit lakes showing the majority have as an upper control saturation with respect to gypsum. Those above were all below pH > 2 and have an iron sulphate–sulphuric acid control.

few years several studies have examined the use of environmental geological models to provide some form of initial prediction mechanism for understanding potential impacts anticipated from mining sulphide-bearing mineral deposits (Ficklin *et al.* 1992; Plumlee 1994; Du Bray 1995; Plumlee & Logsdon 1999; Shevenell *et al.* 1999; Bowell *et al.* 2000).

Mineral deposits do show a variation in metal and anion hydrogeochemistry related to the distinct geological characteristics of these deposits (Figs 4–6). On the basis of the above discussions, it can be observed that the important aspects of metal deposits that influence MPL hydrogeochemistry will be the speciation and proportion of sulphides, and the presence and abundance of buffering materials, principally calcite. Owing to the nature of mineral deposits, only a few are exploited by open-pit mining and thus the data are biased towards copper porphyry deposits, Carlin-type gold deposits of the western United States and volcanogenic massive sulphide (VMS) deposits (Price *et al.* 1995).

Thus, it can be observed that the high sulphidation epithermal systems and VMS deposits that host tens of per cent sulphides, dominantly pyrite, and are usually devoid of calcite or other buffering agents result in the more acidic metal-rich pit lakes (Fig. 5). These deposits also tend to occur on a large scale and, as such, can cause significant impact, for example the Summitville high sulphidation system in Colorado (Gray *et al.* 1994).

Where carbonates form a large portion of the ore, even where sulphides are present in relatively high concentration pit lake, pH is considerably higher and metal concentration lower. A good example are the disseminated sediment-hosted micron gold deposits of the Carlin belt, Nevada that tend to show low base metal concentrations in the ore and a high proportion of calcite in the alteration zones related to carbonate host rocks (Hofstra *et al.* 1995). Although little data are available for pit lakes developed for sedimentary base metal sulphide deposits, what there is reflects as would be predicted, circumneutral low metal chemistry.

The majority of porphyry pit lake results reflect low metal; non to low-acid generating, but some zones within porphyrys can produce a high potential for acid generation and metal leaching (Bowell *et al.* 2000). Typically, these are from the silicified sulphide-bearing zones that have been partially oxidized and so have associated with the sulphides a series of Cu–Fe sulphate salts and other sources of secondary acidity, such as jarosite. Where they form a significant part of the exposed pit then an acid pit lake can prevail. Another sulphide zone that exists within porphyry is the chalcocite blanket or zone of

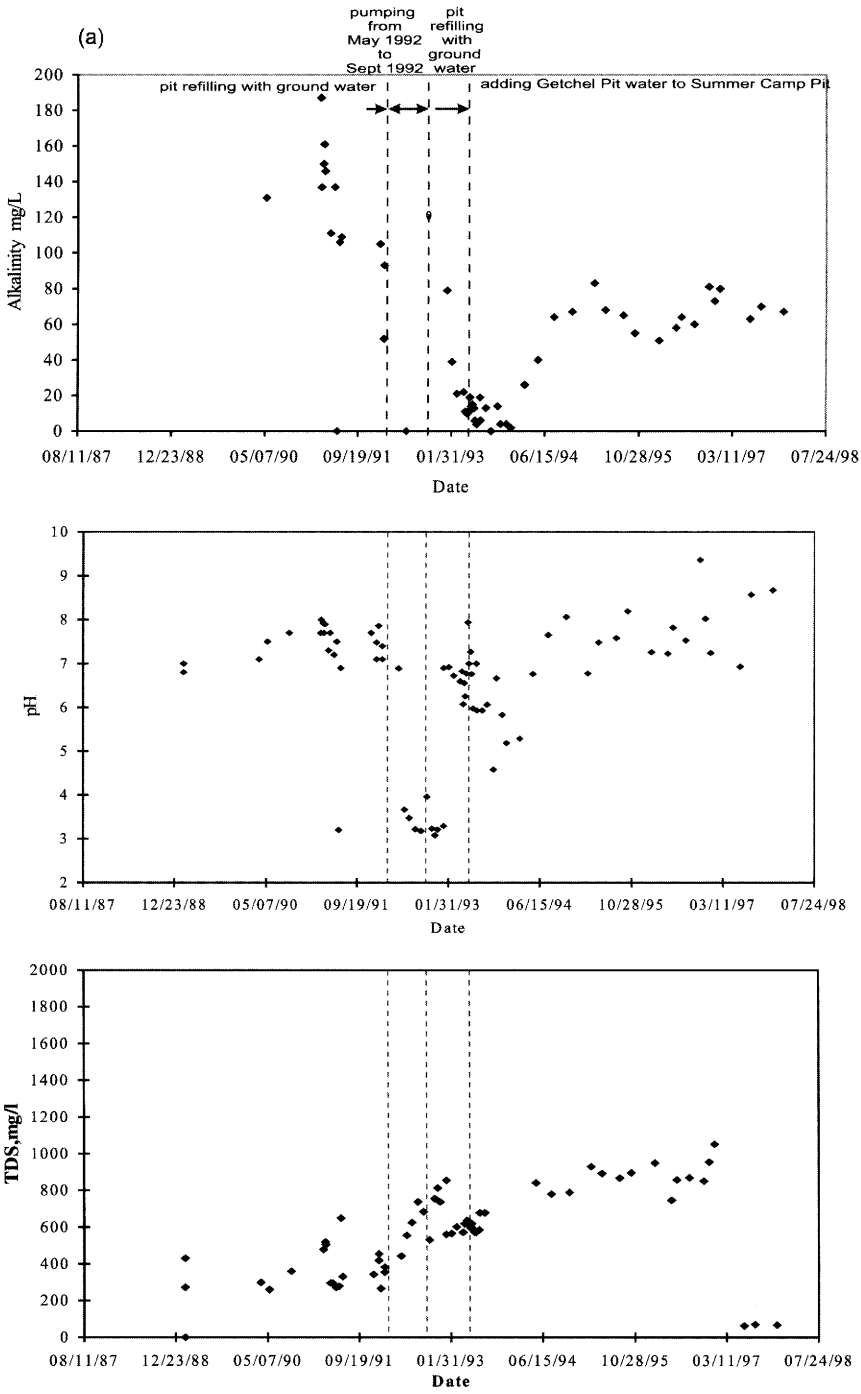


Fig. 13. Geochemical trends over time for Summer Camp Pit lake, 1990–1998.

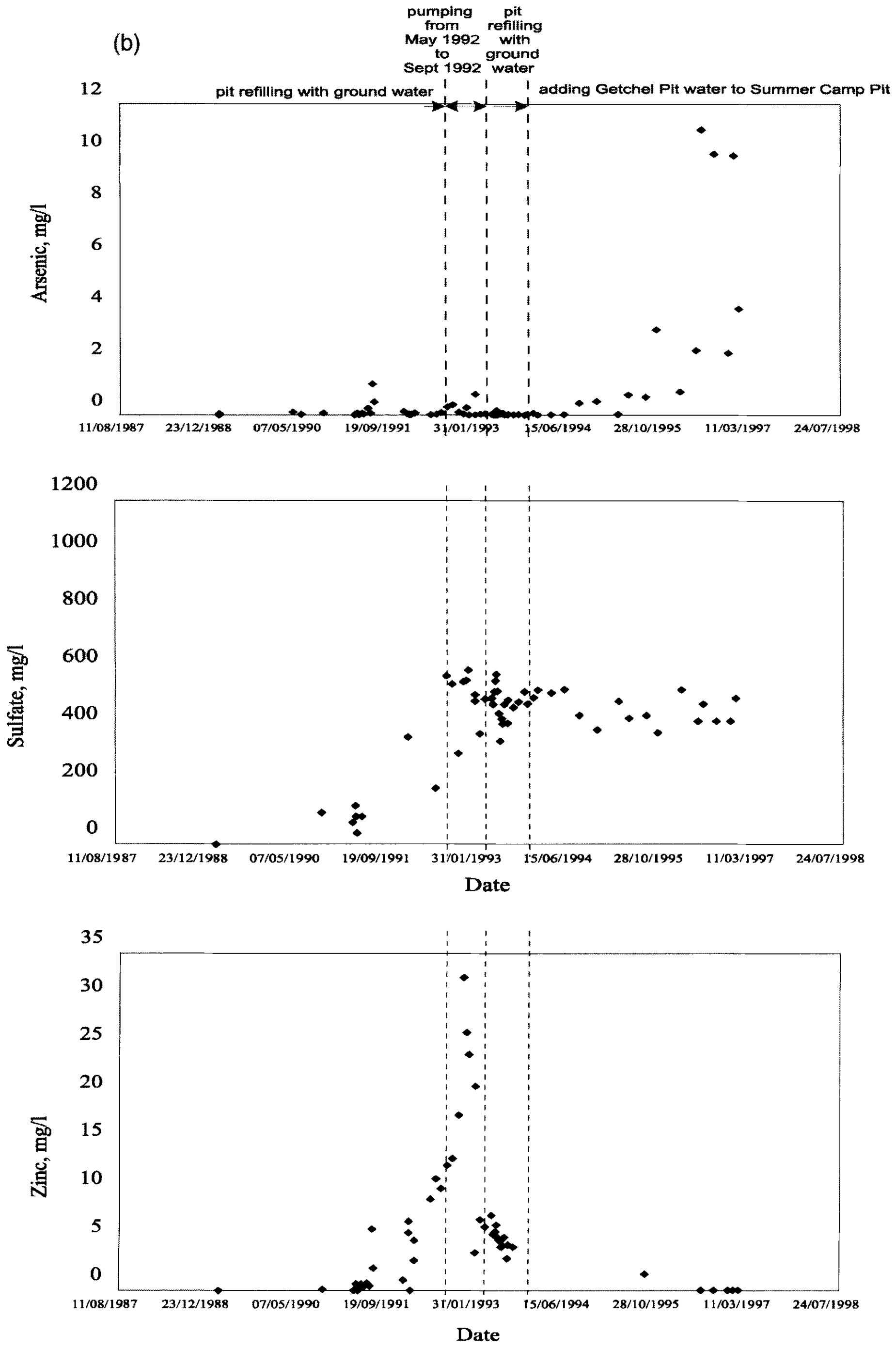


Fig. 13. (b) *(Continued).*

supergene enrichment, this typically comprises of goethite, cuprite, chalcocite and covellite, with minor jarosite and relict pyrite (Lowell & Guilbert 1970; Guilbert & Lowell 1974). If these zones are present then metal leaching can occur at relatively high pH (pH $> 4-5$). Owing to the configuration of chalcocite, it does not produce protons on oxidation but hydroxyl ions and consequently produces alkaline drainage.

Case study of pit lake chemistry: Summer Camp Pit, Nevada

Few detailed examples of pit lake evolution have been published, except for the pit lakes on the Getchell Mine, Nevada that have been subject to several studies from 1995 to 1999 (Barta *et al.* 1997; Tempel *et al.* 1999; Shevenell & Pasternak 2000; Parshley *et al.* submitted). For one of these pits, the period from pre-mining through to cessation of mining and formation of a MPL has been constantly monitored from 1990 to the present (Bowell *et al.* 1998).

Prior to mining in 1990 the Summer Camp Pit (SCP) area was undisturbed and as such was most likely in equilibrium with groundwater. Natural groundwater has an alkaline Ca–Mg–HCO_3 chemistry with variable amounts of arsenic and sulphate, dependent on contact with gypsum and sulphides (Table 4). Possibly this reflects the migration of oxygenated groundwater along the mineralized shear zone in which water reacted with primary sulphides, chiefly arsenian pyrite. The pH is circumneutral, suggesting that either pyrite oxidation was not appreciable or that groundwater alkalinity and host rock acid consumption was sufficient to buffer generated H^+.

During pit development in 1990 water quality remained fairly constant, with a small pool developing in the west of the pit. This had measurable levels of As (up to $0.082\,mg\,l^{-1}$), Se (up to $0.009\,mg\,l^{-1}$), Zn (up to $0.12\,mg\,l^{-1}$), low sulphate ($110\,mg\,l^{-1}$) and TDS ($360\,mg\,l^{-1}$). At this time pH of water around the SCP was circumneutral to alkaline (pH $= 7.7-8.3$). Water chemistry shows low salt load and trace element concentrations, with As below the primary drinking water standard ($0.05\,mg\,l^{-1}$) in the pit sump. Pool alkalinity in March 1991 ranged from 146 to $187\,mg\,l^{-1}$ (Fig. 13a) and pH from 7.3 to 8 (Fig. 13b). Slightly elevated metal/metalloid levels in the pool were recorded (Table 7). By May 1991 acid generation had exceeded available alkalinity in the sump and water pH was acidic (Table 7). The acidic pH was accompanied initially by a low TDS, due to precipitation of evaporative salts like gypsum, melanterite ($Fe^{2+}SO_4{\cdot}7H_2O$), halotrichite ($Fe^{2+}Al_2(SO_4)_4{\cdot}22\text{-}H_2O$) and copiapite ($Fe^{2+}Fe_4^{3+}\,(SO_4)_6(OH)_2{\cdot}20\text{-}H_2O$) (Bowell *et al.* 1998). Adsorption of arsenate at mildly acidic pH (4–6) limits As hydromorphic dispersion but at lower pH (< 3) arsenate can be mobilized, in response to hydrogen ion activity stabilizing arsenic acid (H_3AsO_4) and the increased solubility of HFO and stability of Fe^{3+} in solution. From June 1991 a gradual increase occurred towards the end of operations in December 1991 (Fig. 14).

After pumping was terminated at the end of operations in December 1991 alkalinity was

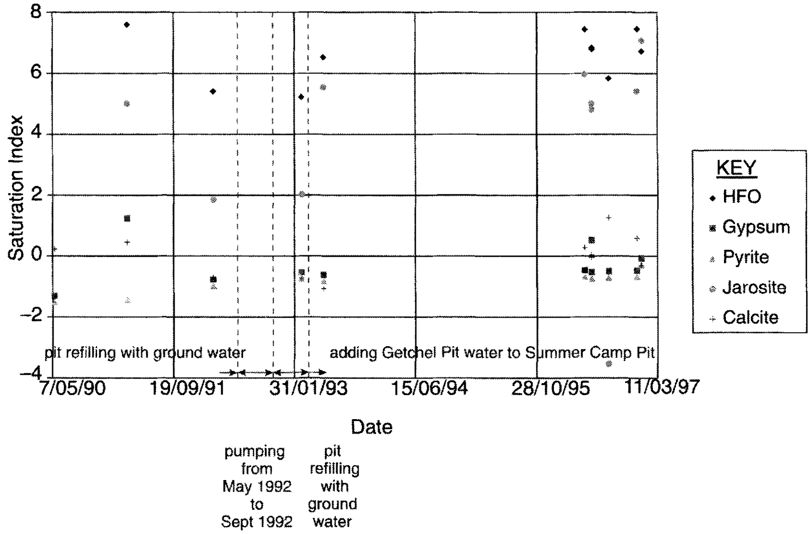


Fig. 14. Saturation Indices for major minerals in Summer Camp Pit lake, 1990–1998.

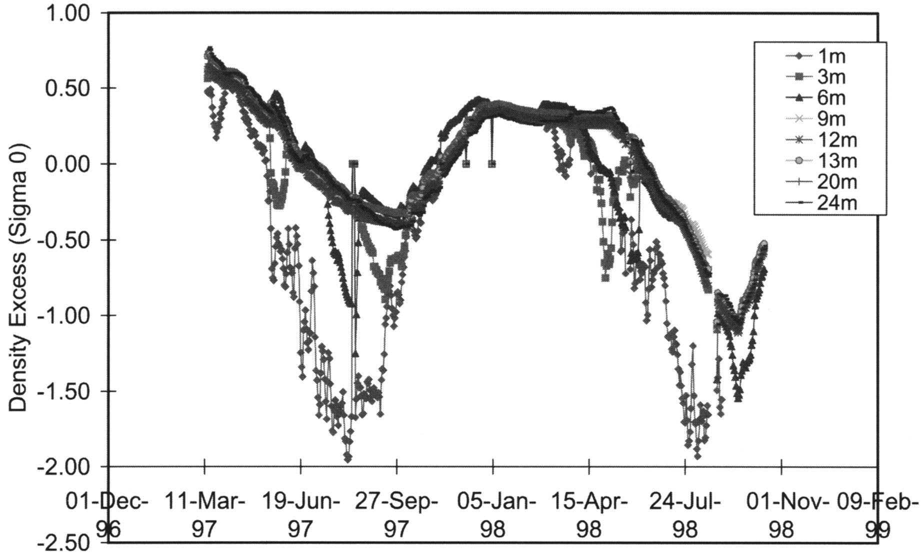


Fig. 15. Density (sigma excess) plot with time for the SCP. Depths are set at various intervals to record changes within the epilimnion (above 9 m), metalimnion and hypolimnion (below 20 m).

steadily consumed until April 1992, when all available alkalinity was consumed as acid generation exceeded alkalinity recharge (Table 7). The zero alkalinity observed is most probably not due to cessation of buffering but, rather, due to increased rates of acid generation. This increase in acid generation correlates to flushing of secondary acid salts as the water level recovers in the pit. During this period pH fell from 7–7.5 to 6.89 in April 1992 and by May 1992 decreased to 3.67 (Fig. 13b). In the absence of excess carbonate alkalinity, water pH was buffered from May 1992 by hydroxides and silicates, so remained in the range pH 3–4 (Sverdrup 1990; Kwong & Ferguson 1997).

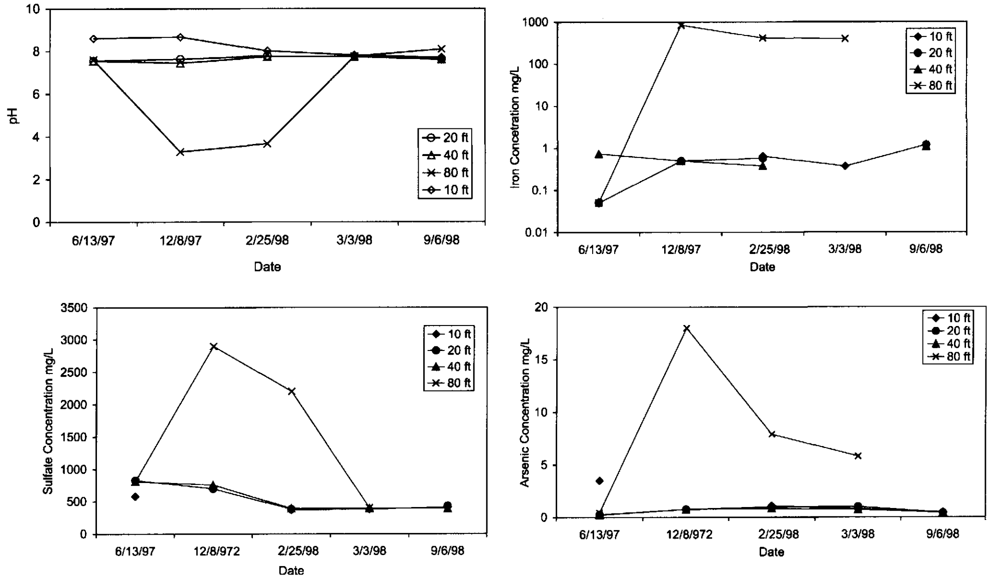


Fig. 16. Chemistry–time plots for the SCP showing depth variations in the values of pH, sulphate, Fe and As.

The slow accumulation of dissolved iron compared to sulphate is most probably due to a greater portion of iron being reprecipitated as secondary minerals such as hydrous ferric hydroxide. Arsenic and selenium during this period do not show significant increases, probably due to adsorption onto ferric hydroxide and clay minerals. Zinc levels show a steady increase from the end of operations, even at neutral pH. This is most probably due to secondary processes such as dissolution of soluble zinc minerals like smithsonite ($ZnCO_3$) or goslarite ($ZnSO_4{\cdot}7H_2O$) or ion exchange of Zn with other divalent cations during clay mineral–water interactions. Smithsonite dissolution might occur in response to increased acid production and be utilized in the buffering process along with calcite carbonate.

Water was abstracted from SCP for operational use from May 1992 to September 1992. The high rate of acid generation was maintained during this period. Most probably this is because pumping maintained the water level such that 'reactive' pit walls were exposed and these contributed metals, sulphate and acidity to the pit lake through sulphide oxidation and secondary mineral leaching due to water level recovery and rainwater surface run-off. The low pH environment was mitigated in late 1992 with the diversion of HCO_3-bearing water from other flooded open pits and the underground operations elsewhere on the Getchell property (Fig. 13a). Following the addition of alkaline water into the SCP, pH increased to circumneutral levels (Fig. 13a). Total dissolved solids have remained relatively constant, with the water chemistry being essentially a Na–Ca–SO_4 type with the

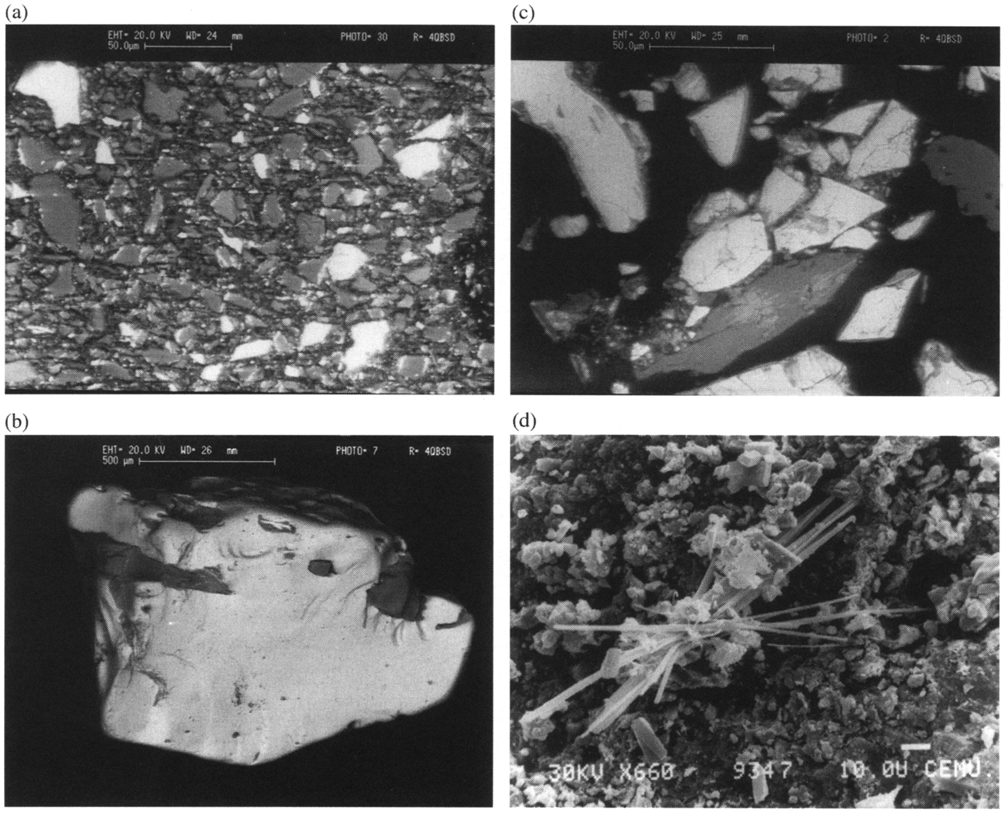


Fig. 17. Photomicrographs of sulphides from pit sediments and sulphates from pit walls. (**a**) Section showing euhedral to subhedral crystals of mackinawite $(Fe,Ni,Co,Zn)_9S_8$, sphalerite (ZnS) and orpiment (As_2S_3) in kaolinite–quartz matrix, SCP hypolimnion sediment. Note sphalerite and orpiment are most probably detritus grains, whilst mackinawite is probably authigenic. (**b**) Backscatter image of mackinawite euhedral crystal showing negligible corrosion, SCP hypolimnion sediment. (**c**) Backscatter image of orpiment euhedral crystal showing negligible corrosion, SCP hypolimnion sediment. (**d**) Halotrichite, chalcanthite and gypsum on wall-rock. Sternberg lode, Copper Flat Pit lake, Hillsboro County, New Mexico.

main mineralogical control being gypsum saturation (Fig. 14).

Further variations in pit lake water quality reflect changes in the chemistry of pumped mine water rather than pit lake processes. Although not discussed here in detail, the nature of the stratified pit lake can be observed in the density plots for the pit lake set at various depths (Fig. 15). As can be observed for much of the year, the basal layer is considerably denser than the other two layers but in winter this changes as turnover occurs (Fig. 15). Over time the magnitude of this turnover would become less, as a permanent hypolimnion forms in the deep (20 m) pit lake. A crucial impact of turnover is that it acts as a 'self-cleansing' event and a post-turnover lake (such as the data shown for June 1998, Table 4) shows lower TDS water than pre-turnover (as shown for February 1998 for SCP, Table 4). Turnover events such as these could be both seasonal and, possibly, longer-term multi-year events. Similar processes will occur in other deep pit lakes, for example the Sleeper Mine in Nevada where the pit lake is over 60 m deep.

Chemical variations in the pit lake over the same period reflect its stratified nature, with low pH, high sulphate, As and metals in the basal layer for much of the year (Fig. 16). On turnover, the basal layer is briefly aerated resulting initially in higher pH and lower metals, but with the aeration comes oxygen and sulphide oxidation occurs in the basal sediments. This leads to low pH and high metals as stratification reforms. A more detailed study of the limnological–depth stratification of this pit lake is currently being prepared (Parshley *et al.* submitted).

Attenuation of metals occurs in the basal sediments of the SCP through sulphidization in the hypolimnion. In the hypolimnion of Summer Camp pit lake, sulphate-reducing bacteria have been identified (Gannon *et al.* 1996). Within this zone, sediments have been found through diagnostic leach studies to contain high metal concentrations associated with the reduced fraction (Bowell & Parshley 1999). The diagnostic leach scheme used in this study involved a modified Tessier selective extraction procedure (Bowell & Parshley 1999). From mineralogical analysis the phases in this fraction have been confirmed as authigenic sulphides not observed in bedrock geology, and include mackinawite ([Fe, Ni, Co, Zn]$_9$S$_8$) and greigite (Fe^{2+}Fe$_2^{3+}$S$_4$), as well as pararealgar, sphalerite and pyrite. The latter three all show authigenic morphologies (Fig. 17) but they do occur within the pit wall-rock and thus a detritus origin cannot be ruled out. Similar processes have been observed in deep-sea anoxic sediments (Morse 1994) and natural wetlands (Kwong & Van Stempvoort 1994; Rees 1998).

Utilizing all this information, a conceptual model was developed to assist understanding of the development and geochemical–limnological environment within the SCP lake (Fig. 18). This model reflects the internal and external processes that control the water quality observed within the mine pit lake. At the SCP an important external

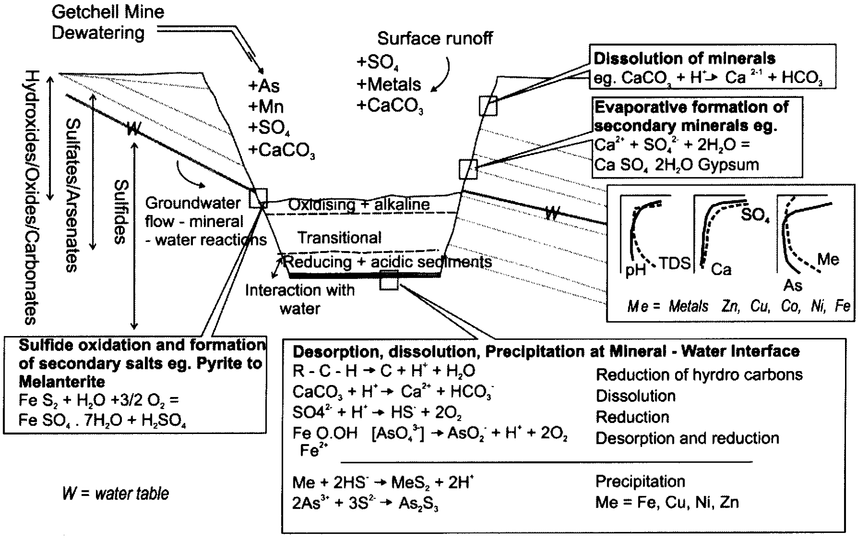


Fig. 18. Conceptual model developed for the Summer Camp Pit (SCP) based on the data collected in the field and by laboratory analysis to explain the complex interlinked limnological and geochemical mechanisms that control pit lake water quality.

control is the discharge of underground mine water into the pit, this practice has now ceased.

Conclusions

A review of the major processes influencing the hydrogeochemistry of MPLs has been presented. The major controls on MPL can be related to:

- limnology of the pit lake;
- geochemical processes within a pit lake;
- geology of the exposed wall-rocks and type of mineral deposit.

At the present time, methods for predicting the future water quality in mine pit lakes involve hypothetical mechanistic and empirical models to reflect the major chemical and physical processes operating within a MPL. These major processes include groundwater inflow, wall-rock leaching, pit wall run-off, precipitation, evaporation, lake hydrodynamics, and geochemical equilibrium and speciation. Most of these methods are still in the process of development. Refinement of such models and general understanding of the environmental assessment of pit lakes will be improved through characterizing the conditions in existing MPL.

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