

Acid Mine Waters in South Africa and Their Amelioration

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Abstract

Acid mine waters formed as a result of chemical and bacterial oxidation of pyrites constitute one of South Africa's biggest water pollution problems. Three principal stages are involved in the formation of such waters, the first two involving oxidation and the third hydrolysis. This third stage, which is the most acid-forming of the three, is promoted by ageing and indicates that prompt removal of water from mines will result in a considerable saving of neutralizing agent. Hydrated lime is the most suitable neutralizing agent. Although the form in which iron is present, i.e. ferrous or ferric, determines the pH at which iron can be removed by precipitation, it is the total acidity that determines the lime requirement for full neutralization. This can very easily be determined after complete oxidation of the iron to the ferric form with hydrogen peroxide.

Introduction

Acid mine waters occur wherever pyritic formations come into contact with air and water resulting in acid sulphate contaminated waters which constitute one of the biggest water pollution problems in South Africa. As the name implies, the great majority of these waters result from mining activities, past and present, and they are formed both underground and at the surface. Much of the underground water (8 100 m³/d from the central and eastern Witwatersrand alone) is treated as described by Van Staden (1979) before release to public streams but this is not universal practice at present. In addition gold mine dumps on the Witwatersrand occupy a total area of about 80 km². All of these contain appreciable amounts of pyrites which, as a result of rainfall and weathering, produce strongly acid waters at the surface, most of which are not treated.

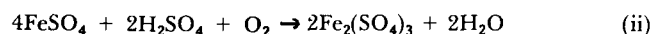
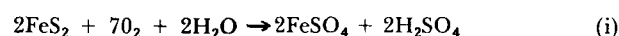
South African coal always contains some pyrites and constitutes a further source of acid mine waters in the coal mining areas of the eastern Transvaal and northern Natal. In the eastern Transvaal the terrain is relatively level and while considerable amounts of such waters come to the surface and find their way into streams, much water remains underground, particularly where workings have been abandoned. In northern Natal, however, many of the coal seams occur in mountainous country and frequently emerge at the surface on steep slopes. As a result, the number of point sources from which acid waters emanate tends to be more numerous than in the Transvaal but at each point source the volume tends to be less. This makes any attempted treatment and amelioration of water quality more difficult.

The development of sulphate acidity has been extensively studied and reported, especially in soils where it gives rise to so-called cat clays or acid sulphate soils. These occur mainly in tidal swamp areas, notably in the tropics, but numerous other

occurrences have been authenticated including one in Uganda (Chenery, 1954) and one in Rhodesia (Thompson, 1972).

In soils the oxidation stages to produce acidity from sulphides must usually be preceded by anaerobic reduction stages to produce the necessary iron sulphides in the first place. However, in the case of acid mine waters these initial stages are not involved.

According to Ivarson, Ross and Miles (1978) the three main reactions involved in the production of sulphuric acid from pyrites can be written as follows:



basic ferric sulphate

These authors state that reactions (i) and (iii) are chemical reactions but that due to the low rate of the chemical oxidation of FeSO₄ at pH values below 4.0 compared to the high rate in the presence of *Thiobacillus ferrooxidans*, reaction (ii) is mainly bacteriological. However, the important point to note is that reactions (i) and (ii) are oxidation reactions that require aerobic conditions, while reaction (iii), the most acid-producing, is essentially a hydrolysis reaction that can proceed without air.

This study was undertaken to determine the range in chemical composition of acid waters from the more important sources and to investigate the applicability and consequent effects of reaction (iii) in regard to water quality improvement by neutralization.

Materials and Methods

A total of 30 acid mine water samples was analysed in some detail. Of these 18 were of coal mine origin (streams, small dams and waters pumped from underground) one from gold mines (45 000 m³/d of combined waters from several mines being pumped by East Rand Proprietary Mines to the High Density Sludge treatment plant, described by Van Staden, 1979, for neutralization), and 11 originated from gold mine dumps (seepages, streams and small dams).

For the investigation, selected representative samples were aged at ambient temperatures under aerobic and anaerobic conditions for periods ranging from one and two and a half months. pH, conductivity and the concentrations of ferrous and ferric iron were then re-determined. Neutralization experiments using calcium hydroxide and calcium carbonate were also performed on selected samples to assess the efficiency

of these materials in improving the quality of the waters.

Results obtained in the ageing and neutralization experiments necessitated further investigations. A few samples in which most of the iron was present in the ferrous form were oxidized at ambient temperatures with the minimum amount of 30 % H_2O_2 required to convert all of the iron to the ferric state since through this step the lime requirement for acid waters can readily be determined regardless of the original oxidation state in which iron was present.

Analytical methods

Fe(II) was determined by potassium permanganate titration. Fe(II) and Fe(III) as above after treatment in a Jones reductor, the Fe(III) being obtained by difference.

Al by atomic absorption spectrophotometry.

Total acidity by titration with caustic soda using screened methyl red indicator (pH 6 end point) as described by Thompson (1979), applicable only if the iron is present in the trivalent state.

H^+ inferred by difference between total acidity and sum of Fe(III) and Al, where applicable.

Ca^{++} and Mg^{++} by EDTA titration after removal of iron and aluminium.

Na^+ and K^+ by atomic absorption spectrophotometry after removal of iron and aluminium.

Cl^- by titration with silver nitrate after removal of iron and aluminium.

Sulphates were not determined since they account for almost all of the anions present in these acid waters. However, unless such waters are heavily contaminated with cations other than those listed above, sulphate content can be inferred by subtracting chloride where appreciable, from the sum of cations including hydrogen.

Results and Discussion

Chemical composition of mine waters

Depending on origin and other factors, including dilution due to mixing with normal groundwaters, there are considerable differences in pH and salinity, particularly in acid coal mine waters. The highest conductivity recorded to date for coal mine water was 625 mS/m. In general, the waters originating from gold mine dumps are by far the most saline and acidic. The principal acid cations are hydrogen, iron and aluminium species. There are also large variations in the state in which iron is present and this is important since on neutralization all of the Fe(III) is precipitated below pH 6,0 whereas precipitation of Fe(II) was found to be complete at about pH 7,8.

The results of analysis of some typical acid waters from coal mines, a combined gold mine sample and samples from gold mine dumps are given in Table 1.

As indicated earlier it is generally accepted that the formation of acid sulphate waters from pyrites is fundamentally a process involving oxidation. It is therefore logical to expect that the iron will be predominantly in the ferric state. However, Dutrizac and MacDonald (1974) showed that the acidic ferric ion is a very effective leaching medium and that this property is primarily due to its oxidizing potential, and consequently ferric salts are reduced to the ferrous state.

In almost all of the coal mine waters so far examined, the iron was in the ferric state but in three instances the ferrous iron content was appreciable, sample 3 (Table 1) being one of these. This particular water was stagnant and occurred in an excavation into which a considerable amount of topsoil, apparently rich in organic matter, had subsided. In the other two instances (analyses not shown) contamination with municipal sewage effluent containing organic matter probably accounted for the appreciable ferrous iron contents.

TABLE 1
ANALYTICAL DATA FOR ACID WATERS FROM MINES AND MINE DUMPS

Sample	Coal mines			Gold** mine	Mine dumps		
	1	2	3	4	5	6	6a
pH	4,1	2,45	2,48	4,72	2,01	1,56	1,39
Cond. mS/m	73,3	211	237	498	1060	3095	3060
Total acidity me/l	1,54	18,22	n.d.*	n.d.	211,5	n.d.	n.d.
Fe(II) me/l	n.d.	0,06	2,15	11,33	trace	162,7	133,0
Fe(III) me/l	n.d.	3,28	4,44	trace	49,9	89,4	5,5
Al me/l	n.d.	5,01	8,33	1,67	101,4	202,8	91,67
H me/l	n.d.	9,87	n.d.	n.d.	60,2	n.d.	n.d.
Ca me/l	4,62	1,72	1,25	18,77	6,42	22,4	10,14
Mg me/l	2,02	0,83	0,70	16,24	9,25	42,6	9,91
Na me/l	0,79	0,23	0,13	8,42	1,18	2,71	2,22
K me/l	0,08	0,04	0,03	0,16	0,01	1,15	1,45
Cl me/l	0,31	0,24	0,41	3,06	0,56	1,3	0,75

* n.d. = not determined

**This combined water from several mines is pretreated with lime underground to about pH 5,0 to reduce corrosion of steel pipes and pumps.

At the time of sampling, the entire iron content of the pretreated combined gold mine waters (being pumped to the surface for further treatment) was in the ferrous form (sample 4, Table 1). In fact, had the ferric iron content been appreciable, almost all of it would have been precipitated by the pretreatment to pH 5 or even 4.7. The completely ferrous state can therefore only be attributed to contact with reducing agents, e.g. iron pyrite and as a result of reaction with pumps, piping, and any other iron objects that come into contact with the water underground.

Most of the acid waters from gold mine dumps have a transparent brown to dark brown colour and the iron is almost entirely in the ferric state due to contact with atmospheric oxygen. Sample 5 is typical of such waters that apparently originate mainly from surface run-off. However, the iron in sample 6 from the primary dam of the older Modder Deep mine dump was predominantly in the ferrous state, although much ferric iron was also present. This water originates mainly from a permanent spring at the base of the dump. Analysis of this spring water (Sample 6a) shows that the iron is almost completely in the ferrous state. As described by Dutrizac and MacDonald (1974) this is readily explained by oxidation within the dump of iron pyrites and other sulphides by the acidic ferric sulphate medium. In fact several workers including Matic and Mrost (1964) in South Africa and Harrison, Gow and Highson (1966) in Canada, have investigated the extraction of uranium from mine dumps by such media. However, limited depth of aeration within slimes dump material prevents regeneration of the ferric ion, and appears to be a major constraint.

Ageing

Samples 2, 3, 5 and 6 shown in Table 1 were among the samples that were aged at ambient temperature for periods ranging between one and two and a half months.

After some time the coal mine waters (samples 2 and 3) began to develop brown precipitates whether aged aerobically (sample 3) or anaerobically (sample 2). In the case of the much more acid and saline mine dump waters (sample 6) no precipitate developed within a one month period, but oxidation by air resulted in a colour change from greenish brown (ferrous and ferric) to dark brown (ferric). Visually there was no change in waters in which all or virtually all of the iron was already in the ferric form, e.g. sample 5 of Table 1, and the analyses were not repeated.

Details of treatments and changes in analytical data are given in Table 2.

From this table it is evident that the pH of the coal mine waters (samples 2 and 3) decreases and the conductivity increases. This can readily be explained by the hydrolysis of ferric sulphate to insoluble basic ferric sulphate plus free sulphuric acid as illustrated by reaction (iii). Confirmation that the precipitates were in fact basic ferric sulphates was obtained from X-ray diffractograms. However, with the mine dump waters in which most of the iron is in the ferrous form, the reverse takes place i.e. pH rises and there is a very marked drop in conductivity. This is doubtless the result of oxidation of ferrous sulphate to ferric sulphate during which free sulphuric acid is consumed, as indicated by reaction (ii). The extent of the drop in conductivity is due to the fact that the equivalent conductance of the hydrogen ion is about 5 to 6-fold that of the other ions present. Thus the consumption of appreciable amounts of free sulphuric acid, and consequently hydrogen ions, will have a very marked effect in lowering conductivity.

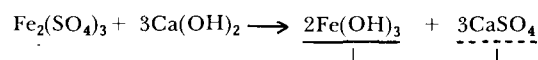
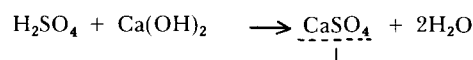
TABLE 2
CHANGES IN ANALYTICAL DATA RESULTING
FROM AGEING OF ACID MINE WATERS

	pH	Cond. mS/m	Fe(II) me/l	Fe(III) me/l
Sample 2 original	2.45	211	0.06	3.28
Sample 2 aged anaerob. 2½ months	2.38	258	n.d.*	n.d.
Sample 3 original	2.48	237	2.15	4.44
Sample 3 aged aerob. 2½ months	2.29	296	n.d.	n.d.
Sample 6 original	1.56	3095	162.7	89.4
Sample 6 aged aerob. 1 month	1.89	1670	6.65	244.4

*n.d. . . not determined

Quality improvement

Amelioration of acid mine water quality is best achieved by neutralizing with hydrated lime, particularly if the acidic species are present in high concentration because precipitation of sparingly soluble calcium sulphate can result in a marked reduction of total dissolved salts (TDS). The reactions involved are:-



The reactions for aluminium sulphate and ferrous sulphate, if the latter is present, are similar to that for ferric sulphate above.

In the process of neutralization the hydroxides of iron and aluminium are precipitated. As mentioned earlier, precipitation of ferric iron is complete at pH 6.0 but in the case of ferrous iron precipitation is only complete at about pH 7.8. Precipitation of calcium sulphate occurs whenever the conductivity due to the acidic species exceeds about 280 mS/m. However, the minimum conductivity attainable on neutralization will also be governed by the concentration of other salts, e.g. sodium salts if these are present, such as in sample Z, Table 3.

In order to illustrate the reduction in conductivity that is attainable under laboratory conditions a slurry of calcium hydroxide made up with a minimum of water was thoroughly stirred into several acid mine waters until a pH of between 7.5 and 8.0 was obtained. After settling the conductivity of the clear supernatant liquid was determined. These results are given in Table 3.

TABLE 3
CONDUCTIVITY OF MINE WATERS BEFORE AND AFTER COMPLETE NEUTRALIZATION WITH CALCIUM HYDROXIDE

	pH	Original		After Neutralization to pH 7,5–8,0	
		Cond. mS/m		Cond. mS/m	
Sample 2	2,45	211		178	
Sample 3	2,48	237		217	
Sample 5	2,01	1060		292	
Sample 6	1,56	3095		277	
Sample Z	2,02	1202		490	

Sample Z was an acid mine water that had been contaminated with industrial effluent and had a sodium content of 8,78 me/l compared with less than 3 me/l for similar samples in Table 1.

As expected, the greatest reduction in conductivity occurs in the very saline acid mine dump waters in which the acidic species account for most of the salts present. Because of the very large amounts of hydrated lime that would be required to neutralize even relatively modest amounts of mine dump waters such as those above, similar neutralization experiments were carried out using calcium carbonate. Two levels of liming were tested, firstly stoichiometrically calculated amounts and subsequently a large surplus, approximately twice the stoichiometric amount. The results are shown in Table 4.

One of the main reasons for the much poorer results obtained with calcium carbonate is that at ambient temperatures the solubility of CO₂ maintains the pH at a level that is too low to effect the precipitation of any of the ferrous iron and also much of the ferric iron. On boiling, results approaching those obtainable with calcium hydroxide can be obtained but this is of academic interest only.

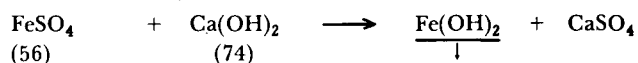
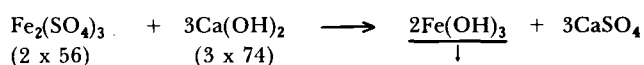
TABLE 4
CONDUCTIVITY AND pH VALUES OF MINE WATERS BEFORE AND AFTER PARTIAL NEUTRALIZATION WITH CALCIUM CARBONATE

	Original		Stoich. amount		2x Stoich. amount	
	pH	Cond. mS/m	pH	Cond. mS/m	pH	Cond. mS/m
Sample 5	2,01	1060	3,53	722	4,88	619
Sample 6	1,56	3095	3,80	1650	5,02	1460

Oxidation with hydrogen peroxide

The ageing experiment showed clearly that oxidation of appreciable amounts of ferrous iron (sample 6, Table 2) consumes

free sulphuric acid in accordance with equation (ii). However the precipitation of ferric iron requires 50 % more neutralizing agent than ferrous iron, as shown below:-



On the other hand, precipitation of ferric iron is complete at pH 6,0 whereas with ferrous iron a pH of 7,8 is necessary. This suggested that in order to obtain a definite, reproducible ready means of determining total acidity, and hence hydrated lime requirement, all of the iron would have to be in the ferric form.

In a further set of experiments total acidity to the pH 6,0 level was determined by titration with caustic soda on two acid mine dump waters (samples 6 and 6a) before and after oxidation with H₂O₂ of all of the iron present, and pH and conductivity were also re-determined after oxidation. The amount of 30 % H₂O₂ (a few drops per 100 ml) required for complete oxidation involved a dilution factor of less than one per cent, thus introducing a negligible error on the subsequent conductivity measurement. The results are shown in Table 5.

TABLE 5
pH, CONDUCTIVITY AND TOTAL ACIDITY AT THE pH 6,0 LEVEL OF MINE DUMP WATERS BEFORE AND AFTER OXIDATION

	Original			After oxidation		
	pH	Cond. mS/m	Tot. Acidity me/l	pH	Cond. mS/m	Tot. Acidity me/l
Sample 6	1,56	3095	532,0	1,97	1620	741,0
Sample 6a	1,39	3060	240,8	1,94	1319	433,3

As expected, oxidation by H₂O₂, which takes place at ambient temperatures within seconds, has the same effect on pH and conductivity as aerobic ageing (c.f. analytical data for sample 6 in Table 2) and the increase in pH and decrease in conductivity also occurs. In addition there is the apparent contradiction that total acidity to the pH 6,0 level *increases* very considerably but this is because at the pH 6,0 level all ferric iron is involved in the neutralization reactions whereas most ferrous iron is not. In other words, when the iron is in the ferric state neutralization to pH 6,0 is fully stoichiometric whereas with iron in the ferrous state it is not. This experiment thus confirms that oxidation with H₂O₂ enables total acidity, and hence lime requirement, to be readily determined.

Conclusions

In the formation of acid sulphate waters reaction (iii) described by Ivarson, Ross and Miles (1978) is the most acid-forming. It is an hydrolysis reaction that takes place over an appreciable

period of time and thus occurs whenever acid water is stored or stagnates above or below ground. This is an important aspect because it strongly suggests that waters percolating into the reactive or acid-producing zones of a mine should be removed for amelioration by neutralization as soon as possible. In this way a considerable saving in neutralizing material can be effected. Hydrated lime is the most effective neutralizing material because, for high concentrations of the acidic species a considerable reduction in TDS can be obtained through precipitation and removal of calcium sulphate which is sparingly soluble.

The form in which iron is present is also an important factor, ferric iron being completely precipitated at pH 6,0 whereas for iron in the ferrous state a pH of about 7,8 is required. This has an important bearing on the assessment of lime requirement. In order to calculate this, total acidity must be determined. This determination is most conveniently performed by titration with caustic soda to a pH 6,0 end point provided that all of the iron has previously been oxidised with H_2O_2 to the ferric state.

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