Pergamon

0892–6875(95)00109–3

OXIDATION OF PYRITE AND ARSENOPYRITE IN SULPHIDIC SPOILS IN LAVRION

K. KOMNITSAS, A. XENIDIS and K. ADAM

National Technical University of Athens, Laboratory of Metallurgy
GR-157 80 Zografos, Athens, Greece

ABSTRACT

This paper aims to present the aspects of oxidation of pyrite and arsenopyrite in the sulphidic spoils in Lavrion and to assess the environmental impact of this process. Sulphidic spoils, under the combined action of atmospheric oxygen, water and bacteria are oxidised and toxic elements are released and migrate to surrounding areas contributing to widespread soil contamination and severe deterioration in the quality of surface and underground waters. The critical factors which control the generation of acidic waters are availability of oxygen and water, temperature, bacterial activity and rate of oxygen diffusion through the pores in the upper zones of spoils. Special emphasis will be given in the oxidation of sulphidic spoils at Lavrion, Greece, where the generation of acidic waters causes widespread contamination. This study is focused in the first part on the preferential oxidation of arsenopyrite. Flotation products containing pyrite and arsenopyrite were subjected to bacterial leaching tests at 3% w/v pulp density and the degrees of oxidation were calculated and compared to with previous experimental studies. These results provided the basis to assess the behaviour of the above minerals in waste stockpiles. Moreover, and in order to assess the oxidation and precipitation mechanisms, several samples were collected up to a depth of 20 cm from the surface from the same spoils profile, where successive layers of oxidation products were present and characterised chemically and mineralogically. The above information is critically evaluated for the determination of the environmental impact of the oxidation of sulphide phases in spoils.

INTRODUCTION

At Lavrion area, in Eastern Attica, Greece, the intensive mining and metallurgical activities over the past 100 years for the production of lead and silver, have generated huge volumes of mining and metallurgical wastes which exhibit different chemical and mineralogical composition. These tailings act as pollution sources and contribute to the widespread soil and water pollution of the surrounding area. They exhibit high acid generation potential, the characteristics of EP toxicity and monitoring of pore water revealed extremely high concentrations of toxic elements [1]. Following a rainfall, acidic ponds are formed on the spoils with the following indicative analysis: pH=1.5–2.5, EMF=450–600 mV, Pb=0.7–5 ppm, Zn=1 g/l, Cd=2–5 ppm, As=1g/l. Sludge analyses revealed the presence of *T. ferrooxidans* strains.

Acidic water generation results from the oxidation of sulphide minerals, mainly pyrite and is believed to be the most important factor for the contamination of surface and ground waters in mining areas or in areas where mining/milling wastes have been disposed.

The natural bacterially mediated oxidation of sulphide minerals occurs under acidic conditions with sulphuric acid being the major solvent and ferric iron participating in the overall reaction as a strong oxidising agent.

The oxidation of sulphide minerals generally occurs at shallow depths above the water table and results in the production of acidic waters often containing increased levels of heavy metals and other constituents. The most important factors that influence oxidation are oxygen availability, presence of bacteria and depletion of acid consuming minerals. Oxidation rates are enhanced in the presence of oxidising bacteria *T. ferrooxidans*. These bacteria are aerobic, acidophilic and chemolithotrophic and their optimum conditions for growth are pH 1.5–3.0 and temperature 30–40°C.

MECHANISMS OF BACTERIAL OXIDATION

Bacterial oxidation of sulphide ores and concentrates is mainly based on the action of the bacteria *T. ferrooxidans*. These bacteria are used to accelerate the rate of sulphide minerals oxidation by breaking down the sulphide lattice [2,3,4]. Therefore, these phases which otherwise could have been oxidised in a long time by the use of oxygen and water, are oxidised much faster in case when microorganisms are present and local conditions favour their growth. *T. ferrooxidans* is able to utilise not only inorganic sulphur compounds but also ferrous iron simultaneously, as oxidisable inorganic substances. Many strains of this organism have been isolated, their differentiation being based upon capacity to oxidise either elemental sulphur or various sulphide minerals. *T. ferrooxidans* requires a source of nitrogen, phosphate and trace amounts of calcium, magnesium and potassium. Its energy for growth is obtained from the oxidation of ferrous iron, soluble and insoluble sulphides, sulphur and soluble sulphur compounds. *T. ferrooxidans* are encountered in a wide range of natural environments, but their presence is mostly associated with increased concentrations of sulphide minerals.
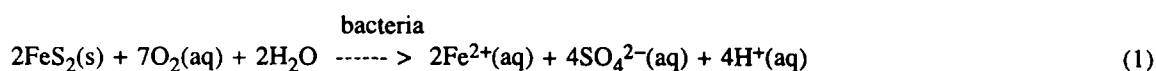
Emphasis is placed upon the tolerance of the culture to the metals released from the dissolution of minerals and its ability to oxidise both sulphur and iron. *T. ferrooxidans* can tolerate 40 g/l iron, 70 g/l copper, 119 g/l zinc and 70 g/l nickel and strains can be made adaptable by successive subculturing to a variety of metals such as cobalt, uranium, chromium and arsenic [7,8].
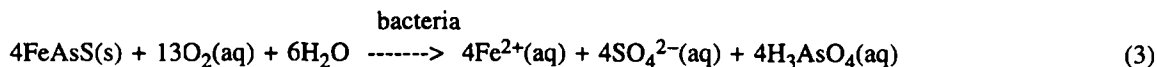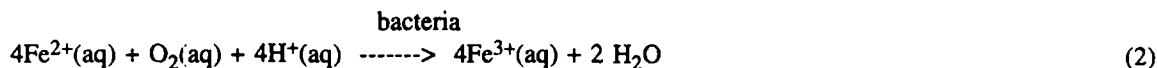
Other microorganisms that oxidise sulphide minerals include *Thiobacillus thiooxidans* and *Leptospirilum ferrooxidans*. The thermophilic strain *Sulfolobus* can leach sulphide minerals at temperatures as high as 70°C, but their use is reportedly limited.

Bacterial oxidation of pyrite and arsenopyrite may proceed either directly or indirectly [5,6,7,8]. Direct mechanisms involve catalysis of the oxidation reactions by direct bacterial action and therefore require physical contact between bacteria and the sulphide particle surface under aerobic conditions; indirect mechanisms involve oxidation of the sulphides mainly by the action of bacterially produced ferric iron in solution [9]. Both mechanisms operate concurrently but their extent to the total oxidative attack varies depending on the type of bacteria, the sulphide substrate and the environmental conditions during the oxidation [10].
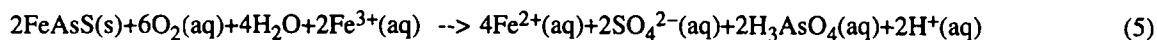
The main reactions describing pyrite and arsenopyrite bacterial oxidation are summarised below:
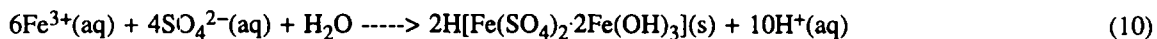
Direct mechanism

$$\underset{\text{bacteria}}{2FeS_2(s) + 7O_2(aq) + 2H_2O \;\text{-----}>\; 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq)} \tag{1}$$

bacteria
$$4Fe^{2+}(aq) + O_2(aq) + 4H^+(aq) \text{ -------> } 4Fe^{3+}(aq) + 2 H_2O \tag{2}$$

bacteria
$$4FeAsS(s) + 13O_2(aq) + 6H_2O \text{ -------> } 4Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H_3AsO_4(aq) \tag{3}$$

Indirect mechanism

$$FeS_2(s) + 2Fe^{3+}(aq) \text{ --------> } 3Fe^{2+}(aq) + 2S^0(s) \tag{4}$$

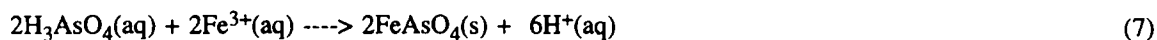$$2FeAsS(s)+6O_2(aq)+4H_2O+2Fe^{3+}(aq) \text{ --> } 4Fe^{2+}(aq)+2SO_4^{2-}(aq)+2H_3AsO_4(aq)+2H^+(aq) \tag{5}$$

Ferrous sulphate is re-oxidised by *T. ferrooxidans* (equation 2) while elemental sulphur is further oxidised with the following reaction:

bacteria
$$2S^0(s) + 3O_2(aq) + 2H_2O \text{ -------> } 2SO_4^{2-}(aq) + 4H^+(aq) \tag{6}$$
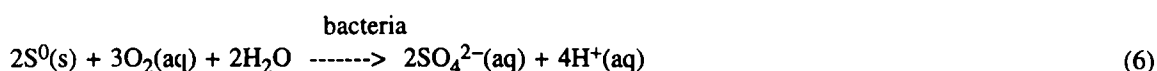
In parallel, secondary precipitation reactions may occur, depending on pH and solution composition, leading to the formation of ferric arsenates, ferric hydroxide, basic ferric sulphates and jarosites:

$$2H_3AsO_4(aq) + 2Fe^{3+}(aq) \text{ ----> } 2FeAsO_4(s) + 6H^+(aq) \tag{7}$$

$$2Fe^{3+}(aq) + 6H_2O \text{ ----> } 2Fe(OH)_3(s) + 6H^+(aq) \tag{8}$$

$$Fe(OH)_3(s) + SO_4^{2-}(aq) + 2H^+(aq) \text{ -----> } Fe(OH)(SO_4)(s) + 2H_2O \tag{9}$$

$$6Fe^{3+}(aq) + 4SO_4^{2-}(aq) + H_2O \text{ -----> } 2H[Fe(SO_4)_2 \cdot 2Fe(OH)_3](s) + 10H^+(aq) \tag{10}$$

Panin *et al.* [11] suggested that the direct mechanism is based on electrochemical interactions intensified by bacteria. Bacteria are adsorbed on the mineral surface both physically, by the forces of molecular interaction, and chemically, by the formation of chemical bonds between the cell and the elements of the mineral lattice. However, the mechanism of electrochemical process intensification on the sulphide minerals surface has not yet been fully identified. It has been proved, though, that bacteria, while in contact with the mineral, tend to change the electrode potential, depolarise the mineral surface through oxidation of S and Fe^{2+}, and increase the Eh of the medium producing highly oxidising conditions.

Furthermore, it is well documented in literature that during leaching of mixed sulphide minerals exhibiting different rest potentials, galvanic conversion occurs, significantly enhancing the leaching process [12]. Galvanic contact between the different conducting and semi-conducting minerals leads to the preferential dissolution of certain less noble minerals acting as anodes, by nature of electrochemical relativity. Thus, in the presence of pyrite, arsenopyrite will be the first mineral phase to be oxidised at much higher oxidation rates [11,13]. The presence of bacteria accelerates this galvanic conversion. Berry *et al.* [9] concluded that bacteria do not preferentially attack one sulphide mineral in a mixture of sulphide minerals, but act by producing the oxidising agent (Fe^{3+}) and the lixiviant (H_2SO_4) which assist oxidation of the mineral phases. Preferential oxidation is, thus, a chemical phenomenon due to the galvanic pairing, and selective oxidation is not due to biological selection of the substrates.

EXPERIMENTAL PROCEDURE

Materials

The chemical and wet screen size analyses for both flotation products used in this study, containing pyrite and arsenopyrite, are shown in the following Tables 1 and 2.

TABLE 1 Wet screen size and chemical analysis of pyrite concentrate

Size (mm)	Weight %	Fe (%)	As (%)	S (%)
+0.25	1.46	36.16	0.8	44.9
-0.25+0.125	40.82	42.71	1.0	50.97
-0.125+0.088	19.55	42.5	1.2	49.09
-0.088+0.063	11.37	42.9	1.2	48.62
-0.063+0.044	10.23	42.12	1.4	48.5
-0.044	16.56	38.96	2.3	42.5
Total	100.00	41.91	1.32	48.59

The pyrite fraction of this concentrate is 87.7%, while the arsenopyrite fraction is 2.87%.

TABLE 2 Wet screen size and chemical analysis of arsenopyrite concentrate

Size (mm)	Weight %	Fe (%)	As (%)	S (%)
+0.125	1.81	11.2	9.6	10.5
-0.125+0.088	2.59	13.90	10.92	12.02
-0.088+0.063	3.96	17.90	15.64	13.47
-0.063+0.044	8.65	25.06	23.16	19.04
-0.044	82.99	33.33	30.88	23.87
Total	100.00	31.10	28.71	22.49

The arsenopyrite fraction of this concentrate is 62%, while the pyrite fraction is 20.7%.

Bacterial Culture

The bacterial culture used in this experimental study is the iron oxidising *T. ferrooxidans*, which has been grown in the Laboratory of Mineral Processing of University College Cardiff, Wales, U.K., on a variety of metal sulphide concentrates and shown to be adaptive to growth in the presence of high concentrations of iron and arsenic.

Shake flasks — Leaching Technique

All tests were conducted in 250 ml Erlenmeyer flasks. 3 g of the mineral concentrate were added into the flask, followed by the addition of 100 ml of 9K medium acidified to pH 1.7 with the addition of conc. H_2SO_4. The flasks were then placed into a heated at 30° C water bath, aerated and agitated for several days. An inoculum of *T. ferrooxidans* with a concentration of 1×10^9 cells per ml of suspension per 1% w/v pulp density was employed in all experiments and correction for evaporation made prior to sampling by the addition of acidified water.

Chemical and Mineralogical Analyses

All elements in solution were measured using a Perkin Elmer Atomic Absorption Spectrophotometer. Suspension Eh was measured by a platinum/calomel electrode combination. Mineralogical analysis was carried out by XRD techniques for the identification of the oxidation products present in sulphidic spoils. Digestion techniques were also used in order to perform mass balance calculations.

RESULTS AND DISCUSSION

Leaching tests

In order to study the preferential oxidation of arsenopyrite, flotation products containing pyrite and arsenopyrite were subjected to bacterial leaching tests and the degrees of oxidation for both mineral phases were calculated and compared to with previous experimental studies. The effect of particle size on the degree of oxidation was also examined. These results will provide the basis to assess the behaviour of the above minerals in waste stockpiles.

Pulp density was maintained at 3% w/v and the particle sizes were +0.25 mm, −0.25+0.125 mm, −0.125+0.088 mm, −0.088+0.063 mm, −0.063+0.044 mm and −0.044 mm for the pyrite concentrate and +0.125 mm, −0.125+0.088 mm, −0.088+0.063 mm, −0.063+0.044 mm and −0.044 mm for the arsenopyrite concentrate.

As it is well documented in literature [7,8], arsenopyrite dissolution starts immediately in the presence of bacteria within an Eh range 390–450 mV and proceeds much faster than the dissolution of pyrite according to equations (3) and (5), indicating that arsenopyrite presents a higher oxidation potential as compared to pyrite.

Pyrite dissolution starts at higher Eh values and is enhanced by the presence of high concentrations of bacterially produced ferric iron in solution. Ferric iron is produced by the oxidation of ferrous iron, according to equation (2).

The effect of particle size on the oxidation of pyrite and arsenopyrite for both concentrates is seen in Figures 1–4.
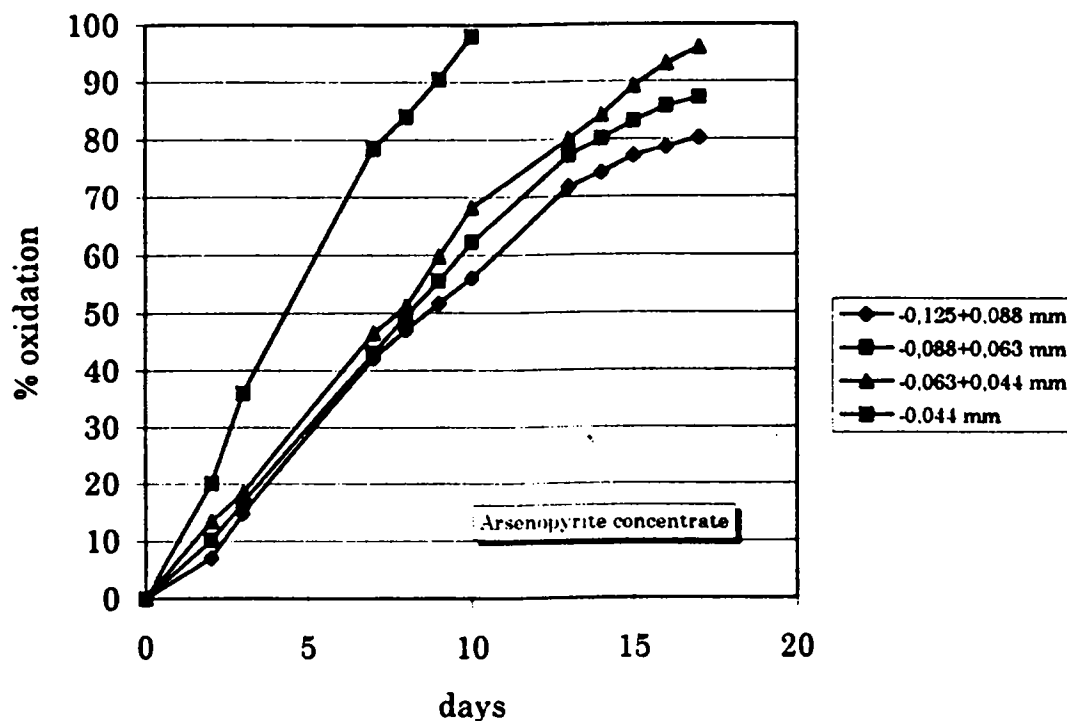

Fig.1 % FeAsS oxidation

From the data presented the following observations can be made:

For the arsenopyrite concentrate

The degree of arsenopyrite oxidation increases during leaching of finer concentrates and for the –0.044 mm fraction almost complete oxidation is attained after 10 days. Oxidation rates were much slower for the coarser fractions and after 17 days of leaching the maximum degree of oxidation exceeded 80%.

Pyrite is only partially oxidised and for the –0.125+0.088 mm fraction 15% of the feed material was oxidised after 17 days of leaching. All other fractions show considerable oxidation degrees and the finest fraction was oxidised almost completely after 10 days.
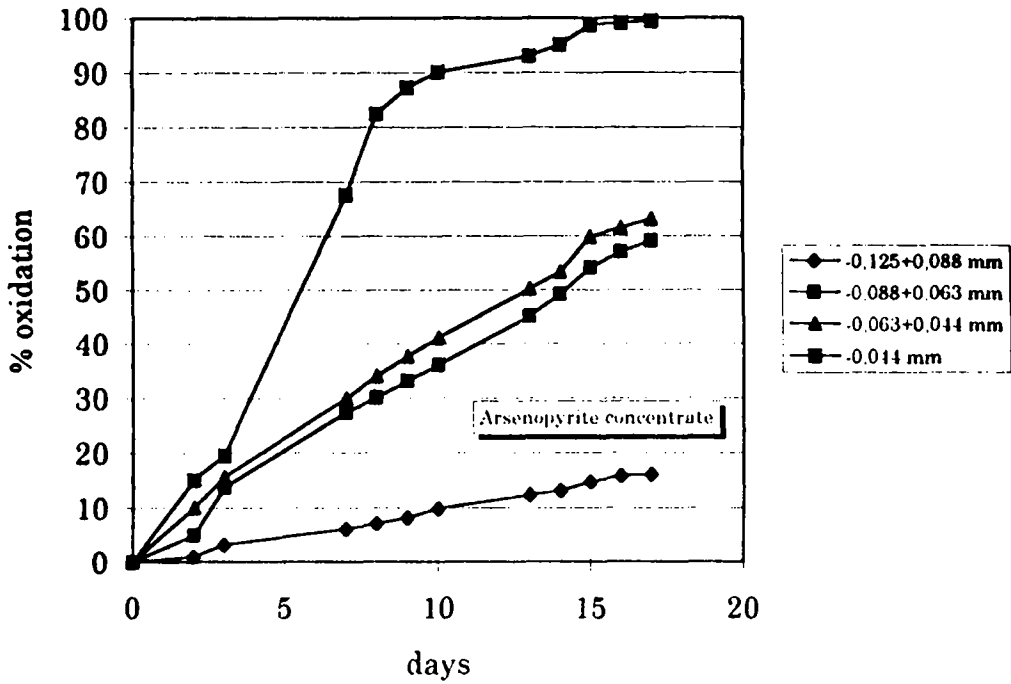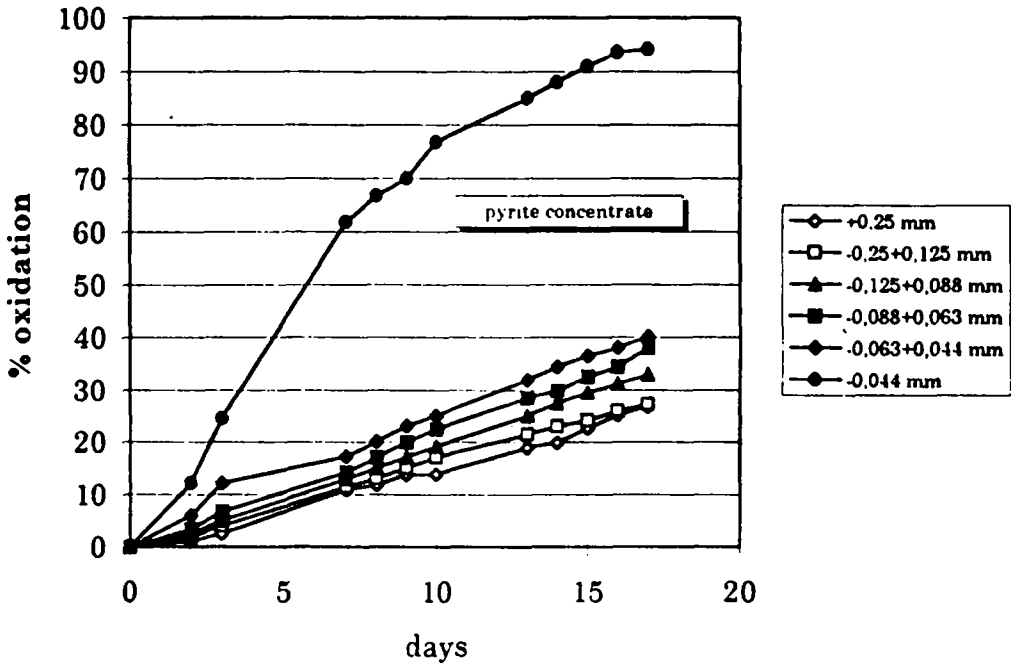
Fig.2 % FeS$_2$ oxidation
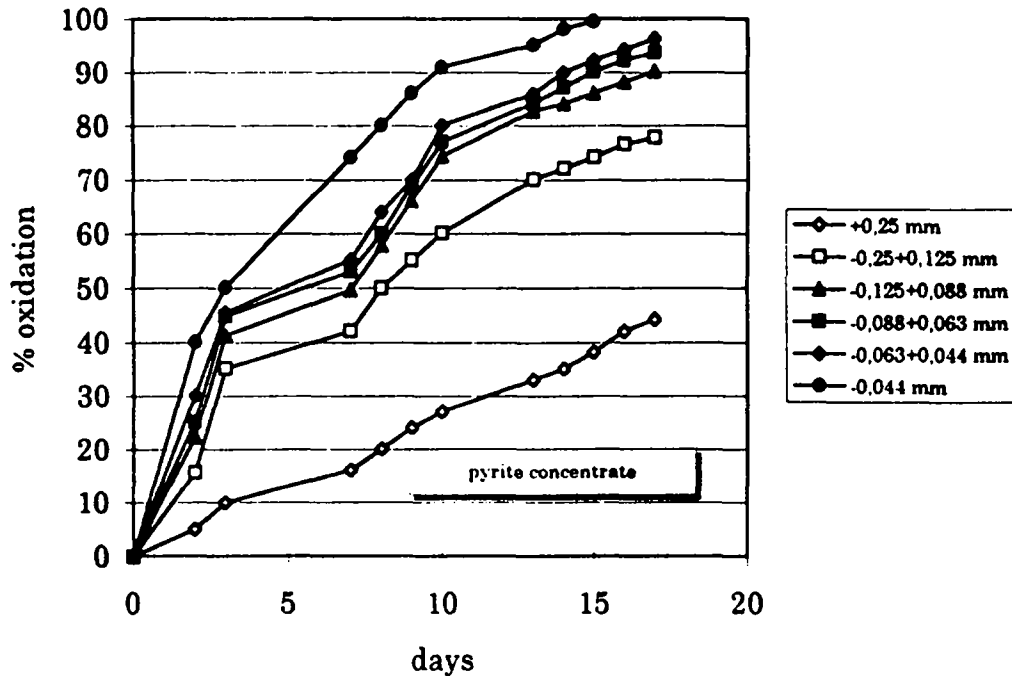
Fig.3 % FeS$_2$ oxidation

Fig.4 % FeAsS oxidation

For the pyrite concentrate

The degrees of pyrite oxidation for all particle sizes examined, apart from the −0.044 mm fraction, were found to be very low and varied between 27 and 40% after 17 days of leaching. The oxidation degree for the finest fraction reached almost 95%. The pyrite fraction of this concentrate is oxidised slower than the similar fraction of the arsenopyrite concentrate and this is mainly attributed to the higher surface:volume ratio present in solution.

Arsenopyrite degrees of oxidation for all particle sizes examined, apart form the coarser one, were found to be very high and varied between 77 and 100%. The arsenopyrite fraction of both concentrates shows similar oxidation degrees and this can be attributed to the low initial pulp density that allows immediate oxidation of ferrous ions in solution to the ferric state.

From these experimental data the preferential oxidation of arsenopyrite can be studied. In order to demonstrate the selectivity of arsenopyrite versus pyrite oxidation, the following selectivity index [7] is calculated and presented in Table 3, as a function of the particle size, for the 17 days retention time leaching tests.

$$S.I=(\%FeAsS\ oxidised/\%FeS_2\ oxidised)\ /\ (\%FeAsS\ _{feed}/\%FeS_2\ _{feed})$$

From these experimental data it is clearly seen that high selectivity indexes are calculated for the coarser size fractions, where preferential oxidation of arsenopyrite is observed at shorter leach periods. For the finer size fractions, where improved liberation of both mineral phases is attained and pyrite oxidation proceeds much faster due to the greater reactive surface area exposed in solution, selectivity indexes drop dramatically.

These observations concerning arsenopyrite selectivity are supported by previous experimental studies [14], where an arsenopyrite concentrate assaying 69% FeAsS and 7% FeS_2 was subjected to bacterial leaching tests under much better leaching conditions (in a pachuca reactor with the use of bacterially produced ferric liquor assaying 10 g/l Fe^{3+}).

Taxiarhou *et al.* [7] have demonstrated that selectivity indexes increase when operating at higher pulp densities (up to 30%). This is explained by the fact that pyrite oxidation is initiated at later stages of leaching where the oxidation of the more active arsenopyrite is almost complete. Where operating at higher pulp densities, EMF of the pulp decreases to values below 500 mV, thus making the oxidising conditions not strong enough to sustain complete dissolution of the nobler pyrite.

TABLE 3 Selectivity of bacterial oxidation vs grain size fraction

Size fraction (mm)	Percentage oxidation (%)		Selectivity index (S.I)
	FeAsS	FeS$_2$	
FeAsS conc.			
-0.125+0.088	80.14	16.12	2.6
-0.088+0.063	87.12	59.11	0.6
-0.063+0.044	96.00	63.15	0.5
-0.044	98.12	99.45	0.3
FeS$_2$ conc.			
+0.25	44.25	26.87	72
-0.25+0.125	77.89	27.3	118
-0.125+0.088	90.23	33	94
-0.088+0.063	93.68	38.05	85
-0.063+0.044	96.32	40.11	69
-0.044	99.56	94.12	17

The main conclusions from this experimental part can be summarised as follows:

Both arsenopyrite and pyrite oxidation is encouraged at finer fractions when operating at low solids concentration due to corresponding increases in reactive surface per unit volume ratios. This results in a more rapid release of ferrous ions into solution which can then be oxidised by bacteria to the ferric state producing a rapid increase in ferric ion concentration upon which the role of oxidation depends. Calculated selectivity indexes have demonstrated that arsenopyrite selectivity is reduced during leaching tests of fine grain size fractions when operating at low pulp densities.

Arsenopyrite is the first mineral phase to be oxidised either in its concentrate or as a fraction in a pyrite concentrate. In these series of tests the arsenopyrite fraction of the pyrite concentrate was insignificant and therefore almost complete oxidation was achieved for all size fractions examined.

Pyrite oxidation commences at later stages of leaching, when sufficient concentration of ferric ions and high $Fe^{3+}:Fe^{2+}$ratios exist in solution.

Eh values in these series of tests rose steadily and in case of arsenopyrite concentrate leaching exceeded 550 mV after the 7th day of leaching. All ferrous iron produced initially in solution from the arsenopyrite concentrate was oxidised almost instantly to the ferric state and therefore leaching of both fractions progressed well. In the case of pyrite leaching Eh values rose slower because the initial ferric strength of the solution was not high enough to support oxidation. At later stages of leaching Eh values exceeded 550 mV but this increase had a beneficial effect only in pyrite oxidation rates for the finest fraction. pH dropped steadily for almost all fractions to values ranging between 1.1–1.2 for the arsenopyrite concentrate and between 1.2–1.5 for the pyrite concentrate.

The critical parameter during sulphide minerals oxidation is the reactive surface area. As this increases either by the reduction in size or an increase in solids concentration per unit volume, then a critical state may be reached at which bacteria are unable to convert all the ferrous ions produced to the ferric form. In this series of tests such problem was not encountered because the initial pulp density maintained at very low levels.

Careful grinding is therefore necessary when preparing substrates for bacterial leaching in order to minimise the production of ultra fine particles. When a high percentage of these particles exists in a bacterial ferric system a great number of cells tend to attach to them and become inactive. Therefore the number of free cells in suspension decreases and the rate of production of ferric iron in solution is reduced.

Much higher oxidation rates for both mineral phases should have been attained in case when these tests were conducted in pachuca reactors where better mixing and aeration rates are present.

It is therefore concluded that when pyrite and arsenopyrite are present in spoils, if local conditions such as temperature, oxygen and water availability, permeability, presence of bacteria and particle size of the spoil favour oxidation, both mineral phases will be oxidised and acidic waters will be produced.

Study of oxidation mechanisms in sulphidic spoils

In order to assess the mechanisms of oxidation for pyrite and arsenopyrite in sulphidic spoils, several samples of oxidation products were collected and analysed by XRD and digestion techniques. All samples were collected from the same spoils profile, where successive layers of oxidation products were present up to a depth of 20 cm from the surface. Below that depth no oxidation products were detected.

Furthermore, some distinct surface samples of oxidation products from the entire tailings area were collected and analysed.

Mineralogical and chemical analyses of the oxidation products vs. depth are presented in the following Tables 4 and 5.

TABLE 4 Mineralogical analysis of the oxidised products vs. depth

	Layer No.	1	2	3	4	5	6	7	8	9
	Depth (cm from surface)	0-5	5-5.5	6-7	7-7.5	7.5-9	9-10	10-11	11-19	19-
FeS_2	Pyrite	3.00	5.00	9.99	11.61	25.71	0	0	28.53	64.79
SiO_2	Quartz	3.70	14.70	16.50	21.80	19.50	31.50	43.90	21.10	3.60
$FeCO_3$	Siderite									22.08
FeAsS	Arsenopyrite	0.39	0.42	0.43	0.22	0.22	1.52	0.22	0.22	2.17
$FeAsO_4.H_2O$	Scorodite	4.60								
$CaSO_4.2H_2O$	Gypsum	1.29	15.91	3.59	21.50	5.59	10.38	1.04	2.58	1.72
$Ca(Mg.Fe)(CO_3)_2$	Ankerite							20.00	10.74	
$CaCO_3$	Calcite					3.25	8.72	15.49	5.84	
$Fe_2(SO_4)_2(OH)_2.3H_2O$	Metahohmanite				10.64		22.28	2.80	4.90	
$NaFe_3(SO_4)_2(OH)_6$	Natrojarosite		40.04		10.97	27.47				
$Fe_4(SO_4)_6.15H_2O$	Kornelite		23.32			11.79				
$FeSO_4.4H_2O$	Rozenite	60.93		34.24	11.73					
$FeSO_4.7H_2O$	Melanterite	24.94		28.33						

TABLE 5 Chemical analysis of the oxidised products vs. depth

Layer No.	1	2	3	4	5	6	7	8	9
Depth (cm from surface)	0-5	5-5.5	6-7	7-7.5	7.5-9	9-10	10-11	11-19	19-
Fe %	21.60	19.20	21.20	15.20	24.00	6.40	4.00	28.00	41.20
S_{total} %	14.25	15.24	19.80	14.02	35.85	6.51	0.98	17.25	36.03
$S(SO_4)$ %	11.40	10.56	8.89	8.86	6.78	6.38	0.65	0.34	0.33
Ca %	0.30	3.70	4.50	5.00	2.60	5.90	6.70	3.00	0.40
As%	1.80	0.6	0.2	0.1	0.1	0.7	0.1	0.1	1.0
Cu%	0.02	0.01	0.01	0.02	0.02	0.03	0.02	0.02	0.02
Pb %	0.25	0.50	0.70	0.40	0.60	0.30	0.40	0.50	0.60
Zn %	0.40	0.10	0.10	0.20	0.90	1.10	1.70	1.30	1.30
Cd (ppm)	40	40	20	40	40	40	40	100	100
Hg %	0.60	0.06	0.05	0.06	0.07	0.40	1.00	0.70	0.20
Al %	0.30	0.60	0.70	0.90	0.90	1.10	1.60	1.50	0.20
Cr %	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02
Mn %	0.30	0.02	0.02	0.04	0.04	1.60	3.40	2.20	1.20
insol. %	3.70	14.70	16.50	21.80	19.50	31.50	43.90	21.10	3.60

From the above analyses the following observations can be made:

The upper zones of spoils are heavily oxidised by the combined action of oxygen, water, temperature and bacterial activity. The main oxidation products detected in the upper zones are: rozenite ($FeSO_4 \cdot 4H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), kornelite $Fe_4(SO_4)_6 \cdot 15H_2O$ and gypsum ($CaSO_4 \cdot 2H_2O$). In these zones, where evaporation phenomena are more intense and therefore ion concentration in pore water exceeds solubility limits, ferrous sulphate compounds precipitate.

Rozenite and melanterite are the first oxidation products to be formed by precipitation reactions. Pyrite and arsenopyrite dissolution is initiated by reactions (1) and (3), while part of the ferrous iron produced is oxidised to the ferric form by reaction (2).

Ferric iron which is produced by reaction (2) reacts partially with pyrite and arsenopyrite according to reactions (4) and (5) and ferrous ions are produced. These ferrous ions are reoxidised to the ferric state. Ferric iron, in the form of hydroxides can be precipitated according to reaction (8). Instead of $Fe(OH)_3$, natrojarosite and kornelite may be precipitated by a combination of reactions (9), (10), (11) and (12).

$$3Fe^{3+}(aq) + 2SO_4^{2-}(aq) + 6H_2O + Na^+ ----> NaFe_3(SO_4)_2(OH)_6(s) + 6H^+ \qquad (11)$$

$$4Fe^{3+}(aq) + 6SO_4^{2-}(aq) + 15H_2O ----> Fe_4(SO_4)_6 \cdot 15H_2O(s) \qquad (12)$$
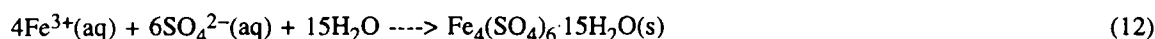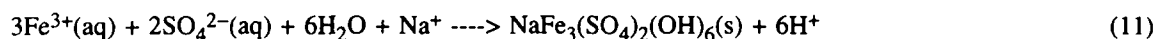
while gypsum is produced according to the following reaction

$$CaCO_3 + H_2SO_4 + H_2O -----> CaSO_4 \cdot 2H_2O + CO_2 \qquad (13)$$

Almost all calcite is converted to gypsum at the upper layers of spoils, due to strong oxidising conditions. At lower layers, where higher concentration of acid consuming minerals and lower oxygen diffusion and water infiltration rates exist, only partial conversion of calcite to gypsum takes place.

Little or no arsenopyrite and calcite is present in the oxidised layers close to the surface. Arsenopyrite is the first mineral phase to be oxidised and precipitated in the form of ferric arsenate and all calcite is transformed to gypsum. Some pyrite still remains unoxidised.

In the middle parts of the oxidised zone almost no precipitation products are present. Metahohmanite $Fe_2(SO_4)_2(OH)_2.3H_2O$ is the only precipitation product that is traced at a depth between 10–19 cm. At this depth calcite is present at percentages between 5–15% wt and acts as pH buffering material. Therefore, acidic waters infiltrating the tailings mass are neutralised, oxidation rates are reduced and limited precipitation takes place.

In the lower part of the examined oxidation zones almost no oxidation products are found and the mineralogical analysis of the spoils is in accordance with the average mineralogical analysis of the spoils mass. The low permeability of the spoils, 6×10^{-6} cm/sec, does not allow easy access of the surface water and oxygen to the underlying layers and therefore oxidation rates at the lower parts of the spoils become extremely slow. Furthermore, the high calcium content of the lower layers of spoils buffers pH of the infiltrating water and therefore reduced oxidation rates are observed. This is also confirmed by the $S(SO_4)$ content of the spoils profile as seen in Table 5.

The intense oxidising conditions existing at the surface of the sulphidic spoils are confirmed by the formation of acidic ponds after rainfalls with the following indicative analysis [1]: pH=1.5–2.5, Eh=450–600 mV, Pb=0.7–5 ppm, Zn=1 g/l, Cd=2–5 ppm, As=1g/l, SO_4^{2-} 10–30 g/l. In addition, the surface layers exhibit extremely negative net neutralisation potential (NNP), up to 1000 kg $CaCO_3$/t, indicating the potential of these layers for acid generation. These acidic solutions infiltrate the spoils and may contribute to minerals dissolution and consequent ion mobilisation and transfer to lower zones of spoils.

Furthermore, several distinct samples of oxidation products were collected from surface points of the entire sulphidic spoils area and analysed. The main mineralogical components found in these samples were rozenite ($FeSO_4 \cdot 4H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$), starkeyite ($MgSO_4 \cdot 4H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), scorodite ($FeAsO_4 \cdot 4H_2O$), szomolnokite ($FeSO_4 \cdot H_2O$), ankerite $Ca(Mg,Fe)(CO_3)_2$ and hohmanite $Fe_2(SO_4)_2(OH)_2 \cdot 7H_2O$.

Ferric arsenates, such as scorodite, are formed by secondary precipitation reactions in areas where the arsenopyrite content of the surface tailings was high according to reactions (5) and (7).

CONCLUSIONS

The main conclusions derived from this experimental study are:

Oxidation of pyrite and arsenopyrite in sulphidic spoils generates acidic solutions which accelerate mineral phases dissolution and therefore heavy metals and other constituents are released, migrate by a number of mechanisms and pollute surrounding areas.

Arsenopyrite is the first mineral phase to be oxidised. Pyrite dissolution starts at later stages and is enhanced by the presence of high concentrations of bacterially produced ferric iron.

The critical factors which control oxidation of pyrite and arsenopyrite in sulphidic spoils and the consequent generation of acidic waters are availability of oxygen and water, temperature, permeability, enhanced bacterial activity and rate of oxygen diffusion through the pores of the upper zones of spoils.

The main oxidation products formed at the upper zones of spoils are hydrated ferrous sulphate compounds which are produced by precipitation reactions following the dissolution of the mineral phases. At lower zones hydrous ferric sulphate compounds and jarosites are produced either directly or by secondary precipitation reactions. The depth at which oxidation products are formed and precipitate depends on the permeability of the tailings, which controls oxygen diffusion and water infiltration rates.

ACKNOWLEDGEMENTS

REFERENCES

1. Kontopoulos, A., Komnitsas, K., Xenidis, A. & Papassiopi, N., Environmental characterisation of the sulphidic tailings in Lavrion, *Minerals Engineering*, **8 (10)**, 1995 (in press).
2. Adam, K., Stefanakis, M. & Kontopoulos A. Bacterial Oxidation of the Olympias Arsenical Pyrite concentrate, *Biotechnology in Minerals and Metal Processing*, eds B.J. Scheiner, F.N. Doyle, S.K. Kawatra, SME, Littleton, Co, 131–138 (1989).
3. Brierley, C.L., Microbiological Mining, *Sci. Am.*, **247**,2, 42–51 (1982).
4. Komnitsas, C. & Pooley, F.D., Mineralogical Characteristics and Treatment of Refractory Gold Ores, *Minerals Engineering*, **2**(4), 449–457 (1989).
5. Karavaiko, G.I., Chuchatin, L.K. & Pivovarova T.A. *et al.* Microbiological leaching of metals from arsenopyrite containing concentrates, *Fundamental and Applied Biohydrometallurgy*, eds R.W.Lawrence, R.M.R.Ebner, Elsevier Science Publishing, Amsterdam, 115–126.
6. Imai, K., On the mechanism of bacterial leaching, *Metallurgical Applications of bacterial leaching and related microbiological phenomena*, eds L.E. Murr, A.E. Torma, J.A. Brierley, Academic Press, N. York, 275–295 (1978).
7. Taxiarchou, M., Adam, K. & Kontopoulos A., Bacterial Oxidation Conditions for Gold Extraction from Olympias Refractory Arsenical Pyrite Concentrate, *Hydrometallurgy*, **36**, 169–185 (1994).
8. Komnitsas, C. & Pooley, F.D. Optimization of the Bacterial Oxidation of an Arsenical Gold Sulphide Concentrate from Olympias, Greece, *Minerals Engineering*, **4**(12), 1297–1303 (1991).
9. Berry, V.K., Murr, L.E. & Hiskey, J.B., Galvanic interaction between chalcopyrite and pyrite during bacterial leaching of low-grade waste, *Hydrometallurgy*, **3**, 309–326 (1978).
10. Groudev, S. & Frenay, J., Mineral Biotechnology: current state and future prospects, *Veme Forum of Applied Biotechnology*, Gent Belgium, (26 Sept. 1991).
11. Panin, V.V., Karavaiko, G.I. & Polkin, S.I., Mechanism and kinetics of bacterial oxidation of sulphide minerals, *Biogeotechnology of Metals*, eds G.I. Karavaiko, S.N. Groudev, Moscow Centre of International Projects, GKNT/UNEP, 197–215 (1985).
12. Mehta, A.P. & Murr, L.E., Fundamental studies of the contribution of galvanic interaction to acid–bacterial leaching of mixed metal sulphides, *Hydrometallurgy*, **9**, 235–256 (1983).
13. Atkins, A.S., Studies on the oxidation of sulphide minerals (pyrite) in the presence of bacteria, *Metallurgical Applications of bacterial leaching and related microbiological phenomena*, eds L.E. Murr, A.E. Torma, J.A. Brierley, Academic Press, N. York, 403–425 (1978).
14. Komnitsas, C. & Pooley, F.D., Oxidation of arsenopyrite in bacterial ferric solutions, *Hydrometallurgy 94 Conference Proceedings*, eds. Chapman and Hall, Cambridge, 361–367 (1994).