GEOCHEMICAL PROCESSES CONTROLLING MINEWATER POLLUTION

D. Banks, Holymoor Consultancy, United Kingdom

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Abstract

Minewater is a subset of groundwater, subject to broadly similar hydrochemical processes. In "normal" groundwaters, access to oxidising species is poor and acid-base reactions tend to dominate over oxidation reactions. Acid-base reactions such as carbonate dissolution and silicate hydrolysis consume protons and carbon dioxide, and release alkalinity and base cations. In mines, the atmospheric environment is rapidly introduced to the deep reducing geosphere (or *vice versa* in the case of mine waste deposits). This carries the possibility of intense and rapid oxidation of sulphide minerals such as pyrite, to such an extent that these acid-generating redox reactions may dominate over acid-base "neutralisation" reactions and result in the phenomenon of "acid rock drainage" (ARD). In ARD, a negative correlation is typically observed between pH and concentrations of many metals and metalloids, base cations and sulphate. This correlation is due to (i) genetic co-variation – generation of protons, sulphate and metals in sulphide weathering reactions, (ii) pH-dependent solubility of many ARD-related metals and (iii) low pH intensifying carbonate dissolution and silicate hydrolysis to release aluminium, silica and base cations. This paper examines the reactions involved in ARD generation and neutralisation, and attempts to clarify key concepts such as pH, Eh, alkalinity, acidity and equilibrium constants.

PART 1: AN OVERVIEW

Introduction

Groundwater is often defined as water occurring within the subsurface geological environment. Mine water is thus merely a type of groundwater, subject to the same geochemical processes as "normal" groundwater. Mine water often appears very different to the pure spring water beloved of poets and bottled water manufacturers, however: it may be highly acidic, brightly coloured and packed full of salts and potentially toxic metals. So what is it that creates the difference between our flask of Evian and our sampling bottle of mine water from San José silver/tin mine? Why are some mine waters alkaline (Banks et al., 2002b), while others are acidic and rich in aluminium, iron and other metals (Banks, 1994)? This paper attempts to provide an introduction to some of the answers. We should start, however, by examining, in outline, some of the processes which give all groundwaters (including mine waters) their characteristic chemical signatures.

The Hydrochemistry of Groundwater

Every groundwater has its own unique hydrochemical fingerprint. This is derived from the interplay of various processes at various stages along the groundwater's flow path:

Recharge Chemistry

Groundwater may retain some of the characteristics of the water (rainfall, snowmelt or infiltrating river water) that was the source of its recharge. For example, newly recharged groundwater will often contain:

- An isotopic signature (^{2}H, ^{3}H, ^{18}O) characteristic of the rainfall at the geographic location, time and altitude of recharge
- An "atmospheric" chloride content, which may increase with decreasing distance from the coast (due to marine aerosols in the atmosphere, Banks et al. 1998).
- A content of atmospheric "pollutants" from industry or motors: nitrate, sulphate, chloride
- A high content of dissolved oxygen

Soil Zone

The soil zone is a highly microbiologically active environment. Respiration within the soil zone produces CO_2. Thus, groundwater leaving the soil zone will often be charged with high concentrations of dissolved CO_2 (with an isotopic ^{13}C signature reflecting soil zone processes).

Water-Rock Interaction

This innocent term covers a huge range of geochemical processes that describe various ways in which groundwater reacts with minerals in the subsurface. The most important of these will be discussed in the next section. In general, water-rock interaction processes in "normal" groundwater tend to result in:

- Consumption of dissolved O_2 and CO_2
- Elevation of pH and production of alkalinity
- Release of base cations

Mixing

Along its flow path, groundwater may mix with other water "facies", e.g.

- Mixing with deep saline "formation" water within the aquifer
- Mixing with intruding saline water from a surficial source (e.g. sea water)

Water-Rock Interaction

The main reactions taking place between water and mineral phases in the subsurface fall into four main categories:

Dissolution Reactions

E.g. halite: $NaCl \leftrightarrow Na^+ + Cl^-$

or fluorite: $CaF_2 \leftrightarrow Ca^{++} + 2F^-$

Ion Exchange Reactions

These often take place on the surface of minerals such as clays:

e.g. $\text{Ca-clay} + 2Na^+ \leftrightarrow Na_2\text{-clay} + Ca^{2+}$

Acid-Base Reactions

The most common rock-forming minerals (carbonates, silicates) are bases that consume protons (acid) on reacting with groundwater. Note that dissolved carbon dioxide is regarded as an acid, as it dissociates to release protons:

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

Examples of acid base reactions include the weathering of calcite or plagioclase feldspar:

$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$

$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \leftrightarrow 2Na^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 + 4SiO_2$

Note that these reactions tend to:

- consume CO_2 and elevate pH
- release bicarbonate alkalinity
- release base cations

In most "normal" groundwaters, these types of reactions dominate, resulting in groundwaters of neutral to slightly alkaline pH (Frengstad & Banks, 2000), dominated by base cations (Ca^{++}, Mg^{++}, Na^+) and bicarbonate.

Redox Reactions

Here, electrons are transferred between reacting species, causing *oxidation states* to be altered. For example, the oxidation of organic matter:

$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$

Oxidation reactions often (but not inevitably) release acid. Reduction reactions often consume acid and release alkalinity. For example, the (bacterially catalysed) oxidation of pyrite releases protons (acid):

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

What is so Special About Mine Water ?

The earth's immediate subsurface is a reaction front between the atmosphere (generally oxidising and acidic) and the geosphere (generally reducing and basic). Groundwater is the circulating medium which carries atmospheric reactants (oxygen, carbon dioxide) into the geosphere. The zone of groundwater circulation is typically the zone where redox and acid-base reactions occur.

In normal groundwater environments, the contents of oxidisable minerals (e.g. pyrite) are so low *or* the access to oxidising species (e.g. oxygen) is so poor, that acid-base reactions (which consume protons) dominate over redox oxidation reactions (which may generate protons). Thus, "normal" groundwaters have typically neutral to slightly alkaline pH (Frengstad & Banks, 2000), dominated by base cations (Ca^{++}, Mg^{++}, Na^{+}) and bicarbonate.

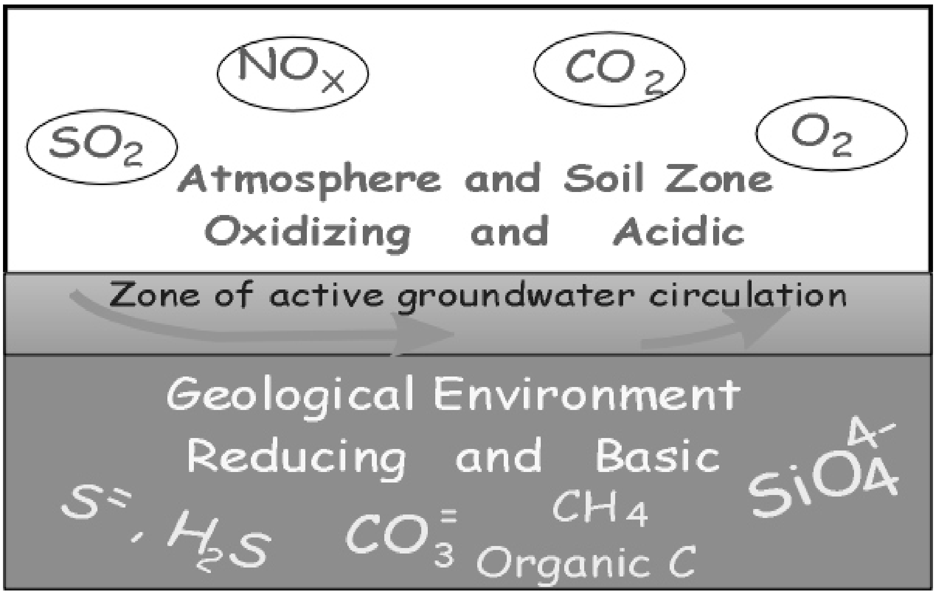

Fig. 1: The zone of groundwater circulation is a reaction front between the oxidising, acidic atmosphere and the reducing, basic geosphere. The zone of groundwater circulation is characterised by acid-base and redox reactions. The rate of reaction will increase where flaws in the geosphere (e.g. mines) allow rapid circulation of water and oxygen, or where geosphere material is transported directly to the surface environment (mine waste tips).

When we dig mines, we introduce the rapid circulation of oxygen and water into the deep geosphere, in zones where there are high concentrations of oxidisable minerals (sulphides). Similarly, when we create mine waste tips, we are bringing deep sulphide-rich geosphere up into the atmosphere, with often excellent access to circulating water and oxygen. Thus, i*n mine or spoil tip environments, oxidation reactions may dominate over acid-base (neutralization) reactions, resulting in the phenomenon of* ***acid rock drainage (ARD)***.

Thus, where sulphide oxidation is the dominant reaction:

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

mine waters may be dominated by:

- Low pH
- Elevated sulphate concentrations
- Elevated concentrations of metals

It should here be noted that not all sulphide minerals release protons on oxidation:

$ZnS + 2O_2 \leftrightarrow Zn^{2+} + SO_4^{2-}$

$PbS + 2O_2 \leftrightarrow Pb^{2+} + SO_4^{2-}$

However, if pyrite/marcasite is also present, the acidic environment generated will assist in mobilising other metals such as Zn and Pb, whose solubility is pH-dependent.

Characteristics of Mine Waters

Tables 1 and 2 present analytical characteristics of various mine waters from metal sulphide mines (Table 1) and coal mines (Table 2). Table 3 shows leachates from selected mine waste tips. From the Tables, the following points should be noted:

- There is considerable variation in mine water chemistry, even amongst mines of the same type. This can be ascribed to factors such as: access to and rate of circulation of water and oxygen, neutralisation potential of host rocks and ambient groundwater, morphology and mineral content of sulphide minerals, age of mine discharge. Particularly aggressive (i.e. metal-rich, acidic) mine waters would thus be expected where:
    - Mines or spoils have a high pyrite content, especially if fine-grained
    - Mines or spoils have good access to oxygen (i.e. unflooded mines)
    - Water throughput is low. Lack of dilution may produce very aggressive mine waters (e.g. San José)
    - Recent flooding of a mine has resulted in a “first flush” of accumulated pyrite weathering products from a mine
- Metals mines generally have the potential to generate more aggressive mine waters than coal mines.
- The most aggressive discharges emanate from recently flooded (or, sometimes, pumping) mines.
- As pH and alkalinity increase, contents of metals, sulphate and base cations generally decrease. This is due to several factors:
    - Metals, protons and sulphate are all released upon sulphide weathering. A co-variation in these parameters would thus be expected
    - Low pH promotes hydrolysis of carbonates and silicates, thus releasing base cations to the water
    - Low pH promotes solubility and mobilisation of most heavy metals (including Fe, Zn, Cu, Al, Pb etc.)
- Chloride concentrations are independent of pH.

The final water in Table 3 is from natural landslipped, broken strata (pyritiferous Millstone Grit shales) at Mam Tor mountain, Derbyshire, UK. This demonstrates that “acid rock drainage” can have a purely natural origin (Vear & Curtis, 1981, Banks, 1997, Banks et al*.,* 1997a).

Tab. 1: Hydrochemical characteristics of three different metal sulphide mine waters:

Mine	**San José Bolivia**	**Kongens Gruve Norway**	**Magpie Sough UK**
Flow rate (l/s)	8	5.8 (average)	-
Temperature (°C)	20.8	n/a	n/a
pH	1.47	2.7	7.2
Alkalinity (meq/l)	0	0	4.28
Cl^- (mg/l)	32670	n/a	19
SO_4^{2-} (mg/l)	8477	901	33
Ca^{2+} (mg/l)	1780	47.8	98
Na^+ (mg/l)	17256	n/a	8
Fe (mg/l)	2460	134	<0.0005
Al (mg/l)	559	33.1	0.005
Mn (mg/l)	27.4	n/a	<0.0002
Zn (mg/l)	79.4	36.3	0.074

San José., Bolivia: a pumped discharge from a tin/silver polymetallic sulphide mine (Banks et al,. 2002a).

Kongens Gruve, Norway: gravity discharge from an abandoned a Cu/Zn massive sulphide mine (Iversen & Knudsen, 1997).

Magpie Mine, UK: old gravity discharge from a PbS/barite/fluorite deposit hosted in limestone (Edmunds et al., 1989, Banks et al., 1996).

Tab. 2: Hydrochemical characteristics of four different coal mine waters:

Mine	**Ynysarwed Wales**	**Dunston Chesterfield, UK**	**Morlais Wales**	**Mine No. 3 Svalbard**
Flow rate (l/s)	15–35	c. 20	c. 100–200	c. 0.056
Temp. (°C)	-	9.4	14.2	4.7
pH	4.2	6.3	6.9	8.2
Alkalinity (meq/l)	2.76	3.74	6.07	36
Cl^- (mg/l)	32	26	25	236
SO_4^{2-} (mg/l)	1554	210	455	7.43
Ca^{2+} (mg/l)	222	64.5	91.8	15.5
Na^+ (mg/l)	109	51.4	155	925
Fe (mg/l)	180	10.6	26.6	<0.01
Al (mg/l)	<0.5	<0.045	<0.01	<0.02
Mn (mg/l)	6.1	1.26	0.93	0.004
Zn (mg/l)	0.061	<0.007	<0.002	0.055

Ynysarwed (new discharge, unpublished analytical data, sampled 15/9/94), Carboniferous Coal Measures of South Wales.

Dunston (historic discharge, Banks et al. 1997a), Carboniferous Coal Measures of UK East Midlands

Morlais (c. 20 year-old discharge, Banks et al. in prep), Carboniferous Coal Measures of South Wales

The Svalbard mine water is a pumped discharge from the active Mine No. 3, Bjørndalen, near Longyearbyen, Svalbard, in Tertiary strata (Banks et al., 2002b).

Tab. 3: Three leachates from mine waste tips, and one leachate from natural landslipped pyritferous strata (Mam Tor).

Mine	**Løkken Norway**	**Sverdrupbyen Svalbard**	**Orgreave Yorkshire, UK**	**Mam Tor Derbyshire, UK**
Flow rate (l/s)	0.84	c. 0.25	c. 0.033	c. 0.8
Temp. (°C)	-	1.9	-	3.4
pH	2.11	2.7	7.4	3.08
Alkalinity (meq/l)	0	0	4.72	0
Cl^- (mg/l)	-	7.0	625	7.9
SO_4^{2-} (mg/l)	17036	1077	2370	1480
Ca^{2+} (mg/l)	330	48.2	136	197
Na^+ (mg/l)	n/a	18.0	947	6.8
Fe (mg/l)	4720	179	0.27	27.3
Al (mg/l)	580	27.5	<0.022	51.3
Mn (mg/l)	n/a	3.2	0.33	23.9
Zn (mg/l)	87.4	1.3	0.059	1.04

Løkken, Norway. Mine waste from a Cu/Zn mine in a massive sulphide ore (Arnesen et al., 1994).

Svalbard. Coal mine spoil tip, Sverdrupbyen, Longyearbyen. Tertiary coals (Banks et al., 2002b).

Orgreave, near Sheffield, UK. Coal mine spoil from a deep Carboniferous Coal Measures mine. The formation water is saline and alkaline and has not yet been fully flushed from the mine waste (Banks et al., 1997a).

The "First Flush" Phenomenon

While a mine is worked and dewatered by pumping, sulphide oxidation proceeds in dewatered strata. Intermediate oxidation products (sulphate and hydroxysulphate minerals) accumulate in these unsaturated strata.

$$FeS_2 + 7/2O_2 + 8H_2O \leftrightarrow FeSO_4.7H_2O + SO_4^{2-} + 2H^+$$

Examples of these intermediate products include:

- Melanterite: $Fe^{II}SO_4.7H_2O$
- Jarosite: $HFe^{III}_3(SO_4)_2.(OH)_6$, $NaFe_3(SO_4)_2.(OH)_6$
- Coquimbite: $Fe^{III}_2(SO_4)_3.9H_2O$
- Alunite: $KAl_3(SO_4)_2.(OH)_6$
- Jurbanite: $AlSO_4OH.5H_2O$

These secondary products may form stalactites, stalagmites, efflorescences and growths in abandoned mines, as was observed in the San José mine in Oruro, Bolivia (Banks et al., 2002a).

When the mine closes and floods, rising mine water levels dissolve and mobilise all these accumulated secondary products and acidic pore waters, resulting in a highly potent "first flush" of concentrated mine water.

$$KAl_3(SO_4)_2.(OH)_6 + 3H_2O \leftrightarrow K^+ + 3Al^{3+} + 2\,SO_4^{2-} + 6OH^- + 3H_2O$$
$$\leftrightarrow 3Al(OH)_3 + K^+ + 2\,SO_4^{2-} + 3H^+$$

With time, the high initial acidity and metal concentrations of the first flush decay. The concentrations often seem to follow a quasi-exponential decay curve, indicative of flushing out of accumulated oxidation products (*"vestigial"* acidity/contaminant loading) from the mine system with fresh recharge water. The concentrations tend, in the long term, towards a steady state contaminant loading that reflects new, ongoing (*"juvenile"*) acidity production from pyrite weathering.

Figure 2 shows the decay of "first flush" concentrations following the overflow of Wheal Jane tin mine in Cornwall. In fact, Younger (2000) and Younger et al. (2002) have studied empirical data and found that the time taken for exponential decay flushing (t_f) can be related to the time taken for the mine to fill with mine water following cessation of pumping (t_r). In other words, the rate of decay is related to the floodable mine volume, as one would expect in a flushing model. Younger (2000) and Younger et al. (2002) found that t_f is approximately equal to four times t_r (Figure 3).

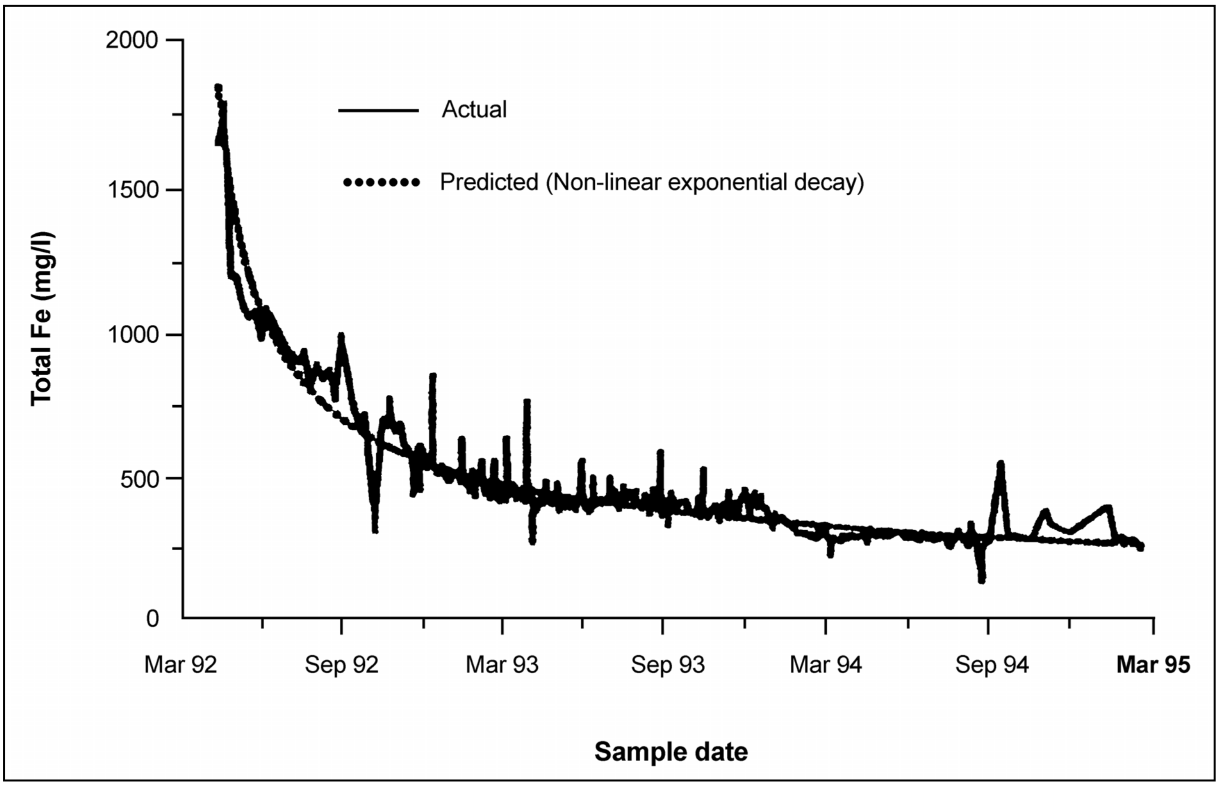

Fig. 2: Evolution of contaminant loading from Wheal Jane tin mine, following its overflow in 1992. Note the exponential decay of "first flush" concentrations towards a steady state (after Younger et al., 2002).

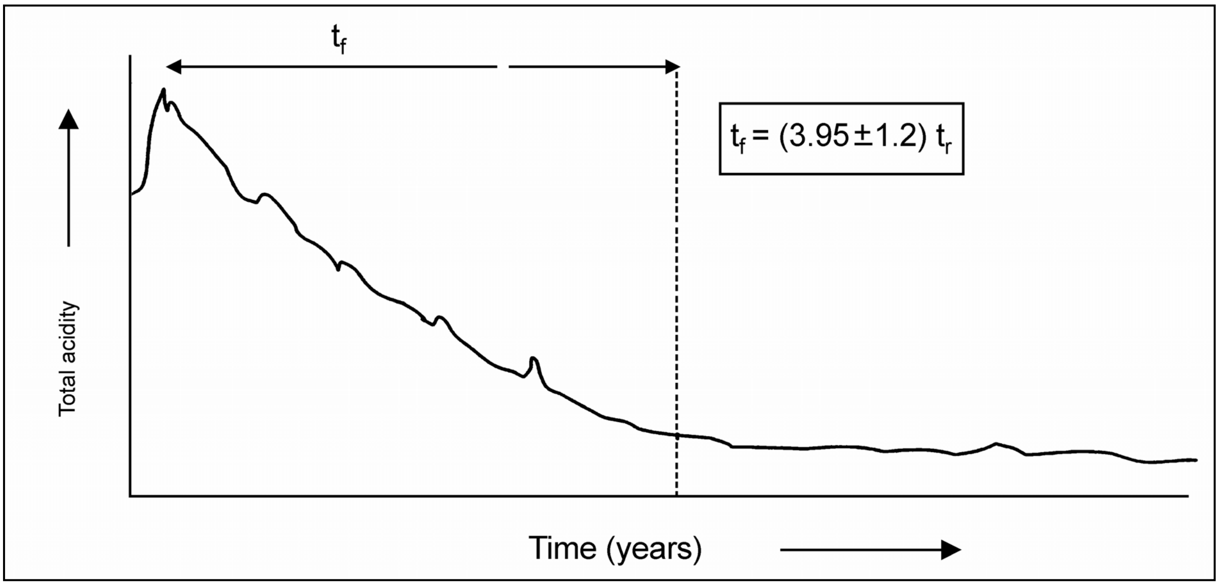

Fig. 3: *Time taken for decay of "first flush" concentrations to a steady state condition (after Younger et al., 2002).*

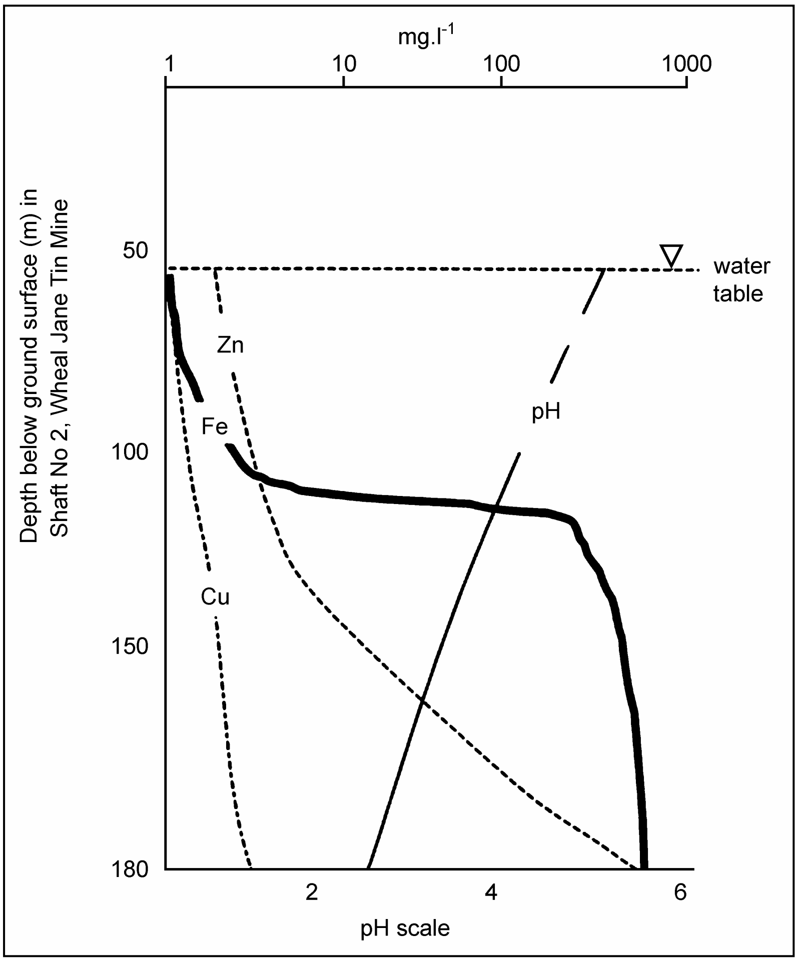

Fig. 4: *Stratification of chemistry during flooding within Wheal Jane tin mine, Cornwall (after Younger et al., 2002). Note that such stratification may be destroyed by turbulence once the mine overflows or is pumped (Nuttall et al., 2002).*

It should be remembered, however, that the volume being actively flushed *may* not be the total volume of the mine. Some mine systems develop a stratification (see Figure 4), where only the upper portion of the mine is being actively flushed, and the lower part contains "stagnant", highly contaminated mine water.

Can We Predict the Quality of Mine Drainage Water

Well, no, not really. There are usually too many unknown variables. We can, however, make some general observations.

1. Acidic, contaminant-loaded mine waters are characteristic of mine systems which are unsaturated, with rapid throughflow of water and good access for oxygen, e.g. workings from surface outcrops, which may be under-drained by a sough or adit (Figure 5a).
2. Flooded workings (especially coal mines), with poor access for oxygen and slow water throughflow, are often characterised by more circum-neutral mine waters (Figure 5b).
3. Some researchers have found tentative correlations between coal mine water iron concentrations and (a) stratigraphical proximity to marine beds in the UK Carboniferous Coal Measures (characterised by high sulphur contents) and (b) distance to outcrop of most closely associated coal seam (MCACS) – Figure 6.

Younger (2000), having studied some 81 UK coal mine discharges concluded that:

- If the worked seam was within 25 m (stratigraphically) of a marine bed, peak first-flush concentrations in excess of 100 mg/l Fe could be expected, Otherwise, concentrations not exceeding some 10s of mg/l are likely
- For coal mines >0.5 km from the outcrop of the shallowest worked seam, long term Fe concentrations of around 7 ± 1.6 mg/l were typical. If <0.5 km, an Fe concentration of 19 ± 2.9 mg/l was regarded as characteristic.
- Fe concentrations could be related to the sulphur content of the worked seam, if known (Table 4)

Tab. 4: Fe concentrations (± standard error at 95 % confidence level) for worked coal seams of differing sulphur content, based on 81 British coal mine discharges (after Younger, 2000)

S content of worked seam	**"First flush" peak concentration of Fe, mg/l**	**Long term, post-flush concentration of Fe, mg/l (for discharges < 0.5 km from outcrop of shallowest seam)**
< 1 wt %	0.15 ± 0.27	0.018 ± 0.76
1–2 wt %	98 ± 14	12 ± 8
2–3 wt %	267 ± 40	33.8 ± 22
3–4 wt %	873 ± 163	110 ± 78
4–5 wt %	1494 ± 248	190 ± 127

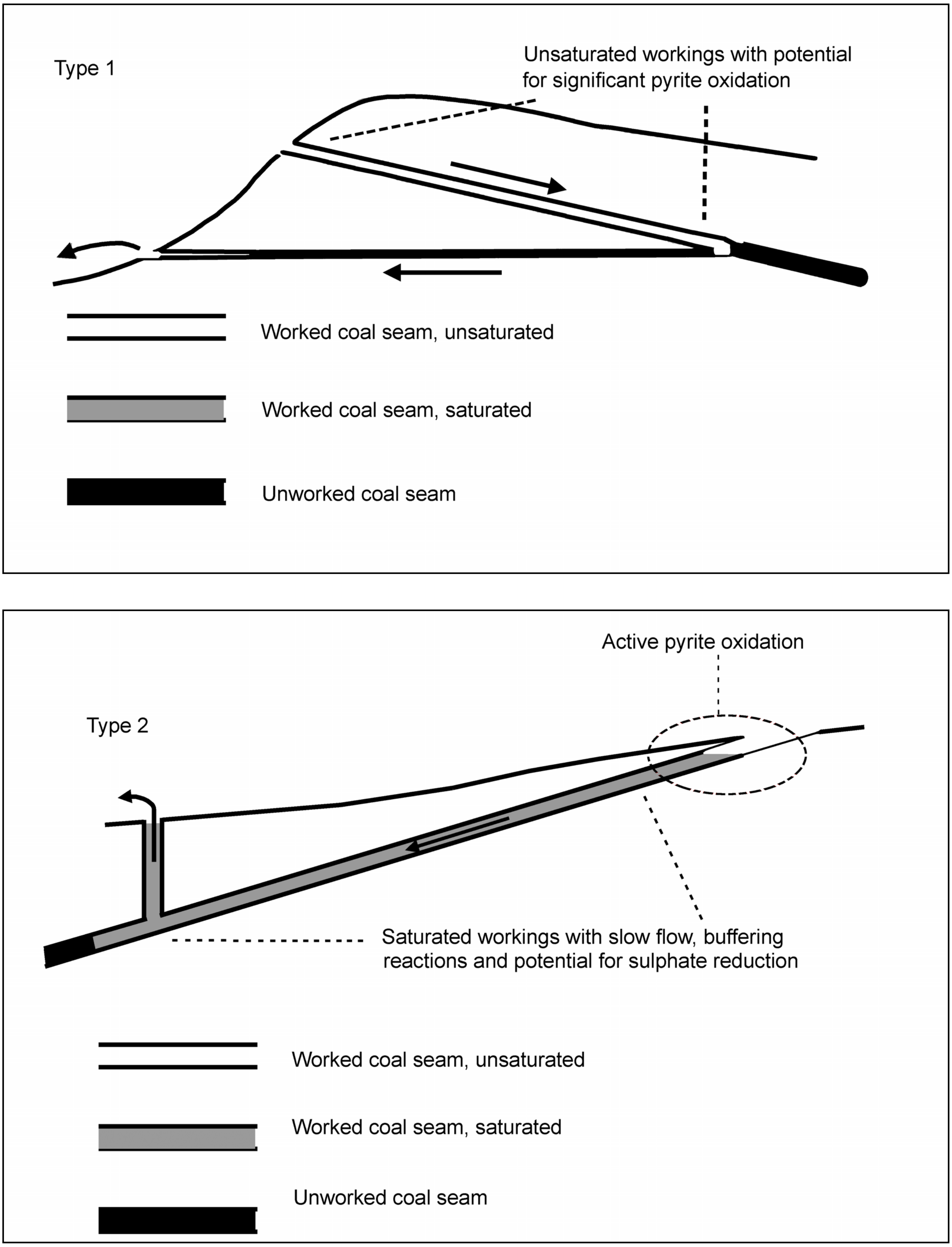

Fig. 5: Coal mine workings which characteristically produce (a) net acidic, aggressive mine waters are derived from unsaturated, under-drained workings. Those (b) producing more circum-neutral, net alkaline waters, are typically from flooded mine systems (after Banks et al., 1997).

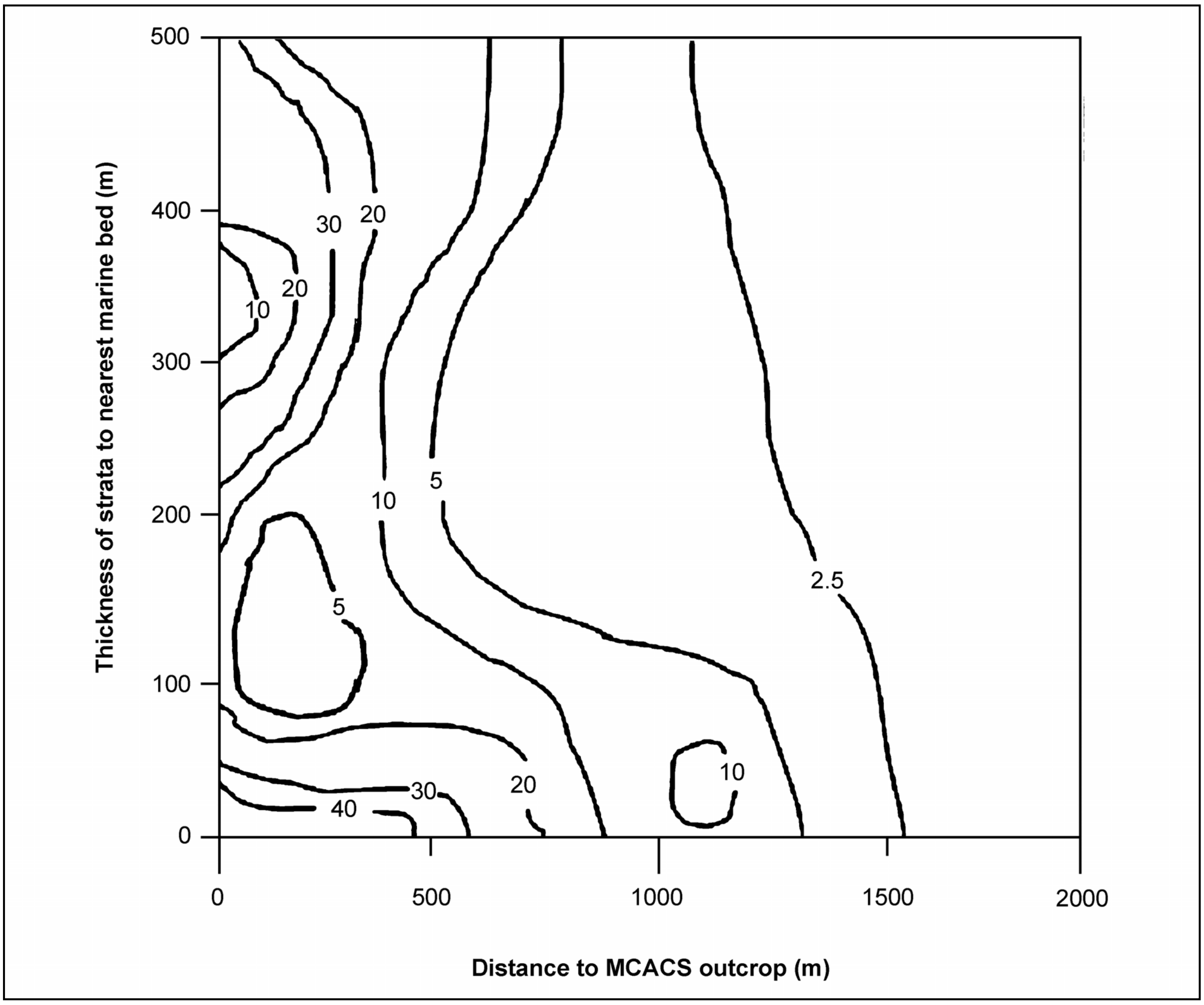

Fig. 6: Contours of total iron (mg/l) in UK mine-water discharges after completion of the main period of flushing, as a function of both stratal thickness to the nearest marine bed and the distance to MCACS(Most Closely Associated Coal Seam) outcrop (after Younger, 2000).

Precipitation of Ochre and Other Minerals in Recipient Watercourses

When minewater emerges from a mine, increased access to oxygen and possible increase in pH on mixing with recipient waters, may cause oxidation, hydrolysis and precipitation of metal oxyhydroxides or other salts. For example, ferrous iron may oxidise and precipitate as an orange ferric oxyhydroxide (*"ochre"*), which may be written as $Fe(OH)_3$ or FeOOH:

$$4Fe^{2+} + O_2 + 4H^+ \leftrightarrow 4Fe^{3+} + 2H_2O$$

$$Fe^{3+} + 3H_2O \leftrightarrow 3H^+ + Fe(OH)_3$$

The combined reaction is thus:

$$4Fe^{2+} + 10H_2O + O_2 \leftrightarrow 4Fe(OH)_3 + 8H^+$$

The overall ochre precipitation reaction is thus proton-generating. It is thus potentially self-limiting: generation of protons may lower the pH to a point where ferric ions no longer precipitate as a hydroxide, *unless* adequate neutralisation capacity (i.e. alkalinity) is present in the water. Similarly, dissolved aluminium may precipitate as a white hydroxide

$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$

However, aluminium is only soluble in the most acidic mine waters. Thus, precipitates from acidic mine waters tend to contain aluminium hydroxide and may be whiter or yellower in colour than those precipitating from more circum-neutral mine waters, which are typically more reddish-orange in coloration.

Many other minerals may be found in stream bed precipitates. In very aggressive mine waters, (for example, San José, see Table 1) both calcium and sulphate concentrations may be high, leading to precipitation of gypsum:

$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4.2H_2O$

PART 2: CHEMICAL FUNDAMENTALS

Master Variable: pH

pH is a measure of the activity of hydronium (hydrogen) ions (protons) in solution

$pH = -log_{10}(H^+)$

where () denotes activity in mol/dm^3 or mol/l. Thus, in water of pH=7, the activity of hydrogen ions is 10^{-7} mole/l or 0.0001 mg/l. In water of pH = 3, the activity is 10^{-3} mole/l hydrogen ions or 1 mg/l.

pH is often described as a *"master variable"* because it controls much of the hydrochemistry of a water sample, and the mineralogical reactions which it can undergo. For example, it controls the solubility of metal ions such as Al, Fe and Zn (Figures 7a,b,c). In these concentration vs. pH diagrams, the solid lines show the concentrations of a variety of metal hydroxide species in the water at a given pH value, while the dashed line shows the total solubility of the metal in water. It will be noted that Al is highly insoluble in water at pH values between 5 and 8 (typical groundwater pH). In acidic and alkaline waters, however, the solubility begins to become significant (i.e. >10^{-6} M).

Ferric iron, in contrast, is practically insoluble (<10^{-6} M) at all pH values greater than around 3–4, a fact which has great importance when treating mine waters. Zinc is, however, more soluble, and its minimum solubility is only reached at appreciably higher pH values than Al and Fe, namely around pH 9–10. This partially explains why Zn is so difficult to remove from mine waters by simple pH adjustment techniques.

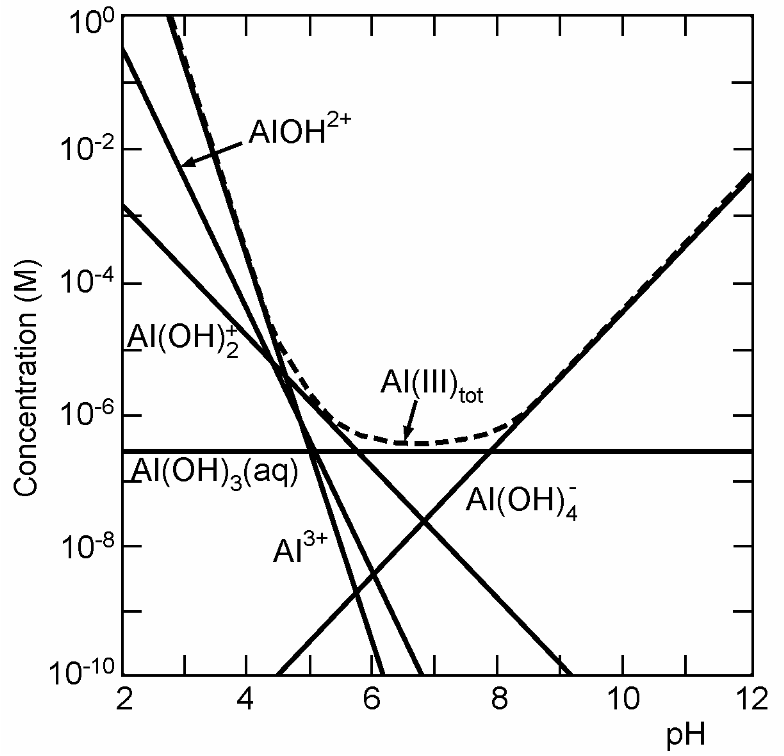

Fig. 7a: pH dependence of solubility of aluminium hydroxide species in water. The dashed line represents total Al solubility (after Stumm & Morgan, 1996 and Younger et al., 2002).

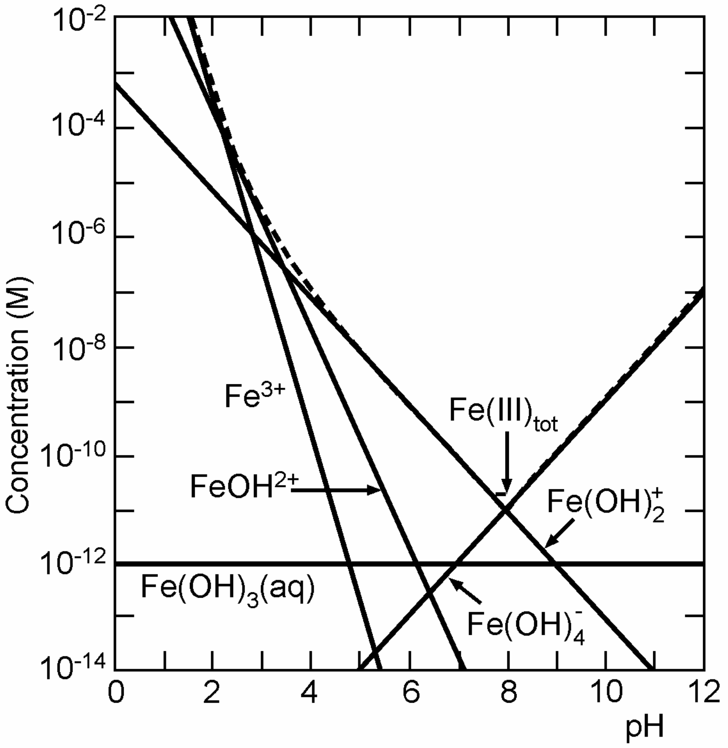

Fig. 7b: pH dependence of solubility of ferric hydroxide species in water. The dashed line represents total Fe^{III} solubility (after Stumm & Morgan, 1996 and Younger et al., 2002).

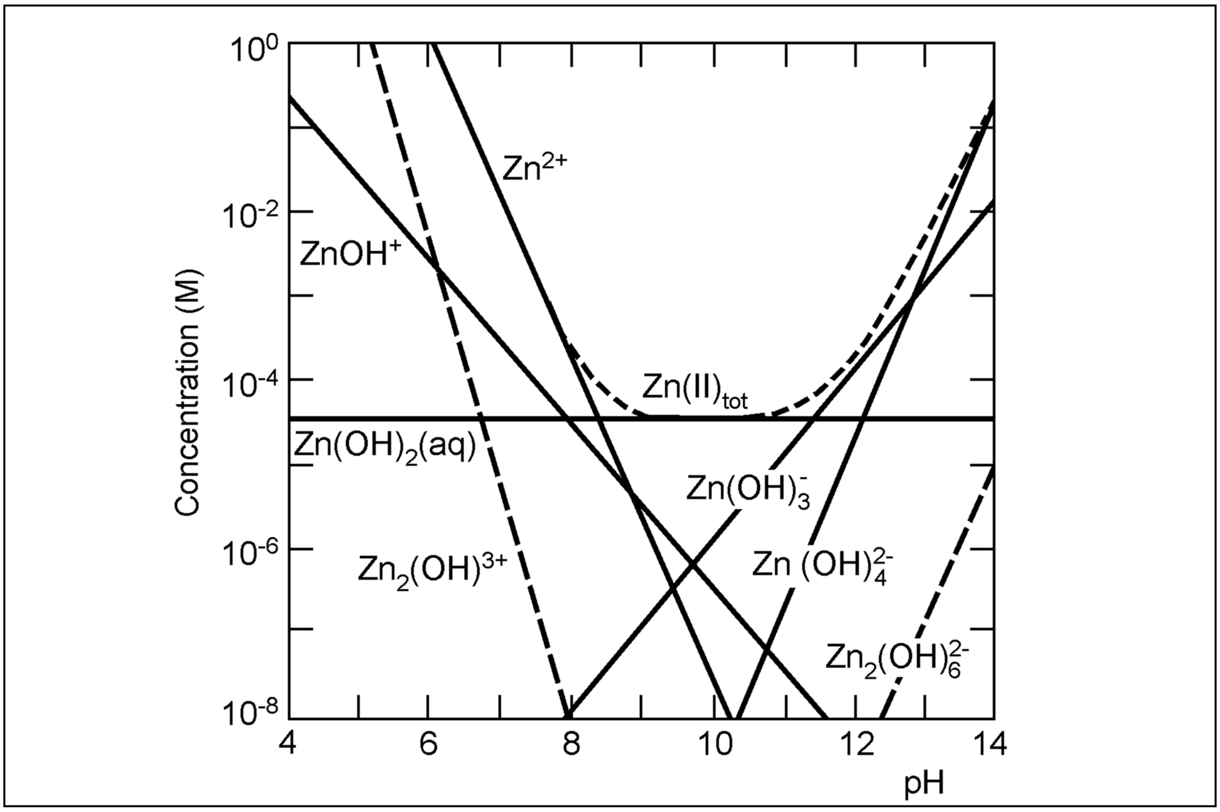

Fig. 7c: pH dependence of solubility of zinc hydroxide species in water. The dashed line represents total Zn solubility (after Stumm & Morgan, 1996 and Younger et al., 2002).

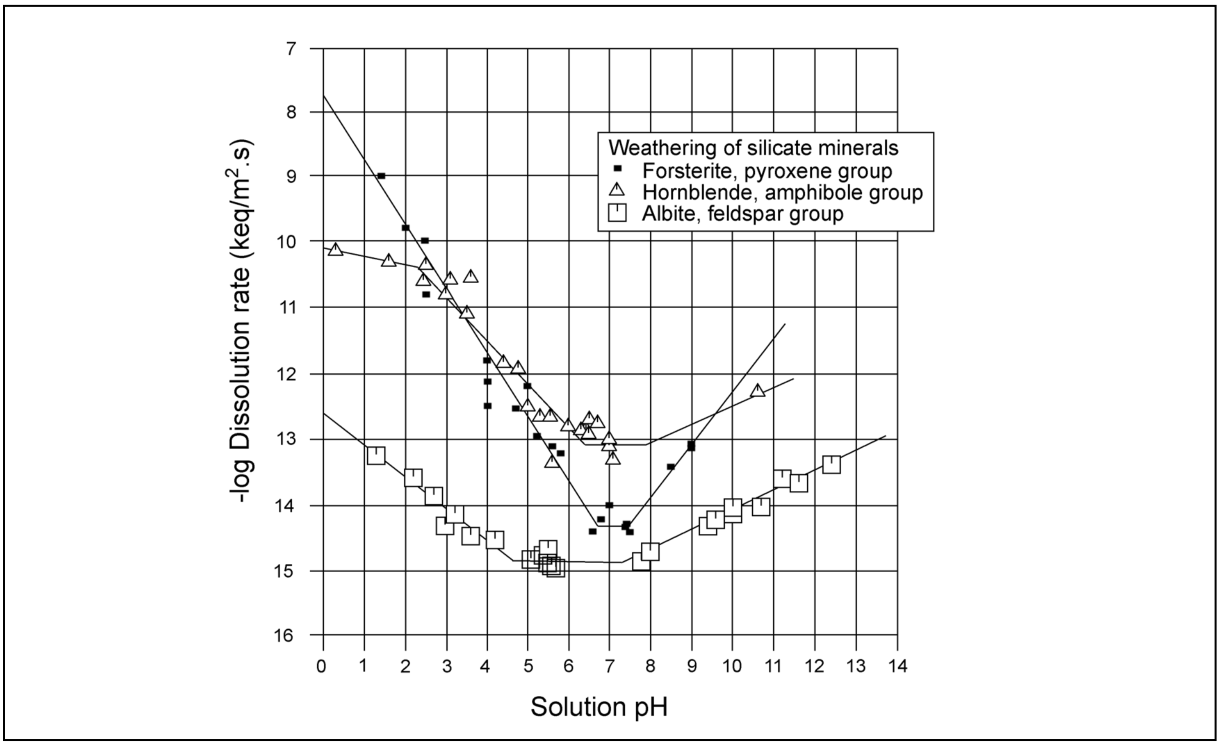

Fig. 8: Experimentally determined reaction (dissolution) rates for selected silicate minerals at varying pH values at 25°C (after Sverdrup & Warfvinge, 1988 and Appelo & Postma, 1996).

pH can also be regarded as a master variable because it controls the rate (Figure 8) and extent of acid-base reactions: i.e. most weathering reactions:

e.g. calcite: $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

plagioclase: $2NaAlSi_3O_8 + 2H^+ + H_2O \leftrightarrow 2Na^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2(aq)$

kaolinite: $Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2SiO_2 + 5H_2O$

Equilibrium Constants

Reversible reactions in solution can be characterised by an equilibrium constant K_{eq} where:

$K_{eq} = \pi$ (products) / π (reactants)

and where ( ) is an activity in mole/dm^3

e.g. for the reaction: $A + 2B = A+B+B \leftrightarrow 2C + D = C+C+D$

$K_{eq} = [(C).(C).(D)]/[(A).(B).(B)] = [(C)^2(D)]/[(A)(B)^2]$

For example, water dissociates reversibly to hydrogen and hydroxide ions:

$H_2O \leftrightarrow H^+ + OH^-$

The dissociation constant (at 25°C) is:

$K_{eq} = (H^+)(OH^-)/(H_2O) = (H^+)(OH^-) = 10^{-14}$ mol^2/dm^6

NOTE: activity of water and solid phases are, by default, set to unity. Thus, in a neutral solution $(H^+) = (OH^-) = 10^{-7}$ mol/dm^3. In other words, pH = 7 at 25°C in a neutral solution.

Gypsum

If we take, as a slightly more sophisticated example, the precipitation and dissolution of gypsum, we can attempt to answer the question: If gypsum is dissolved in water at 25°C, what activities (concentrations) of calcium and gypsum result ??

$CaSO_4.2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

from hydrochemical data Tables (Appelo & Postma 1996), we can find that, at 25°C, $K_{eq} = 10^{-4.58}$

$K_{eq} = (Ca^{2+}).(SO_4^{2-}).(H_2O)^2/(CaSO_4.2H_2O) = (Ca^{2+}).(SO_4^{2-}) = 10^{-4.58}$ mol^2/dm^6

Thus, as $(Ca^{2+}) = (SO_4^{2-})$, the activity of both calcium and sulphate must be: $10^{-2.29}$ mol/dm^3, for dissolution of gypsum in water at 25°C. If we make the (rather naughty, and strictly untenable) assumption that activity approximates to concentration, we can suggest the *approximate* concentrations of calcium and sulphate on might expect upon gypsum saturation:

Calcium weighs 40,080 mg/mol, thus $10^{-2.29}$ mol/dm^3 Ca = 206 mg/l

Sulphate weighs 96,064 mg/mol, thus $10^{-2.29}$ mol/dm^3 SO_4^{2-} = 493 mg/l

Programs such as MINTEQA2 (USEPA 1991) and PHREEQC (Parkhurst, 1995) allow more rigorous calculations to be made, taking full account of speciation of ions, and calculation of activity coefficients.

We can thus state that mine waters containing *more* than the above activities of calcium and sulphate will tend to have a tendency to precipitate gypsum. We can define a *Saturation Index (SI)*, the ratio of the product of the activities of the relevant ions to the K_{eq}:

$SI = \log_{10}[(Ca^{2+}).(SO_4^{2-})/K_{eq}]$

If SI = 0, an equilibrium exists. If SI>0, there is a tendency for gypsum to precipitate and the water is said to be *oversaturated* with respect to gypsum. If SI<0, there is a tendency for gypsum to dissolve and the water is said to be *undersaturated* with respect to gypsum.

For example, the San José mine water of Oruro, Bolivia (Table 1) contains:

1780 mg/l Ca = 0.044 mol/dm^3

8477 mg/l sulphate = 0.088 mol/dm^3

If we again make the rather naughty assumption that concentration approximates to activity (and if we ignore temperature):

$SI = \log_{10}[(Ca^{2+}).(SO_4^{2-}) / K_{eq}] = \log_{10}[(0.044)(0.088)/10^{-4.58}]$

$= \log_{10}(0.00387) + 4.58 = -2.41 + 4.58 = 2.2$

Thus, we can guess that the water is significantly *oversaturated* and that gypsum will tend to precipitate in the minewater channel. We should run a speciation program, such as PHREEQC, to confirm this, however, and to take full account of activity effects.

Iron Oxyhydroxide

We can use the concept of equilibrium constants to examine the solubility of ferric hydroxide, to understand how diagrams such as Figure 7b are generated.

$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$

Ferric oxyhydroxide can take a number of forms (amorphous, microcrystalline) and its Keq is difficult to pin down to an absolute value. However, Appelo & Postma (1996) suggest a value of:

$K_{eq} = 10^4 = (Fe^{3+})/(H^+)^3$

Thus, for systems in equilibrium with $Fe(OH)_3$

$\log(Fe^{3+}) = 4 + 3\log(H^+)$

$\log(Fe^{3+}) = 4 – 3pH$

This equation approximately corresponds to the line marked Fe3+ on Figure 7b. So, when pH = 6, $(Fe^{3+}) = 10^{-14}$ mol/dm^3. When pH = 2, $(Fe^{3+}) = 10^{-2}$ mol/dm^3 = 10 mmol/l. This explains the very low solubility of ferric iron at high pH and appreciable solubility at very low pH.

Master Variable: Eh

The redox potential, Eh (measured in mV) describes the redox state of a solution. The lower the value, the more reducing the solution. The higher the value, the more oxidising. Eh is, in fact, a measure of the electron activity of the solution, in the same way that pH is a measure of the proton activity. Eh controls the oxidation state of elements that can exist in several oxidation states, e.g. Fe and S (Figure 9).

Garrells & Christ (1965) produced a diagram illustrating typical Eh and pH conditions for various terrestrial environments (Figure 10).

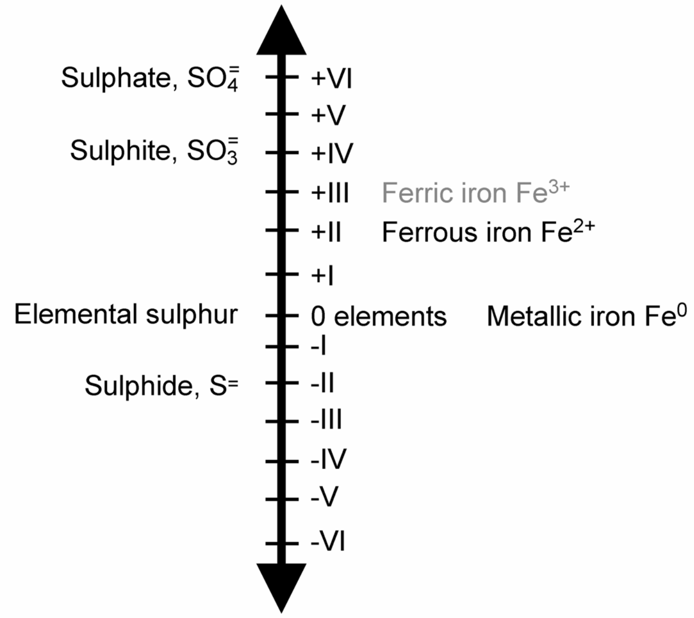

Fig. 9: Redox "ladder" showing some of the possible oxidation states of iron and sulphur.

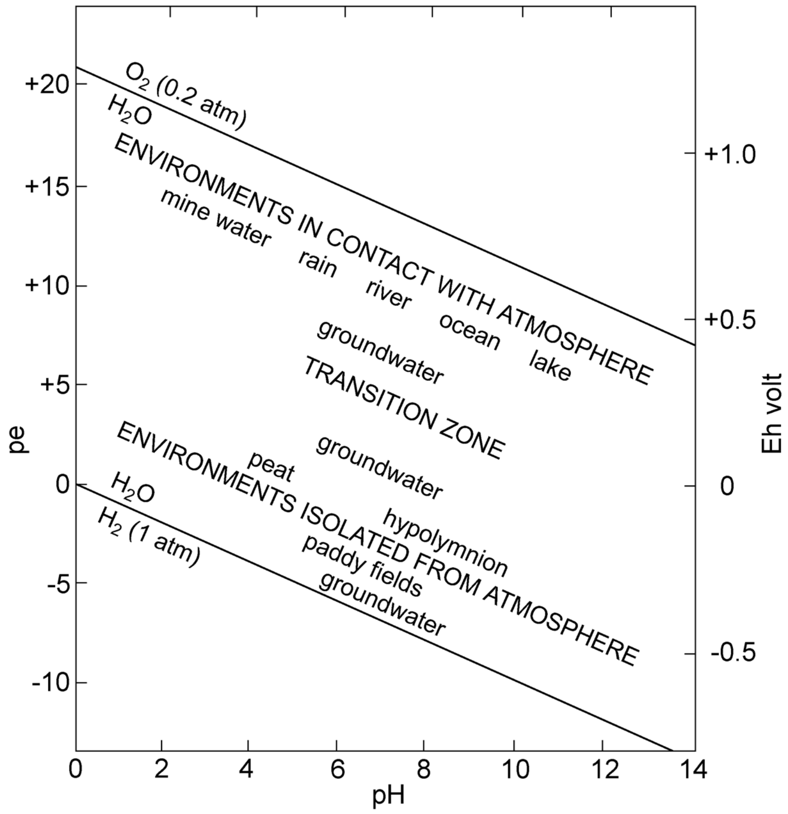

Fig. 10: The stability of water and the range of natural redox and pH environments (after Garrels & Christ, 1965 and Appelo & Postma, 1996).

Figure 10 is an example of a powerful tool used by hydrochemists: the pH – Eh diagram. Such diagrams (Figure 11) show the stable phases of a combination of elements in solution for a variety of Eh and pH values. It is important to realise that each diagram is valid only for specific total element concentrations and for given temperature and pressure conditions. The example in Figure 11 illustrates the following:

- That pyrite is stable in circum-neutral, reducing conditions: i.e. the subsurface geosphere
- By moving vertically from the pyrite field (i.e. by increasing Eh), we see that pyrite becomes unstable and gives way to siderite or ferric oxyhydroxide fields. In acid conditions, as in mine water, dissolved ferrous (and, under extremely oxidising and acid conditions, ferric) ions are the most stable phases.

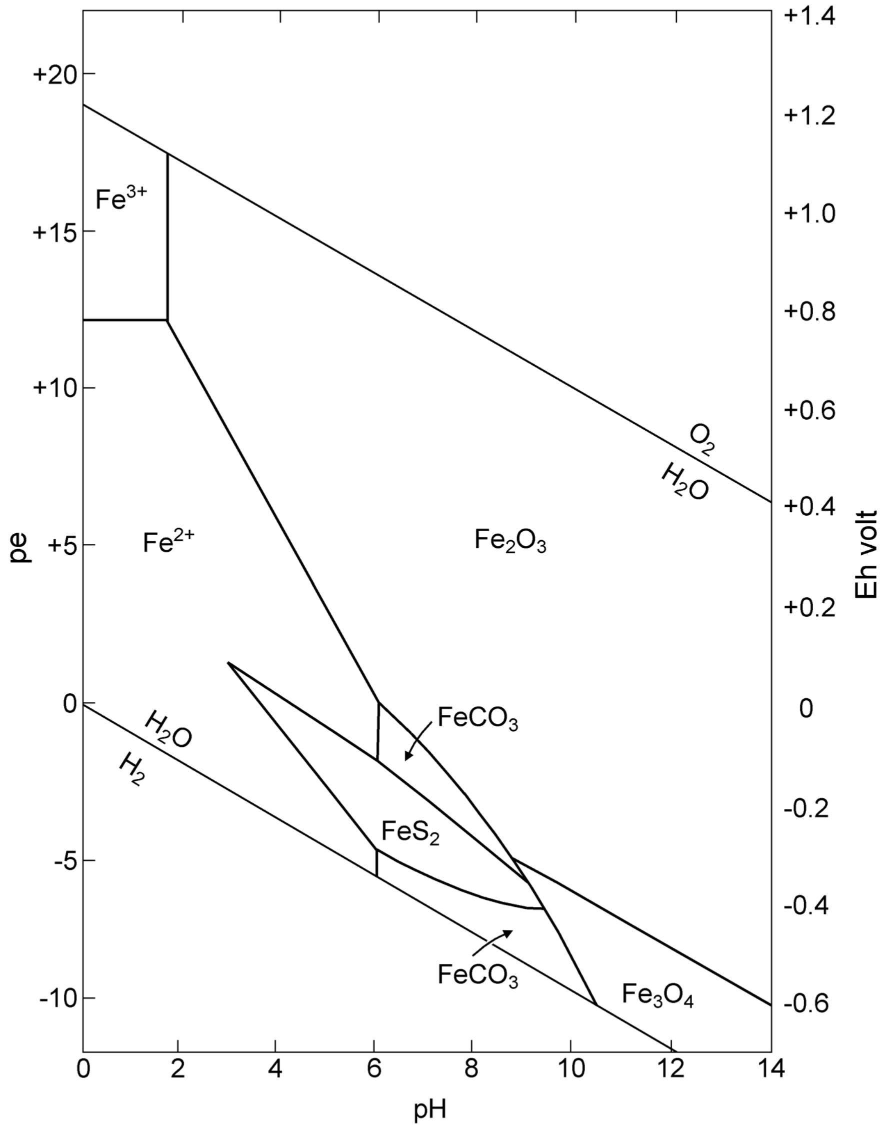

Fig. 11: Eh-pH diagram for the system Fe-C-S-H_2O, where Total S = 10^{-6} M, Total C = 10^{0} M, Fe^{2+} = 10^{-6} M and T = 25°C (after Appelo & Postma, 1996).

Acidity and Alkalinity

These terms cause great confusion to hydrochemists, largely because they are constructed, rather than *a priori* concepts, and because there are several similar, but subtly different, definitions of the concepts. Broadly speaking, alkalinity can be defined as:

- The capacity of a solution to neutralise acid
- The total (in meq/l) of basic species in a solution
- The amount of strong acid (meq/l) needed to reduce the pH of the solution to a given value (often around 4.3)

In most natural groundwaters, alkalinity (in meq/l) can be said to be approximately given by:

$$\text{Alkalinity} = \sum [OH^-] + 2[CO_3^{2-}] + [HCO_3^-]$$

where [ ] = concentration in mmol/l. Similarly, *acidity* can be defined as:

- The capacity of a solution to neutralise alkalis
- The total (in meq/l) of acidic species in a solution
- The amount of strong alkali (meq/l) needed to increase the pH of the solution to a given value (often around 8.2)

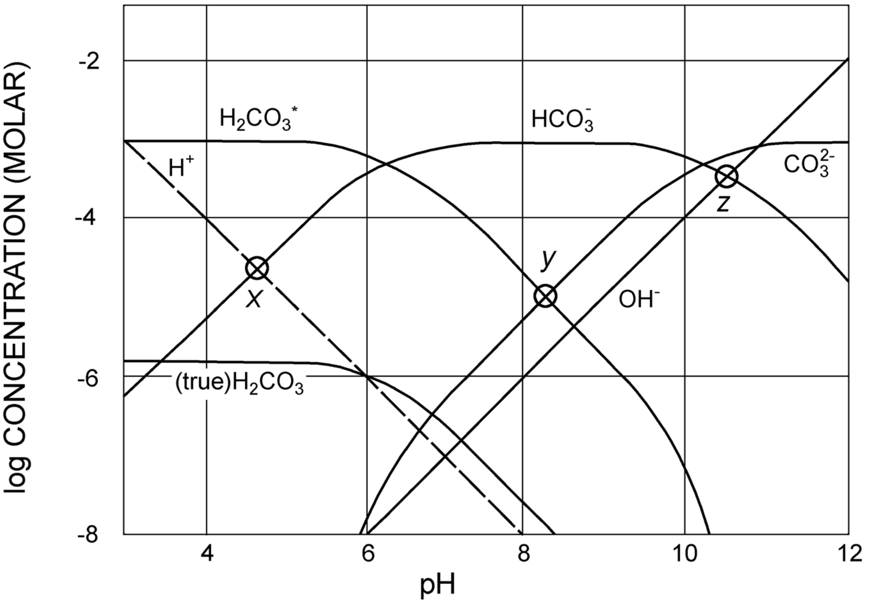

Fig. 12: Concentrations of individual inorganic carbon species in water as a function of pH in a system closed to CO_2 (after Stumm & Morgan, 1996).

One may ask: what's special about pH 4.3 and pH 8.2 as the titration end points. In fact, by the time pH has decreased to pH 4.3 during acid titration, almost all the bicarbonate in a solution has been used up and converted to carbonic acid. Likewise, by the time pH has been raised to 8.2 during an alkali titration, carbonic acid has effectively been converted to bicarbonate in a closed system. In fact, theoretical considerations (Younger et al., 2002) suggest that, for acid mine drainage problems, where mine water is exposed to environments that are open to CO_2 and where the carbonate system dominates, a more suitable end-point for alkalinity and acidity titrations would be pH = 5.64.

Acidity and alkali are best measured in the field by empirical titration. However, acidity can also be estimated from chemical analyses. Acidity is due not only to protons (H^+) but to potentially oxidisable and hydrolysable metals

$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$

$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$

Thus, in a sense, each ferric ion is solution has the ability to liberate three protons (or consume three hydroxide ions) on hydrolysis, and is thus equivalent to three units of acidity.

Similarly:

$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$	Al^{3+} = 3 units of acidity
$4Fe^{2+} + O_2 + 2H_2O + 8OH^- \leftrightarrow 4Fe(OH)_3$	Fe^{2+} = 2 units of acidity
$2Mn^{2+} + O_2 + 4OH^- \leftrightarrow 2MnO_2 + 2H_2O$	Mn^{2+} = 2 units of acidity

Thus, calculated acidity (in meq/l) is given by (e.g. Hedin et al. 1994).

$\text{Acidity} = \sum [H+] + 3[Fe^{3+}] + 3[Al^{3+}] + 2[Fe^{2+}] + 2[Mn^{2+}] + \ldots$ other relevant species

where [ ] is a concentration, in mmol/l. This is only an approximation, however, and is subject to inaccuracies due to the facts that:

(i) not all ferric iron in solution will be in the form of Fe^{3+}. It may form complex species.

(ii) ferric iron and aluminium and other metals may be present in analytical samples in the form of iron oxyhydroxide colloids, or even humic colloids.

If alkalinity of a minewater exceeds acidity, it is said to be “net alkaline”. If acidity of a minewater exceeds alkalinity, it is said to be “net acid”. These concepts have important implications for how mine waters are to be treated: i.e. whether they are suitable for active or passive treatment, whether they can be treated using aerobic wetlands or anaerobic basins.

PART 3: PREDICTING MINE WATER CHEMISTRY

The chemistry of a mine water will be determined by the master variables:

- pH (proton activity), which will be determined by the balance between amounts and rates of proton generating reactions and proton consuming (alkalinity generating) reactions
- Eh (electron activity), determined by access to oxidizing species (e.g. oxygen) and access to reducing species (e.g. organic C)

Some engineers have tried to assess *acidity generating potential* of waste heaps or mines by:

- summing the acid generating species present (e.g. sulphides)
- summing the acid consuming species present (e.g. carbonates)

In the least sophisticated methods, the acid generating species are typically quantified by analysing total S and assuming it is all present as sulphide. The acid consuming species are quantified by assessing the neutralising potential by treatment of crushed rock with hot HCl and then titration. Clearly, this acid-base accounting approach is fraught with problems:

- not all sulphides generate acid
- sulphur may be present as sulphate

- not all sulphide may be exposed to oxygen (heterogeneity)
- hot HCl treatment may overestimate field reactivity
- silicate weathering may also consume protons
- carbonates may not come into effective contact with mine water (heterogeneity)
- rates of reaction are important, as well as quantities
- particle size is not considered

The approach is probably most applicable for homogeneous mine waste tips, over a short-to-medium term time period. More sophisticated techniques use reaction cells and less aggressive conditions and are assessed in some detail by Banwart et al. (2002).

In fact, the pH of the mine water, which in turn will be dominant control on the metal concentrations in the water, will ultimately be controlled by:

- the rates of proton-generating reactions
- the rates of proton consuming reaction

and these rates *may* not be constant with time.

Proton-Generating Reactions

These include, pyrite oxidation and metal hydrolysis

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

$FeS_2 + 14Fe^{3+} + 8H_2O \leftrightarrow 15Fe^{2+} + 2\ SO_4^{2-} + 16H^+$

$Fe^{3+} + 3H_2O \leftrightarrow 3H^+ + Fe(OH)_3$

It should be noted that pyrite can be oxidised both by oxygen *and* by ferric iron, if present in the mine system. Oxidation by Fe^{3+} is considerably faster than by O_2. Thus, production of Fe^{3+} in the mine system by oxidation of Fe^{2+}, which is a typically slow reaction, is often the limiting step in the kinetics of pyrite oxidation (Figure 13).

Reaction cell experiments yield apparent (normalised, lab-determined) reaction rates (r_{py}: dimension $[M.L^{-2}.T^{-1}]$) for pyrite oxidation that are sometimes assumed to be up-scalable to field conditions (R_{py}) by simple factors such as:

- m_{py} , the mass of pyrite present [M]
- a_{py} , the specific surface area $[L^2.M^{-1}]$

$R_{py} = r_{py}.\ a_{py}.\ m_{py}$

However, many more factors will affect pyrite oxidation kinetics than just surface area:

- concentrations of reactants (O_2, Fe^{3+}) – abiotic rate increases as concentrations increase
- temperature (abiotic rate decreases with temperature)
- pH (abiotic rate decreases as pH decreases)
- bacterial activity
  - bacterially mediated pyrite oxidation may be 25–34 times faster than abiotic oxidation
  - bacterially mediated Fe^{2+} oxidation may be 106 times faster than abiotic oxidation
  - Thiobacillus ferrooxidans thrives at a pH range of 1.5 to 3.0.
- nutrient concentrations, temperature will influence bacterial activity

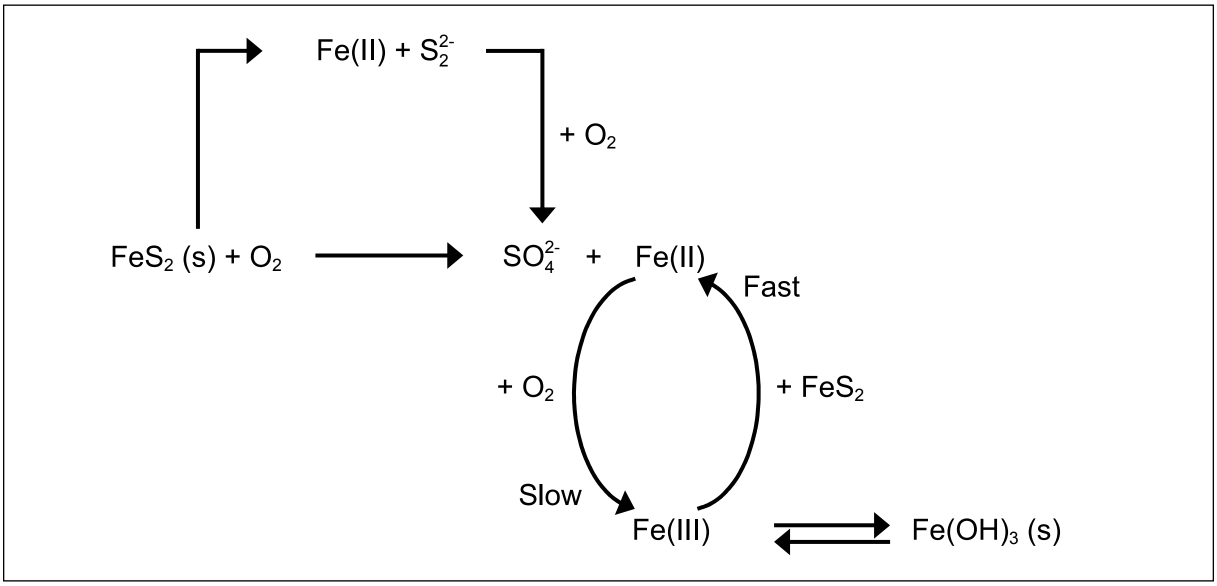

Fig. 13: Simplified diagram illustrating reaction pathways for pyrite oxidation (modified after Stumm & Morgan, 1981).

In other words, *bacteria* cause pyrite oxidation to occur under acidic conditions, and in particular, they catalyse appreciably the rate determining step (Fe^{2+} oxidation). It is open to question whether laboratory reaction cells can adequately simulate *in situ* microbiological conditions.

Although the number of interacting processes involved in minewater biogeochemistry can appear to be so intimidatingly large as to render the prediction of water's hydrochemical composition intractable, it may be possible to dramatically simplify the problem by identifying one rate-determining step. For example, in fine-grained mine wastes, the migration of oxygen into the wastes may be slow enough that it becomes such a rate-determining process, imposing a limit on the biotic or abiotic oxidation of pyrite. The complexity of issues then reduces to a physical problem of characterising the rate of migration of the oxidation front and a chemical problem of quantifying the rate of consumption of oxygen by sulphide oxidation or by organic carbon (which may be a competing process for oxygen).

Proton-Consuming, Alkalinity-Generating Reactions

These include, reaction with carbonate minerals, if present:

$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

FAST

$FeCO_3 + H^+ \leftrightarrow Fe^{2+} + HCO_3^-$

(Note that, although siderite has an immediate neutralising effect, it releases iron that may ultimately hydrolyse and re-release protons, contributing to net acidity).

Bicarbonate, if present in ambient groundwater, may also neutralise protons:

$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2$

Silicate weathering (SLOW)

$2NaAlSi_3O_8 + 2H^+ + H_2O \leftrightarrow 2Na^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2(aq)$

Clay hydrolysis

$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2SiO_2 + 5H_2O$

Sulphate reduction

$2CH_2O + SO_4^{2-} \leftrightarrow 2HCO_3^- + H_2S$

Rates of carbonate and silicate dissolution increase with increasingly acidic pH conditions (Figure 14 and Plummer et al., 1978). However, typically, calcite reacts several orders of magnitude more quickly than pyrite oxidises (especially at low pH) and most silicates react several orders of magnitude slower.

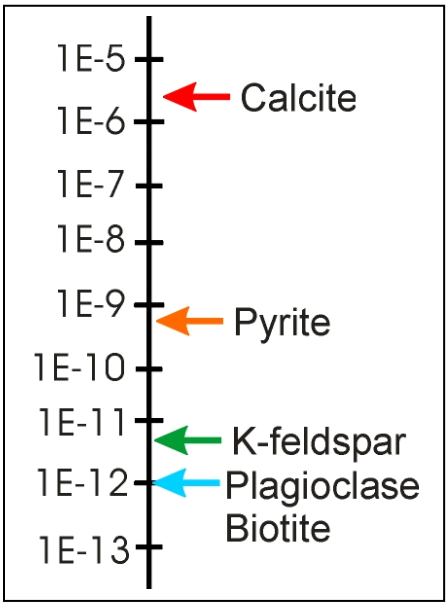

Fig. 14: Schematic showing relative abiotic laboratory mineral reaction rates (mole/ m^2/s) for pH=7 (modified after Younger et al., 2002).

As a result of these differing reaction kinetics, Strömberg & Banwart (1994, 1999) have predicted that minewater chemistry might be expected to evolve over time (see also Wiggering, 1993). In the early life of a mine waste tip, for example, any calcite present would be used up rapidly by the oxidation of pyrite. Thus, initially, the presence of minor amounts of calcite would be expected to maintain a relatively high pH in the leachate from the mine waste. Due to fast reaction kinetics, the calcite would eventually be consumed, if present in less amounts than pyrite. pH would then drop, as silicate weathering would be too slow to effectively neutralise acid generated by pyrite oxidation. With time, however, the pyrite content would diminish and silicate neutralisation might become significant. Thus the leachate draining from a mine waste pile comprising:

- a dominant fraction of silicate waste rocks
- some residual pyrite
- a minor content of calcite,
- residual deep saline and alkaline pore water

might be expected to evolve as through the following four phases, assuming the mine waste behaved homogeneously:

- Phase 1: Flushing of saline pore water from waste rock. Alkaline saline leachate
- Phase 2: Consumption of calcite by acid generated by pyrite weathering. Circum-neutral pH.
- Phase 3: Calcite fully consumed. pH drops dramatically as pyrite oxidation proceeds unbuffered
- Phase 4: Pyrite begins to be used up. Silicate buffering becomes significant. pH rises.

Of course, in real, heterogeneous, mine wastes, the picture will not be so simple. Such flushing and geochemical processes may take places in zones, related to the progressive inward/ downward migration of recharge water and oxygen, or within “hot spots” or preferential pathways with good access to water and oxygen throughflow.

PART 4: FINALLY

Other Types of Mine Water Pollution

Of course, although sulphide oxidation, leading to the phenomenon of acid rock drainage, is the most familiar type of mine drainage pollution, other issues may also arise (Banks et al., 1997b):

- Salinity: saline mine waters may be derived from salt mines, or from deep coal (e.g. Tilmanstone, Kent: Buchan 1962) or metals mines (e.g. San José, Bolivia: Banks et al., 2002a), where deep saline formation waters may be encountered. Alternatively, saline waters may be derived from intrusion of sea water in near-coastal mines. At Tilmanstone, disposal (infiltration) of saline mine waters led to significant contamination of the regionally important Chalk aquifer.
- Ammonium: deep coal mines, especially in shaley, mudstone environments (e.g. in the East Midlands of the UK: Banks et al., 1997a,b) are known to produce pumped mine waters with a high content of ammonium (and a high salinity, Downing & Howitt, 1969). Discharge of ammonium to recipient watercourses is regarded as a significant water quality issue in this context.
- Nitrate: use of nitrogen-based explosives in mining or quarrying can lead to elevated nitrate concentrations in groundwaters. This phenomenon is documented to have led to the contamination of a borehole near a quarry at Kopperå, Norway (T. Moseid, pers. comm.) and is suspected at some Siberian iron ore mines (Banks et al., 2002b).
- Oil/drilling fluids: Contamination by oils or drilling fluids used in the mining or quarrying process is also a recognised threat (Arnesen & Iversen, 1995).
- Radium and barium: in deep coal mine waters, which are low in sulphate (reducing environment), the solubility product of the relevant sulphate mineral (barite) may not be a limiting factor for barium solubility. Thus, elevated concentrations of barium, and its chemical analogue, radium, may occur. This phenomenon is documented from the Tyneside coalfields of the UK, and the Silesian coalfields of Poland (Banks et al., 1997b, Lebecka et al. 1994).
- Organics: the presence of organic micro-contaminants in mine waters from coal or lignite mines is poorly researched. However, a tentative link between refractory fluorescent substances in waters related to lignite exposures with Balkan endemic nephropathy has been suggested (Goldberg et al*.,* 1994).

Minewater: an Environmental Resource

While minewater pollution tends to experience an unremittingly negative press coverage, it should be remembered that mine waters can also be regarded as an environmental resource, as documented by Banks et al. (1996):

- Mine water discharges may provide low-N, bacteriologically pure baseflow to rivers: for example, the Rivers Drone and Dove in Derbyshire and Yorkshire, UK, which are otherwise very highly loaded with sewage effluent.

- Mine water discharges from limestone-hosted sulphide mines can be of high enough quality to be used as sources of drinking water (e.g. Meerbrook Sough, Derbyshire, UK)
- Mine waters can be sources of minerals (such as alkali salts, barium: Tyneside, UK) or can be employed as mineral water spas (Matlock, Derbyshire, UK [Albu et al., 1997] and Joachimstal)
- Ferruginous mine waters have been used in practice as flocculating agents at sewage treatment works (Buxton, Derbyshire, UK: Roberts & Leach, 1985). Ferric sulphate is a recognised flocculent salt.
- Mine water is an ideal source upon which to base heat pump solutions for space-heating and cooling of housing complexes, large commercial developments or public buildings. Examples can be found from Scotland, Norway, Canada and the USA (Banks et al., 2002c, in prep.)

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Contact

David Banks
Holymoor Consultancy
8 Heaton Street, Brampton
Chesterfield, Derbyshire
S40 3AQ
Phone: + 44 1246 23 00 68
E-mail: david@holymoor.co.uk