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THE EFFECTS OF BIO-MECHANISMS ON ACIDIC MINE DRAINAGE IN COAL MINING

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ABSTRACT

The paper outlines the effects of acid mine drainage on the ecology of the surface environment and describes the details of a laboratory test programme that investigated the actual role of micro-organisms in the formation of acid mine water. An example of the corrosive effects of acid mine water on mine pumping equipment is given. The paper enumerates various techniques that can be used to protect pumping equipment and mitigate the effects of pumping acid mine water on the life of pumping equipment.

INTRODUCTION

Mine drainage from surface and underground has been an inseparable part of coal mining operations since historical times. Such drainage inevitably disturbs the ecology of the environment and if the drainage is contaminated, may cause pollution in surrounding water drainage channels.

In the mining of coal deposits - air and water gain access to seams that contain sulphide minerals (pyrite and/or marcasite) which are oxidised, resulting in the formation of large quantities of sulphuric acid. As the main drainage is diluted with water, whether in the mine or on the surface, the pH value rises, resulting in the formation of ferric hydroxide which precipitates. The iron precipitate results in a red 'ochre' deposit which causes discolouration in the river (and is sometimes referred to as 'yellow boy') and may be deleterious to fresh water life and destroy the inherent natural beauty of an unpolluted stream.

The difficulty of preventing such pollution was traditionally recognised in several countries by special exception from statutory liability. In England and Wales, the exception stems from the Rivers (Pollution and

Prevention) Act 1876 followed by the Rivers (Pollution and Prevention) Acts 1951 and 1961 respectively[1]. This provides that the 1951 Act (makes it an offence to cause or knowingly permit any poisonous, noxious or polluting matter to enter a stream) shall not penalise the discharge of water raised or drained from an underground part of a mine, if it is in the same condition in which it is, raised or drained from underground. The acid water condition produced is not restricted only to underground and may form in spoil heap and coal stock piles containing sufficient pyrite. This can produce a contaminated drainage from the base of the heaps, which may cause pollution to surface water course and may be an offence under statutes such as River (Prevention of Pollution) Acts 1951 and 1961 respectively[1].

For a long time the formation of this acid was attributed simply to chemical oxidation of the iron sulphides associated with coal deposits. The isolation of *T. ferrooxidans* from acidic coal mine drainage by Colmer and Hinkle[2] provided definite proof of the presence of microorganism and implicated them as agents partly responsible for the oxidation of pyrite minerals.

However, in certain situations (oxidation of non-ferrous sulphides such as Chalcopyrite ($CuFeS_2$), Galena (PbS), Sphalerite (ZnS) and Pentlandite (Fe,Ni)S etc.,) acid mine drainage from metalliferous operation can be a beneficial method of recovering commercial metal cations from solutions. In fact, the ancient Romans are reported to have recovered iron and copper sulphate from areas where natural leaching was taking place and currently 15 per cent of the United States copper is produced by bacterial slump leaching operations[3,4]. Although bacterial leaching is restricted to sulphide minerals, metals such as uranium can also be solubilised where they occur in association with sulphides.

ROLE OF MICRO-ORGANISM IN ACID MINE WATER

Investigation into the actual role of bacteria in the formation of acid mine waters is comparatively recent, although evidence as early as 1670 records the granting of concessions for the recovery of copper from mine waters and from leach liquors in 1752 at Rio Tinto, Spain[5].

The isolation of *T. ferrooxidans* in 1947 by Colmer and Hinkle[2] generated considerable interest, both in basic biology and ecology of the organism. This motivated research by other investigators into eluding the role of micro-organism in acid mine drainage from coal mines. Temple and Colmer[6,7] confirmed the presence of a sulphur oxidising bacterium in acid drainage waters from a West Virginia Coal Mine and its ability to oxidise ferrous iron. Temple and Delchamps[8] and Leathern et al[9] showed experimentally that these acidophilic iron and sulphur oxidising bacterium isolated from acid drainage from coal mines could oxidise pyrite minerals found in coal.

Many investigators have studied the oxidisation of pyrite in the presence of these bacterial types Ashmead[10], Bryner and Anderson 1957[11], Bryner and Jameson[12], Silverman et al[13], Silverman et al[14], Bryner et al[15], Silverman 1967[16], Mrost and Lloyd[17], Le Roux et al[18], and Silver and Torma[19].

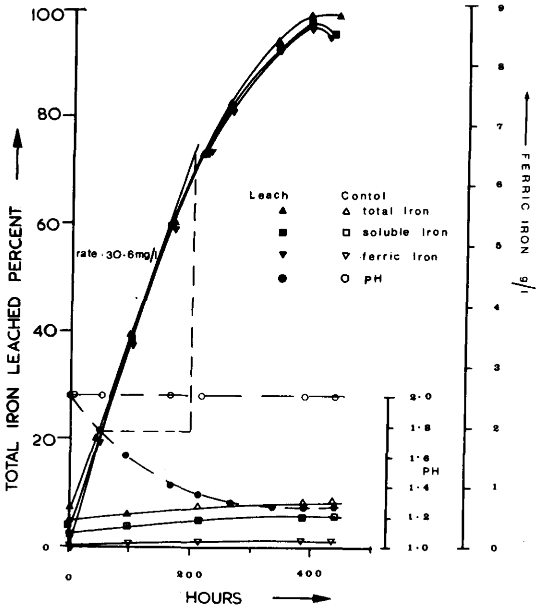

Fig.1. A typical leach test on a 2% pulp density Tharsis pyrite (-45 μm)

Temperature 35°C, initial pH 2.0.

However, information concerned with the kinetics of oxidation of pyrite is limited. This is probably due to a change of emphasis of experimental study since the mid 1960s away from pyrite, (usually considered a gauge mineral sulphide) to the treatment of commercial valuable sulphides of copper, zinc, nickel, etc. This has been primarily the result of environmental aspects in preventing in pollution from sulphur emissions associated with conventional smelting operations. As the use of bacterial leaching of non-ferrous sulphides minerals provides an alternative extraction method to the existing pyrometallurgical and hydrometallurgical processes.

The micro-organism involved in the bacterial oxidation of sulphide minerals in acid solution less than pH 3.0 are the species *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* [20]. These bacteria are classified as members of the genus *Thiobacillus* and are chemosynthetic autotrophic aerobic bacilli. *T. thiooxidans* having the ability to derive energy from the oxidation of inorganic sulphur while *T. ferrooxidans* can utilise both ferrous iron and/or inorganic sulphur.

OXIDATION OF PYRITE IN THE PRESENCE OF BACTERIA

Fig.1 illustrates the complete leaching of a typical Tharsis pyrite at 2% (w/v) in the presence of bacteria providing the pH is not limiting the reaction (pH <0.9 detrimetal[21] and [22]), including the soluble iron and ferric iron in solution compared with a sterile chemical control which resulted in only 8.7 per cent of the pyrite oxidised with respect to time, in the absence of bacteria.

Fig.2 illustrates the bio-mass in µg nitrogen per ml (cellular nitrogen amounts to approximately 14 per cent of dry cell weight of bacteria) measured during the bacterial oxidation of the Tharsis pyrite at 6% (w/v) using the shake flask technique. The graph indicates the total and free cells present as a measure of cellular nitrogen associated with the solids and supernatant respectively. The graph also shows that the supernate yield was only 5 to 8 µg N/ml, which is comparatively low when considering that the original inoculum was 12 to 15 µg N/ml and demonstrates the association of the bacteria with the solid substrata.

Table 1 summarises the free and total cellular nitrogen determinations obtained during the leaching of a variety of substrates by *T. ferrooxidans* in a 5 litre pachuca (air stirred reactor) used to produce cultures for experimental study. The table indicates that in the case of pyrite the bacterial cells preferentially associate with the leach residue rather than the supernate from which bacteria are normally harvested. This difficulty in harvesting cells from pyrite leaching experiments results in bacterial cells harvested from other sulphide substrate as confirmed by other investigators[16,19]. However, the results also indicate that a limited number of bacterial cells are 'free' and able to move around and contaminate mine drainage.

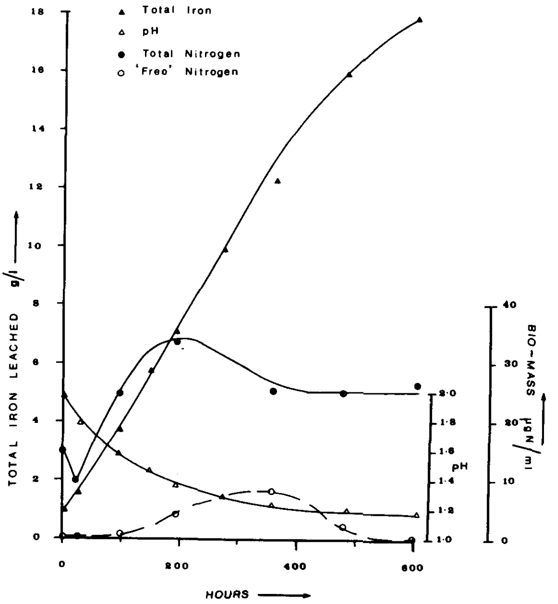

Fig.2. A leach test on the Tharsis pyrite (-45 µm) at 6% pulp density indicating the bio-mass present. Initial pH 2.0, temperature 35°C.

Table 1 Cell Growth Evaluation by Cellular Nitrogen Determinations

Substrate Solid 6% (w/v) Soluble 44 g/l $FeSO_4$	Typical Cellular Nitrogen growth yields		Percentage bacteria associated with solids
	Free nitrogen µg N.ml	Total nitrogen µg N/ml	
Tharsis pyrite	5-10	55-60	87
856 Chalco-pyrite/pyrite	21	40	48
Tynagh sphalerite	33	47	30
Ferrous sulphate	9-11	9-11	100

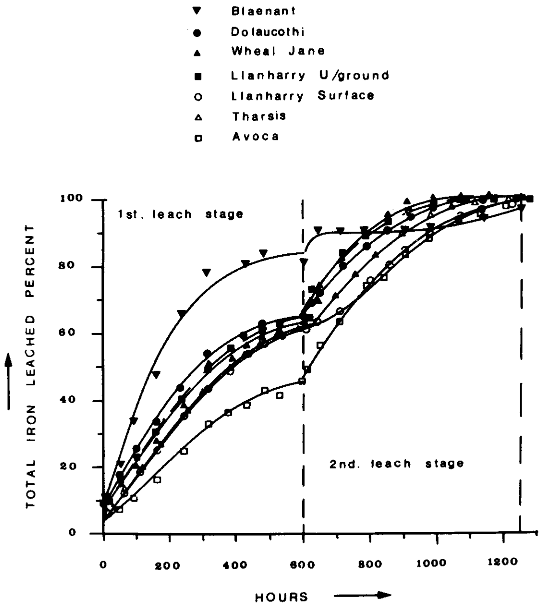

Fig.3. Two stage bacterial leach profile of pyrite samples from various geological origins.
Pulp density 6%, temperature 35°C, initial pH 2.0.

A series of tests were conducted on a variety of pyrite samples from different geological origins to confirm that during the bacterial oxidation of pyrite, the lower pH value of the system was limiting. Fig.3 indicates a typical two stage bacterial leach profile of 6% (w/v) pyrite samples from different geological origins. After the first stage of leaching (600 hours) in which the end pH value were approximately 1.0 the samples were prepared for a repeat leach by resuspension in fresh nutrient salts at a pH of 2.0 and leached to completion. It must be noted that the results have been mathematically corrected to compensate for sampling loss throughout the various leach phases. The leach rates of the respective pyrite samples, as expected were slightly different, and probably caused by sample preparation, size distribution, geological variation during formation and mineralogical factors such as lattice imperfections, non-stoichiometry and porosity [22,23]. It must be stressed that the percentage extracted in Fig.3 refers to the total iron present in the concentrates. In the case of the 96 per cent extraction of iron from the Blaenant pyrite sample, optical microscopy identified the presence of approximately 4 per cent Siderite ($FeCO_3$) as an iron compound impurite[24]. The leach residue was also analysed as a check on the mathematical corrections to compensate for sample loss and a mass balance confirmed the complete bacterial oxidation of pyrite from different geological origins.

Fig.4 illustrates the conversion of ferrous sulphate to ferric in the presence of bacteria. The half life of the reaction corresponds to 25 hours, indicating the speed and ability of the bacteria to promote the oxidation. Experiments carried out on a sterile control showed the rate of chemical oxidation of ferrous sulphate to ferric is remarkably slow and consequently, confirms the importance of bacteria in the regeneration of ferric sulphate.

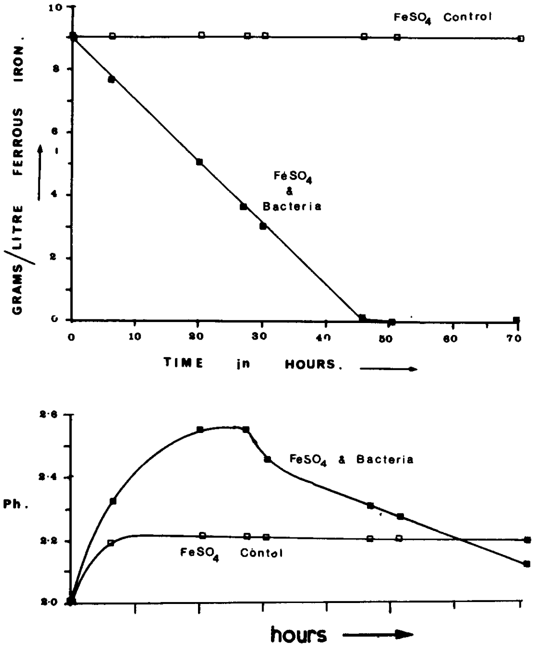

Fig.4. The conversion of ferrous to ferric iron catalysed by the presence of bacteria.

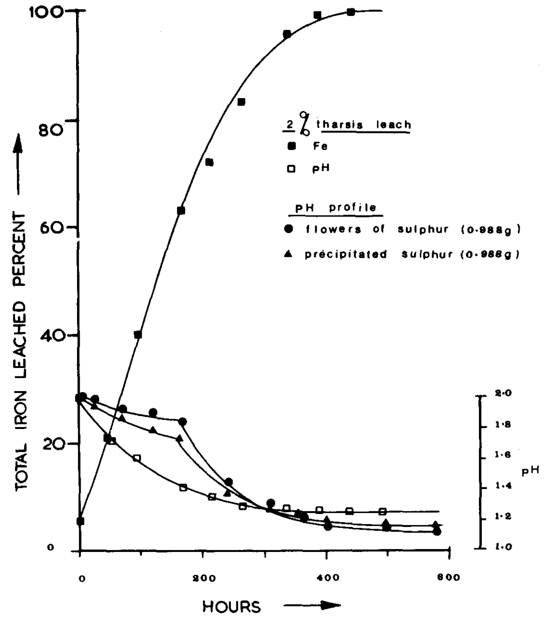

Fig.5. A comparison of the formation of acid during the bacterial leaching of pyrite (2% pulp density) with the equivalent stoichiometric weight (0.988 grams) of precipitated sulphur and flowers of sulphur. Temperature $35^{\circ}C$, initial ph 2.0.

Fig.5 illustrates the formation of acid during the bacterial leaching of precipitated sulphur and 'flowers' of sulphur at the same stoichiometric weight (0.988 g/100 ml) as a typical 2% (w/v) Tharsis pyrite. The slow initial bacterial attack on the two types of sulphur during the first 170 hours was possibly caused by the excretion of wetting agents to lower the surface tension and enable the majority of the floating sulphur particles to be wetted in the culture solution. X-ray diffraction pattern of the two types of sulphur showed an identical 'd' spacing arrangement[22], although only 73.6 per cent of the 'flowers' of sulphur is soluble in carbon disulphide. The slower initial rate of bacterial oxidation on the flowers of sulphur compared with the precipitated sulphur is indicated by Fig.4 and may be caused by difference in particle size of the two types of substrates. The graph indicates that after the first 170 hours the two types of sulphur substrates have a similar pH profile to that of the bacterially oxidised pyrite and demonstrates that the rate controlling step is the conversion of sulphur to sulphuric acid.

MECHANISM

The actual role of the bacteria in the oxidation of sulphide minerals is not yet fully resolved. However, two main mechanisms have been proposed, firstly the direct oxidation of the mineral and secondly the indirect action of ferric sulphate which is regenerated by the bacteria or a combination of both. The bacteria have also been implicated in an electro-chemical mechanism[20]. An experimental study concerned with the indirect mechanism of ferric sulphate oxidation concluded that the action of ferric sulphate was unimportant in the bacteria oxidation of pyrite[24,25].

The experimental study on the complete bacterial oxidation of pyrite have demonstrated that the micro-organisms have a two-fold function in the reaction; firstly they excrete a phospholipid type wetting agent to remove elemental sulphur from the sulphide surface which if it remains is rate limiting. The bacteria then directly participate either by using extra cellular enzymes or membrane diffusion to oxidise the elemental sulphur through various intermediaries to produce sulphuric acid. In this way the necessary acid is produced to lower the pH and maintain the iron in solution. Secondly the bacteria also re-generate ferric sulphate which is involved in the primary oxidation of pyrite. A study of many tests on the oxidation of pyrite during the conditioning period (with no bacteria) has demonstrated the presence of elemental sulphur associated with the particles and the presence of a small quantity of ferric sulphate showing that chemical oxidation does take place but is inhibited.

The bacteria oxidation of pyrite can be represented by a cyclic mechanism from the following equations :-

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \xrightarrow{\text{Bacteria}} Fe_2(SO_4)_3 + H_2O \qquad (1)$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S \qquad (2)$$

$$2FeS_2 + 2H_2SO_4 + O_2 \longrightarrow 2FeSO_4 + 4S + 2H_2O \qquad (3)$$

$$S + 1\tfrac{1}{2}O_2 + H_2O \xrightarrow{\text{Bacteria}} H_2SO_4 \qquad (4)$$

MICROBIOLOGICAL ACTIVITY TO THE DESULPHURISATION OF COAL

In the United Kingdom coal contains sulphur in three forms[26] :

(i) As calcium sulphate and more rarely as ferrous sulphate. This is rarely present in any significant quantity and is generally below 0.03 per cent.

(ii) Organic sulphur intimately associated with the actual molecular structure accounting for 0.8 per cent.

(iii) Pyritic sulphur associated with iron in various forms.

The high sulphur content of coal is therefore usually attributed to the pyritic sulphur present and is normally finely disseminated through the coal matrix. It has been suggested by various coal scientists to have

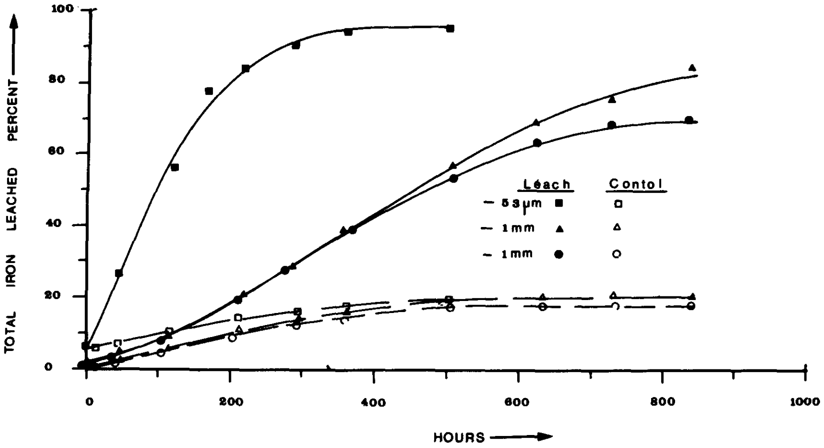

Fig.6. Bacterial leaching tests on the Amman Rider Coal samples of various size fractions. (Δ Sieved O Crushed). Pulp density 10%, temperature 35°C, initial pH 2.0.

been formed by the action of sulphate reducing bacteria similar in type to *Desulphavibrio desulphuricans* of the present day.

Sulphur is detrimental in coal as it contributes to the formation of acid mine waters as well as giving rise to harmful air pollution and corrosion of boiler plant.

A study of pyrite associated with coal in the presence of bacteria was investigated using a sample of Amman Rider Coal containing 5.61 per cent pyrite. Representative samples were prepared as follows for bacterial oxidation :-

(i) Minus 1 mm crushed.

(ii) Minus 1 mm sieved from a representative sample of bulk stock.

(iii) Minus 53 microns (-300 mesh).

The size range of the minus 1 mm is useful for comparison to flotation data and minus 53 micron size ensures a degree of pyrite literation.

Figure 6 illustrates the bacterial oxidation at 10% (w/v) of the respective size fraction of Amman Rider Coal compared to the sterile controls. As expected the fineness of the coal particles influences the degree of bacterial pyrite oxidation together with the retention time of the suspension. Table 2 summarises the leach data with respect to pyrite extraction for the various size fractions.

The result demonstrates that 93.5 per cent of the pyrite can be oxidised. There is a marked increase in the pyrite oxidised from the sieved sample compared to the crushed 1 mm sample and indicates that a higher proportion of the pyrite is liberated and present in the sieved fraction. However, this fraction accounts for only 16.2 per cent of the coal material with a total overall sulphur content of 0.612 per cent.

Table 2 Percentage Pyrite Oxidised

Size fraction	Bacterial Oxidation or pyrite %	Sterile Control pyrite oxidised %
- 53 microns	93.5	25.6
- 1 m.m. crushed	69.0	17.6
- 1 m.m. sieved	85.5	20.7

CORROSIVE EFFECTS OF ACID MINE WATERS ON MINING EQUIPMENT

The problem of mine drainage encountered with low pH values and ferruginous waters entails extensive maintenance of pipe columns and pumps, because of the corrosive nature of the water. Fig.7 illustrates the corrosive effect on a pump impellor operating in water of pH 2.9[27]. Conventional steel of 150 mm diameter pipe columns operating in similar pH values were found to last approximately six weeks before becoming completely ineffective by the corrosive action of the water[27]. The corrosive attack was contained at the bottom and particularly around the 'belled end' of the pipe giving a 'pepper pot' texture which became porous, resulting in the water seeping out on the floor and sides of the roadway causing further damage to rails and steel arches, etc. The effect was prominent at these points because of the combined action of corrosion and friction. This is confirmed by the fact that the steel bends resulted in the same 'pepper pot' texture in only 5 days before being renewed.

The devastating action is not limited to pipes and pumps but to any metallic object in the path of the water, such as, haulage ropes, rails and even miners' boots (nails in sole).

Although, there are various methods available to protect pump equipment and pipe columns such as, stainless steel, bitumen coating, asbestos/cement pipes, fibre glass pipes etc., this results in an increase of capital cost and maintenance of equipment.

SUMMARY AND DISCUSSIONS

It has been shown that the bacterial leaching of pyrite produced insufficient 'free' bacteria to act as seed cultures. This is attributed to the bacterial cells preferentially associating with the leach residue rather than the supernate, however, the results also indicate that a limited number of bacterial cells are 'free' to migrate and contaminate mine drainage.

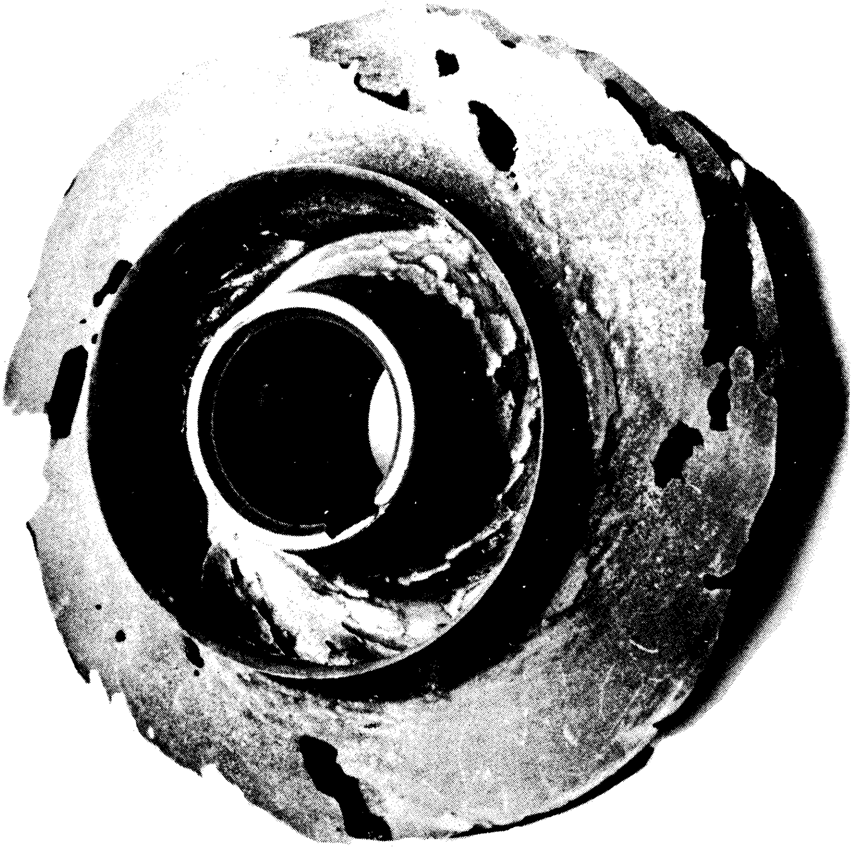

Fig.7. Pump impellor indicating the corrosive nature of the water.

The study has demonstrated conclusively that pyrite samples from different geological origins can be leached to completion in the presence of bacteria provided the pH was maintained in the pH range from 2.0 to 1.0. This result demonstrates that previous speculation on the formation of a protective reation layer on the surface of sulphide particles which accounted for their incomplete oxidation, (or the toxicity of metal in solution) is invalid for iron pyrite.

An experimental study illustrated that the regeneration of ferrous to ferric iron is rapid and the half life of the reaction coincides with the formation of an iron precipitate.

It has been shown that two types of sulphur substrate have a similar pH profile to that of bacterial oxidised pyrite and demonstrates that the rate controlling step is the conversion of sulphur to sulphuric acid.

An experimental study showed that in the complete oxidation of pyrite the micro-organisms have a two-fold function in the reaction; firstly they excrete a phospholipid type wetting agent to remove elemental sulphur formed chemically on the surface of the sulphide particles. The bacteria then directly participate either by using extra cellular enzymes or membrane diffusion to oxidise the elemental sulphur through various intermediaries to produce sulphuric acid. In this way the necessary acid is produced to lower the pH and maintain metal in solution. Secondly the bacteria also regenerate ferric sulphate which is involved in the primary oxidation of the pyrite.

An experimental investigation was undertaken to study the bacterial oxidation of pyrite associated with coal and the effect on sulphuric acid formation associated with mine drainage. The results showed that 93.5 per cent of the pyrite could be removed from a minus 53 micron sample of Amman Rider coal containing 5.61 per cent pyrite. It was found that the size of the pyrite particles together with their distribution are important parameters influencing the bacterial oxidation of pyrite in such samples.

The problem of mine drainage encountered with low pH values and ferruginous water indicates that bacteria are heavily involved in the reaction. This results in an increase of capital cost and maintenance particularly of pumping equipment. The mine waters often cause pollution because they contain toxic metals, oxidised iron which may discolour as well as pollute rivers, or unoxidised iron, which depletes oxygen in river water.

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