MICROBIAL CORROSION OF ALUMINIUM ALLOYS IN MINE WATER

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A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 1990

DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signed

5th day of July 1990

ABSTRACT

Since aluminium alloys are being considered for more extensive use in the mining industry, their susceptibility to corrosion in these environments should be determined. Various aluminium alloy samples, from in situ test rigs on two South African mines, were examined. It was found that their surfaces were colonised by a variety of microorganisms including sulphate reducing bacteria and *Pseudomonas spp.* Pitting and intergranular corrosion were the main forms of attack.

Immersion and electrochemical tests were carried out in mine water under both static and flow conditions. Aluminium alloys 1070, 5182, 6063 and 6261 were exposed to cultures of *Desulfovibrio desulfuricans*, *Pseudomonas aeruginosa* and a mixed strain of sulphate reducing bacteria. Conversion coated and anodized samples were tested under flow conditions only.

The presence of sulphate reducing bacteria in mine water presented an aggressive environment for aluminium alloys leading to pitting at alloying inclusions and intergranular attack. The involvement of FeS in the corrosion process was established. The alloys exposed to *Pseudomonas* cultures also underwent pitting corrosion. Anodizing and conversion coating were effective as temporary measures against microbially induced corrosion provided no defect or damage was present. The alloys were not recommended for use in mine waters.

ACKNOWLEDGEMENTS

The assistance of the following people and organizations is gratefully acknowledged:-

Prof. F.P.A. Robinson for his supervision and advice.

Mr C. Ringas and Mr M. Tullmin for valuable advice and assistance.

Huletts Aluminium for financial assistance and technical input.

Staff of the E.M unit (Wits University) for advice.

Sandra and Robbie for many hours spent printing photos.

University of the Witwatersrand and CSIR for financial assistance.

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1.0 INTRODUCTION

PROBLEM STATEMENT

Aluminium alloys are finding an increasing application for air, drainage, steam and water supply in the mining industry. These alloys are currently being considered for more extensive use as constructional materials in this industry. It is therefore imperative that research be undertaken to determine the susceptibility of such alloys to corrosion in these environments. Preliminary investigations have revealed the presence of microbial growths on aluminium surfaces in mine water. It is now widely recognized that microbes play an important role in processes leading to corrosion of metals, such as iron and stainless steel.

AIMS

This research project was instituted to examine in detail the microbial corrosion of aluminium alloys in mine waters in an attempt to identify the organisms involved, the mechanisms of corrosion, the type of attack incurred, and possible methods of inhibiting microbial growth on the aluminium surface.

JUSTIFICATION

Failures due to corrosion have serious economic consequences and hence mining companies are becoming increasingly aware of the necessity to control and minimize failure of equipment. Use of corrosion resistant alloys and effective water treatment programmes must be properly assessed if maximum benefit is to be obtained. Aluminium has good corrosion resistance due to the stable, extremely hard and tenacious protective oxide layer which forms on its surface. In addition, aluminium alloys have the benefit of a high strength to mass ratio.

BRIEF OUTLINE OF THE PROJECT

This was conducted in 2 main phases:

Phase i

A survey of aluminium samples from test rigs on two South African mines and a literature review were carried out in order to gain knowledge about predominant microbial species.

Phase 2

Small scale laboratory tests in which aluminium alloys were exposed to different static microbial cultures were conducted. Tests were also carried out under flow conditions in a recirculating flow loop system containing a mixed culture of microorganisms. Furthermore, electrochemical tests and weight loss evaluations were carried out. Corroded surfaces were examined using both optical and scanning electron microscopy. Analysis of corrosion product was conducted using the attached EDAX facility. In all tests, controls consisted of sterile medium.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

In the last decade, microbiologically induced corrosion (MIC) - the deterioration of a metal by corrosion processes which occur either directly or indirectly as a result of the metabolic activities of microorganisms - has been recognised as a serious problem. It is not a new phenomenon, however, as corrosion caused by microorganisms was suggested as early as 1891 and then clearly defined by 1910 (1). Corrosion brought about by microbes is often one of the major reasons for material deterioration or failure and is now accepted as a significant contribution to the estimated R4000 million losses that corrosion costs South African industry annually (2). The impact of MIC on industry is widespread. Almost all metals and alloys are affected and the process occurs in most aqueous systems.

There have been numerous review articles on MIC (3 - 9), therefore this review will present a brief overview of the organisms, mechanisms and case histories pertaining to general MIC. The section on MIC of aluminium is, however, more detailed. Mining conditions and factors affecting them are also discussed with respect to their possible influence on aluminium in these environments.

2.2 BACTERIA INVOLVED IN MIC

The first indications that microorganisms may be involved in metallic corrosion processes appeared in the work of Gaines (10) when he concluded that the corrosion of underground iron and steel structures was in part due to bacterial activity. The iron bacterium, *Gallionella* was in fact isolated from corrosion products on a buried steel pipe and high concentrations of sulphur and organic material indicating the presence of sulphate reducing bacteria (SRB) were also detected. The importance of SRB to corrosion was established by van Wolzogen Kuhr in 1922. Since these early investigations were commenced, corrosion of metals due to the action of microorganisms has emerged as a problem of considerable economic importance (3).

Three genera of bacteria closely associated with MIC are also involved in sulphur transformation. The fundamental part played by microorganisms in the cycling of the biological elements in the biosphere is, however, widely recognized. The sulphur bacteria, ie. all those that play a major role in the biological sulphur cycle, have metabolisms which are highly specialized, thus leading them to occupy unusual ecological niches. These organisms affect the economy and environment in a diverse number of ways, principally due to their metabolic activities and the end products they produce (11).

Figure 1 is a schematic representation of the S-cycle. In nature, the S atom is passed through various stages of oxidation by water and soil bacteria, which in so doing, obtain energy for growth. Oxidation of elemental sulphur to sulphates is performed by a group of aerobic bacteria of the

genus *Thiobacillus*. These are also the main organisms concerned with aerobic microbial corrosion. The important organisms in anaerobic conditions are the SRB of the genera *Desulfovibrio* and *Desulfotomaculum*. They reduce sulphates to hydrogen sulphide and probably cause most of the corrosion attributed to microorganisms.

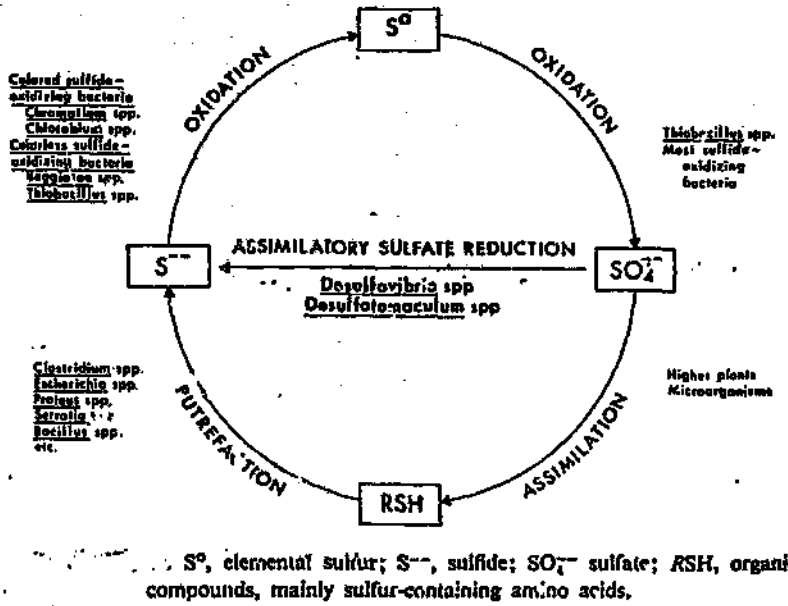

Figure 1. Schematic representation of the sulphur-cycle, from (4).

2.2.1 Sulphate Reducing Bacteria

Sulphate reducing bacteria are among the most destructive environmental organisms and their industrial impact is widespread (12). The SRB are a taxonomically diverse group that are nonetheless related in terms of their physiology and ecology. They are obligate anaerobes that use sulphate as a terminal electron acceptor, reducing it to sulphide. A few species reduce sulphur to sulphide. Some species can optimally use nitrate or fumarate as electron acceptor, while others grow fermentatively, for example on pyruvate (7).

The earliest SRB to be discovered were found in soil - particularly in wet, deoxygenated clayey soils, though they can remain viable for long periods in the presence of oxygen - and in fresh and seawater (13). Isolates, or putative isolates from crude cultures obtained from such sources were habitually grown in lactate-sulphate- inorganic salts liquid media under strictly anaerobic conditions. It is now certain that many of the early workers did not in fact have pure SRB cultures but had other anaerobic contaminating organisms which at that time were difficult to detect.

During the early period, the SRB were considered to comprise only two genera - *Desulfovibrio* and *Desulfotomaculum*. The former were nonsporing Gram negative vibrios mostly motile with polar flagella, while the latter were sporeforming, rod-shaped, Gram positive organisms. The genera contained only 7 and 5 species respectively, and carbon sources of growth seemed restricted to a few compounds such as lactate, pyruvate and malate. This picture has now radically altered due to advances in studies on the nutrition, biochemistry and ecology of the SRB. Nine genera of SRB have now been recognized and these represent a wide range of habitats, morphologies and physiologies. An important feature concerning the role of these organisms in microbial corrosion is the wide nutritional diversity displayed by the sulphate reducers as a group.

2.2.2 Thiobacillus

Bacteria in this genera are small (0,5-1 by 3 µm) rod-shaped cells which may be motile or non-motile. Bergey's Manual lists nine species, most of which are aerobic. They derive their energy from the oxidation primarily of sulphur, thiosulphate, or both to sulphate, thus producing sulphuric acid (4).

2.2.3 Bacteria involved in Iron Transformation

Ferrobacillus

A short, motile, rod-shaped cell, deriving its energy by the oxidation of ferrous iron to the ferric state. These organisms, as well as certain Thiobacilli, are responsible for the leaching process of low grade copper and uranium ores. They accelerate the oxidation of pyrite (FeS) to ferric sulphate and sulphuric acid, which in turn accelerates the rate of removal of copper or uranium (4).

Gallionella

These iron bacteria have unique corrosive tendencies. They are kidney-shaped cells which secrete stalks containing ferric hydroxide. They tend to concentrate chlorides with the result that their deposits are rich in ferric chlorides. This causes general corrosion of steel. On austenitic stainless steels, the effect is more catastrophic with rapid subsurface cavities being formed (6).

Sphaerotilus

These organisms oxidize dissolved ferrous iron to insoluble ferric hydrate, which forms a common sheath for several cells and produces a characteristic star-like filamentous form. Filamentous iron bacteria are responsible for the common, hollow, hemi-spherical tubercles seen in water side steel equipment. They are aerobic and create oxygen depletion under the tubercles. This is corrosive in itself, but is made even more so when it harbours SRB (6).

are bound to the biofilm matrix and readily dissociated for use by the component organisms. Nutrients produced by component organisms also enter the biofilm and micro- colonies of cells capable of primary production of nutrients are often surrounded by heterotrophic organisms that are stimulated by the exudates to grow and produce adjacent microcolonies. The death and cell lysis of primary producers often radically stimulates biofilm growth since biofilms tend to trap and recycle cellular components. Because of the matrix enclosed mode of growth of biofilm bacteria, a substantial ion exchange matrix arises between the component cells and the liquid phase of their environment. Additionally, the gel-like state of the predominantly polysaccharide biofilm matrix limits the access of antibacterial agents to its component bacteria. Therefore biofilm bacteria are substantially protected from surfactants and biocides (16).

2.4 IDENTIFICATION OF MIC

Nearly all confirmed cases of MIC have been accompanied by characteristic deposits. These are usually discrete mounds of corrosion product. Bacterial deposits often have a slimy feeling when fresh and wet, and are generally soft and easily deformed (6).

Some bacteria can oxidize or reduce metallic ions directly, eg. Fe^{2+} can be oxidized to Fe^{3+} which precipitates in a sheath around the cells. These can accumulate as tubercles in pipes. Tuberculation may develop into a general irregular buildup.

The corrosion generated by bacteria may take distinctive forms as well. Corrosion mediated by SRB on mild stainless steels has several characteristic features. Usually the metal surface is distinctly nodular, the raised area consisting of accumulated corrosion products (eg black FeS). On removal, nodules display a hard, black outer crust and a relatively soft accumulation near the metal. A black foul smelling liquid (H_2 S) may also be present in the nodule. Beneath the corrosion product the metal is clearly pitted, in a localized fashion and the metal within the cavity is shiny (17). SRB attack on cast iron typically produces graphitization, while on nickel, high nickel alloys and cupronickels, conical pits containing concentric rings or steps are produced.

Iron bacteria deposits are most often some shade of brown and under their hollow tubercles, hemi-spherical or conical pits are usually found. Under irregular tubercles containing slime formers, corrosion will be similarly irregular (6). Physical identification is usually sufficient evidence, but chemical and microbiological techniques should also be used. For example, acidification of the black FeS should result in H_2 S evolution. Microscope and cultural examinations of corrosion product sampled close to the metal should yield large numbers of bacteria (17). Elemental analyses of deposits can also be useful. High levels of iron, manganese and chlorides usually indicate *Gallionella*. High sulphur points to sulphur oxidizers or reducers. High iron could be a clue to iron bacteria (6).

2.2.4 Slime forming bacteria

Pseudomonas

These organisms proliferate in waters and other industrial environments. They are aerobic oxygen scavengers which secrete large amounts of organic material thereby creating ideal conditions for harbouring SRB. This seems to be their primary role in causing corrosion (6). They have also been associated with degradation of lubricating oils and depletion of oil additives, causing emulsification of the oil and production of organic acids which are aggressive to bearing metals (8).

2.2.5 Other bacteria

A wide variety of bacteria produce H_2S. Other bacteria, such as nitrate-reducers, produce ammonia. Organic acids (eg acetic, butyric) are produced by many bacteria in anaerobic or micro- aerobic environments. All these may play a part in the corrosive processes.

2.2.6 Fungi

Aircraft integral fuel tanks have been reported to harbour large mats of the hydrocarbon-utilizing fungus *Cladosporium resinae* living in the water bottoms under the kerosene. Exfoliation and grain boundary attack on the aluminium alloys occurred beneath the fungal mats leading to perforation and fatigue. This was found to be due to organic acids produced by the fungus as a metabolic by product (8).

2.3 MODES OF GROWTH OF BACTERIA

Costerton (14) has examined the mode of growth of bacteria in industrial aquatic systems and found that they adopt the same mode of growth that is predominant in natural aquatic systems, viz. in thick sessile biofilms. This type of growth develops initially since, due to chemotactic responses, the bacteria are able to seek out higher concentrations of food sources. Nutrients, especially organic substances, are generally in short supply in most aquatic enviro ments but surfaces, including metals, absorb these materials thereby creating areas of relative p enty where organisms establish themselves (15). A bacterial cell initiates the process of irreversible adhesion by binding to the surface using exopolysaccharide glycocalyx polymers. Cell division then produces sister cells that are bound within the glycocalyx matrix, initiating the development of adherent microcolonies. The eventual production of a continuous biofilm on the colonised surface is a function of cell division within micro-colonies and new recruitment of bacteria from the planktonic phase.

Initial colonization of metal surfaces is often by slime forming aerobic bacteria. These, by scavenging the oxygen in the local environment, create anaerobic zones which can then be colonized by SRB. Such structured consortia allow for nutrient trapping which occurs when organic nutrients

2.5 MECHANISMS OF MIC

In order for corrosion to proceed to a significant extent, two conditions have to be met: (a) the anodic and cathodic reactions must remain in balance. (b) the electrolytic cell must continue functioning over prolonged periods. Under aerobic conditions, these conditions are met by the continuous supply of oxygen to the cathode and by the removal of insoluble metal oxides and hydroxides at the anode. Microbial corrosion proceeds by the same electrochemical mechanisms, and the role of microorganisms is either to assist indirectly by establishing the electrolytic cell or directly by stimulating the anodic or cathodic reactions (7).

2.5.1 Anaerobic corrosion by SRB

The effects of SRB on the corrosion of ferrous materials have been studied extensively. Unique features of corrosion caused by these microorganisms are that it occurs at neutral pH in anaerobic environments, oxygen is not involved, and the corrosion products include iron sulphides. Shortly after anaerobic corrosion was discovered, von Wolzogen Kuhr and van der Vlugt associated this type of corrosion with SRB and proposed a cathodic depolarization theory to account for it. Since that time, evidence for and against this theory has mounted and a few new theories have been proposed. The evidence for and against the cathodic depolarization theory and the proposed new mechanisms will be outlined briefly below.

Cathodic depolarization theories

These theories are based on cathodic depolarization of a metal. Briefly, the surface of an immersed iron object becomes organized into transforming anodic and cathodic zones depending on the presence of impurities, millscale etc and local external conditions. Ferrous ions pass into solution at anodic areas and are discharged, in the presence of air, by the oxygen reduction reaction. In the absence of oxygen, the hydrogen evolution reaction occurs at the cathodes. Atomic H arises first and tends to be strongly absorbed onto the metal surface (under acidic conditions it rapidly forms molecular H_2 and is evolved.) If the hydrogen remains on the cathode, its overpotential results in stifling of corrosion (anodic dissolution). The process is thus under cathodic control and the cathode is said to be polarized. Thus in neutral, anaerobic conditions, corrosion of such iron objects should be minimal. In fact, it is often severe in the presence of SRB (13).

(a) Bacterial cell hydrogenase as a depolarizing agent

This theory, first proposed by van Wolzogen Kuhr and van der Vlugt is also referred to as the classical mechanism of anaerobic corrosion. They proposed that cathodic depolarization was achieved by the removal of atomic H from a cathodic metal surface by hydrogenase (the enzyme employed in H_2 S uptake) action of the SRB.

The overall mechanism can be described as follows:

Anodic reaction:	$4Fe \rightarrow 4Fe^{2+} + 8e^-$
Dissociation of water:	$8H_2O \rightarrow 8H^+ + 8OH^-$
Cathodic reaction:	$8e^- + 8H^+ \rightarrow 8H$
Cathodic depolarization:	$SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O$
Corrosion products:	$Fe^{2+} + S^{2-} \rightarrow FeS$ $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$
Overall reaction:	$4Fe + SO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH^-$

Most of the literature on microbial corrosion has been concerned with evidence for and against this theory. Data in support of the classical theory was obtained by Iverson (in 7) and Booth and Tiller (in 7). Both studies employed benzyl viologen as terminal oxidant, thus obviating any potential complication from the production of sulphide. A direct relationship was found between the hydrogenase activity, the cathodic depolarization activity (as measured by polarization and potentiostatic techniques) and the weight loss of mild steel coupons. These studies were carried out using batch cultures of SRB (7, 18).

(b) Iron sulphide as a depolarizer

In later work, however, using semi-continuous and continuous cultures in sulphate medium, Booth et al (19) found that corrosion rates were generally low and a thin ferrous sulphide film formed on the test pieces. After a few months, however, this film fractured, with a considerable increase in corrosion rate. Under these conditions there was little difference between hydrogenase- positive and -negative strains as concerned weight loss. In the presence of higher iron concentration, the corrosion product was in the form of a bulky black precipitate rather than as an adherent film, and with both hydropenase-positive and -negative strains high corrosion rates were found (19, Booth et al in 7). Mara and Williams (20) reached the same general conclusions and suggested that film breakdown in low-iron media resulted from sulphidation of the primary corrosion product mackinawite (FeS_{1-x}) to greigite (Fe_3S_4). Whereas the initial low rate of corrosion was related to bacterial growth rates, after film rupture corrosion was independent of growth rate. The high rates of corrosion thus seemed dependant on ferrous sulphide corrosion product, being influenced too by its physical and chemical form. The iron sulphide was believed to be acting as a cathode with the cathodic reaction involving either the evolution of molecular hydrogen or the entry of atomic hydrogen into the metal or into the defect structure of the sulphide film.

The quantitative importance of cathodic depolarization by solid ferrous sulphide was confirmed (21) when chemically prepared FeS was added to mild steel coupons in a culture of *Desulfovibrio desulfuricans* in medium containing no sulphate. The extent of corrosion was proportional to the amount of FeS added and dependant on its direct contact with the metal surface (7).

(c) Iron sulphide and bacterial hydrogenase as depolarizers

Several workers (13, 22) focused their attention on the iron sulphides of which there are several - all semiconductors. It was found in laboratory cultures that a sulphur-deficient sulphide, mackinawite, arose first; this formed a temporary protective film on the iron surface. As bacterial growth produced more sulphide ions, the film took these up to form stoichiometric FeS and gradually greigite (Fe_3S_4) causing it to thicken and eventually lift, thus exposing base metal. Thereafter metal dissolution was never suppressed by further film formation. Further work suggested that all iron sulphides are cathodic towards iron. The role of SRB in this system could be either to "regenerate" (or depolarize) the FeS, through hydrogenase activity, thus enabling it to remain cathodic, or to produce "fresh" iron sulphide by their growth reaction.

(d) Hydrogen sulphide as depolarizer

In contrast to the above postulated mechanisms, Costello (in 7) proposed that cathodic depolarization activity of the SRB was due to the cathodic activity of the H_2S produced by these organisms. Hydrogenase may play an important secondary role by removing molecular H with the further generation of more H_2S. Also in agreement with other hypotheses, FeS has been reported to act as a cathode.

Corrosive metabolite theory

Iverson (in 7) reported that extensive corrosion of iron had been found using spent culture media from which SRB and sulphide had been removed. The culture filtrates formed a black film on steel coupons after 3 days. This film was rich in iron and phosphorus and on acidification, phosphine was evolved. Iron phosphides have been identified among the corrosion products, but the corrosive metabolite itself has still not been characterized further than as a volatile phosphorous compound. The extent of corrosion in any case is considered to result from the effective competition between the action of sulphide (protective film formation) and that of the phosphorus metabolite (corrosion).

Weimer et al (23) studied the effect of phosphate on the corrosion of carbon steel and on the composition of corrosion products in two-stage continuous cultures of *Desulfovibrio desulfuricans*. It was found that an increase in the phosphate content of the growth medium resulted in an increased corrosion rate of the steel. In addition, analysis of corrosion product revealed that the P content of the product increased dramatically with increasing phosphate concentration in the me-

dium. Chemical analyses indicated that the P was present both as phosphate and an unidentified component, possibly a reduced P species. An explanation to account for the enhanced corrosion by phosphate, was offered as being due to the direct electrochemical effect of P-cortaining corrosion product stimulating cathodic depolarization. Chemical analyses also indicated that sulphur was present in the corrosion product almost exclusively in the form of sulphides. The importance of sulphides on corrosion was acknowledged and the suggestion made that ferrous sulphides were responsible for the growth of the corrosion product, but that subsequent reactions might alter the composition and structure of these products.

The sulphur theory

Schaschl (24) examined the corrosive action of sulphur under anaerobic conditions, and found that its solubility was influenced by sulphide, pH and temperature, and that only dissolved sulphur could act as a corrodant. He proposed that the corrosion occurred by a concentration cell mechanism analagous to an oxygen concentration cell under conditions of differential aeration, with the principal role of the bacteria being to promote the concentration cell action by shielding the underlying metal (anode) from the higher concentrations of dissolved sulphur in the surrounding medium.

Bates (25) has reinterpreted the action of sulphur, proposing that polysulfides (S_x^{2-}) are the cathodic reactants. Since microbial corrosion is the result of a community of organisms, certain species of bacteria can produce elemental sulphur during their metabolic processes. This sulphur can then act as a cathodic depolarizer as mentioned previously.

It has also been suggested (Maldonado-Zagal in 7) that the high local acidity generated in particles of solid sulphur reacting with water could be responsible for the high corrosion rates of iron and steel.

2.5.2 Aerobic Corrosion

Corrosion by concentration cell formation

A large number of microbial species, generally aerobic, can cause biofouling of metal and other surfaces in damp or wet environments. Such biofilms usually contain several species of organism and the greater part of the mass of the biofilm generally consists of extracellular polymeric material.

Absorption of oxygen and other nutrients by such microbial growths cause concentration cells to be set up between the interior of the growth and the immediate environment. In such an electrochemical cell, the oxygen-depleted zone beneath the coherent biofilm is anodic with respect to the exposed metal bordering the growth and anodic dissolution occurs. Fig. 2 shows diagramatically the mechanism of anode formation by a differential aeration cell set up under a microbial colony. Active growth of the organisms keeps the oxygen concentration near to zero in

the centre, but once the electrochemical cell is established and the colony increases in bulk, even the death of organisms in the interior of the colony need not destroy the cell since there is now a substantial mechanical barrier to the ingress of oxygen. A serious additional problem arises if the anaerobic conditions at the centre of the colony initiate growth of any SRB that became entrapped in the colony in the early stages of growth (26).

Iron bacteria, such as *Gallionella* and *Sphaerotilus* are commonly associated with tubercle formation and corrosion of water distribution pipelines. The raised hard deposits (mainly ferric hydroxide) formed by the action of these bacteria acts in the same way as bacterial biofilms ie corrosion results from oxygen concentration cells, with the added possibility of the presence of SRB (7).

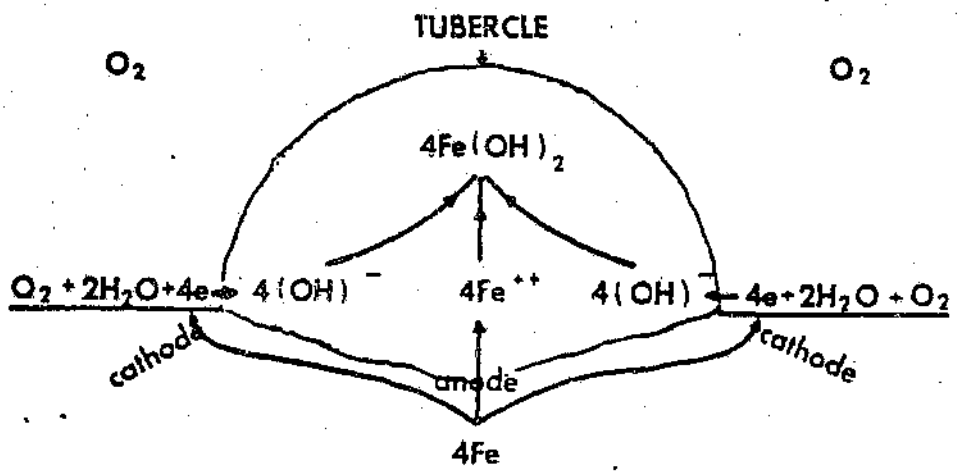

Figure 2. Oxygen concentration cell, from (9).

Corrosion due to products of bacterial activity

Products of bacterial metabolism which can cause corrosion are mainly organic and inorganic acids. Other products, particularly organic sulphur compounds, may be corrosive in some situations.

The most important inorganic acid producing organisms are species of *Thiobacillus* and *Ferrobacillus* which are both capable of producing sulphuric acid. *T. thiooxidans, T. thioparus* and *T. concretivorus* are capable of oxidizing sulphur via sulphite, thiosulphate and tetrathionate to free sulphuric acid, thereby leading to lowered pH values and removal of protective films from metal surfaces.

Ferrobacillus ferrooxidans oxidizes ferrous ions to the ferric form. The ferric salts thus produced oxidize reduced sulphur compounds to sulphuric acid. In nature the organism is often associated with the oxidation of pyritic deposits. Acid waters thus produced in mines have been shown to be corrosive to pumping machinery (3).

Cases of corrosion of iron, copper and Al due to organic acids associated with mould growth have been reported (3). The fungus *Cladosporium resinae* has frequently been associated with corrosion of Al fuel tanks, particularly in aircraft. This phenomenon has been attributed to the action of organic acids secreted by the organism (27).

2.6 INDUSTRIES AFFECTED BY MIC

Considerable progress in understanding the mechanisms involved in and improved techniques for detecting MIC over the past two decades has led to an increased awareness of this type of corrosion. This is especially true in South Africa where the recent droughts, limited water resources and increasing limitations on effluent discharge to the environment have resulted in increased recycling and re-use of water. Concurrent to this, industries have noted an increase in microbial corrosion with MIC often becoming one of the major reasons for material deterioration/failure (2).

Corrosion induced by bacteria is a widely recognized phenomenon in the oil and gas industries bringing about corrosion of pipelines and machinery, reduction in the value of oil and gas by raising the sulphide content and by producing toxic H_2S (11, 28-31).

The pulp and paper industry continuously copes with corrosive bacteria in their processes leading to corrosion of machinery and blackening of paper pulp (11, 32).

In the metal working industry, there have been numerous cases of microbial contamination of emulsions lubricants and coolants used in machinery, wire drawing, rolling and deep drawing operations. The results were serious corrosion of drawing dies, wire and sheet products and staining or alteration of surface finish (33). MIC problems are also found in cooling water systems (32, 34, 35), heat exchangers (34, 36) and condensers (37).

The anaerobic corrosion of buried pipelines by SRB is one of the best known economic activities of this group. Conditions for growth of bacteria are ideal in the soil/pipe environment (11, 38).

Other industries (2) in which corrosion has been attributed to MIC include:
breweries
chemical manufacturing
mining
petroleum
waste water treatment
marine.

2.7 METALS AFFECTED BY MIC

Almost all engineering materials can be damaged by the effects of the activity of some microbial groups. There are many citings in the literature of the susceptibility of mild steel and iron to MIC especially to SRB attack (15, 19, 39-41). Stainless steels are also susceptible to damage, (mainly pitting) especially in anaerobic environments (32, 36, 37, 42). Damage by bacteria to copper and nickel (43-46) and to high Ni alloys in natural waters (42) has also been reported. In the 1950's and 60's microbial deposits in Al alloy fuel tanks on jet aircraft plugged fuel lines and perforated the tanks and structural members (47). Any material immersed in sea water is very susceptible to MIC. The surface is likely to be colonized by a wide range of organisms both macro- and microscopic leading to severe corrosion beneath the fouling layer (46, 48-53).

2.8 MIC OF ALUMINIUM

In this section, the results of research on the MIC of aluminium and its alloys reported in various environments, are surveyed in an attempt to establish : (i) factors affecting microbial corrosion (ii) predominant organisms involved in corrosion (iii) mechanisms of microbial corrosion.

Particular attention is then paid to the mining industry and factors that could affect aluminium corrosion in this environment.

2.9 CORROSION OF ALUMINIUM

2.9.1 Oxide layer and corrosion

Aluminium is an active metal and oxidizes rapidly when exposed to water or air. This results in a thin, continuous film of oxide on the metal surface which generally protects the metal from further attack in mildly aggressive environments. The corrosion resistance of aluminium depends on the stability and continuity of this film or passive layer. If the film becomes damaged locally under conditions which do not allow for repassivation, localized corrosion in the form of pitting or inter-granular attack takes place (54). Fig. 3 is a Pourbaix diagram for aluminium in water illustrating the potential and pH range of aluminium oxide stability and corrosion. The range of oxide stability covers the range of water stability from a pH of about 4,5 to 9 which encompasses most natural waters. The stability and continuity of the protective film is affected by aggressive ions, complexing agents, local shifts in pH and crevices (54).

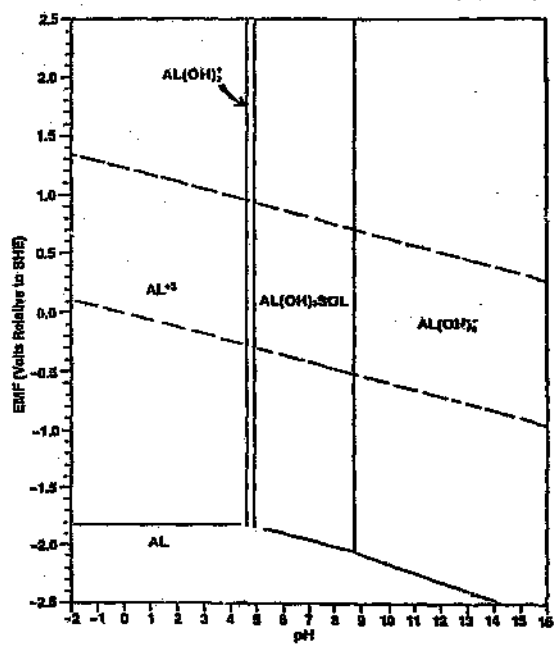

Figure 3. Pourbaix diagram for aluminium in water, from (54).

Pitting corrosion of aluminium occurs in the pH range 4,5 to 9 since outside this range general corrosion takes place due to the dissolution of the surface oxide film. The pitting process involves adsorption of the reactive anion on the oxide-covered surface; reaction of the adsorped anion with the aluminium ion in the aluminium oxide lattice; thinning of the oxide film by dissolution and finally, direct attack of the exposed metal by the anion under the influence of the anodic conditions set up. Potentiostatic polarization techniques have been widely used to study corrosion of aluminium in different inorganic media. The pitting potential obtained is used as one of the principal electrochemical parameters. The pitting potential (Ep) of a metal is the potential below which the metal remains passive and above which pitting takes place (55). Pitting potentials depend to a certain extent on the electrolyte composition especially with respect to aggressive anions eg Cl^- and also to anions eg chromates, which inhibit corrosive processes, displacing Ep to high anodic regions. An increase in aggressive substances decreases Ep and pitting therefore occurs more easily.

2.9.2 Effects of alloying on corrosion

The principal alloying elements of aluminium are Cu, Mg, Si, Zn and Mn. A large variety of minor alloying elements such as Fe, Cr, Ti, Pd, Bi, Ni, B, Va, Zr, Br are also used. Fig. 4 illustrates the effect of alloying on corrosion resistance. Alloying elements impart important changes on aluminium such as permitting heat treating and ageing of the metal, increasing strength and hardness, refining grain structure, decreasing ductility and reducing cracking (56).

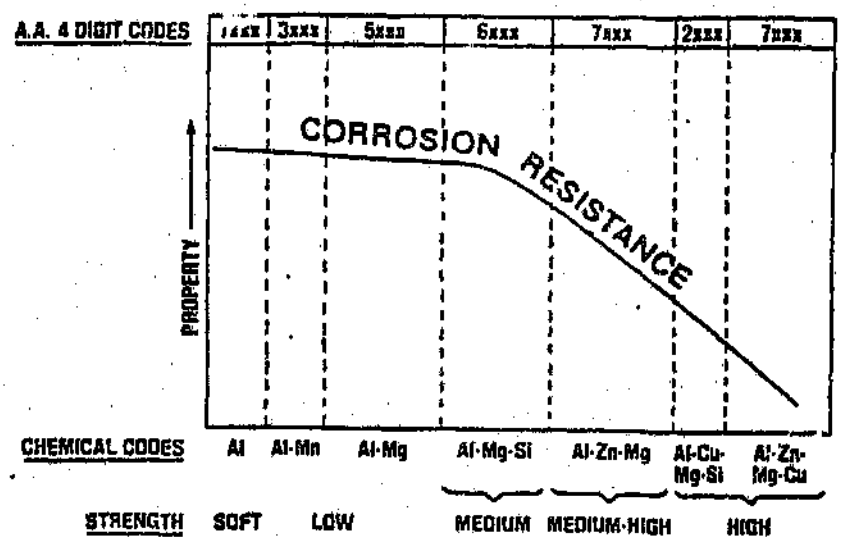

Figure 4. Effects of alloying on the corrosion resistance of aluminium, from (57).

The electrochemical potential of secondary phases or precipitates relative to aluminium is of great importance. Iron and silicon in commercially pure aluminium form constituents that are cathodic to aluminium. Since they form cathodic points over which the film is weak, they may promote electrolytic action in the surrounding aluminium.

High strength Al-Cu alloys have poor corrosion resistance and the amount of copper in the alloy has a strong influence on its electrode potential. Al and Mn form compounds having almost the same electrode potential as the aluminium itself and thus these alloys have good corrosion resistance. Al-Si alloys have good corrosion resistance since silicon in solid solution has a minor influence on the electrode potential of aluminium. Silicon particles within the alloy promote galvanic corrosion. Mg is an important alloying element for aluminium and the solid solution formed is anodic to aluminium. Al-Mg alloys are as corrosion resistant as commercially pure aluminium, and even more resistant in salt water and some alkaline solutions. The Al-Mg-Si alloys often have a very similar electrode potential to pure aluminium as the silicon makes the solid solution more cathodic and in the ratio 2Mg:1Si, this balances out the anodic effect of the Mg (58).

2.10 CASES OF MICROBIAL CORROSION OF ALUMINIUM

Aluminium and its alloys find microbial enemies in many places : in airplane parts, jet fuel lines and fuel storage tanks, tap and seawater; in natural and artificial media; in aerobic and anaerobic

environments. With the increased use of Al as a prime fabrication material, the problem of its corrosion has come to the forefront in certain engineering applications (59).

2.10.1 Corrosion in fuel/water systems

The aircraft industry, both military and commercial, was first faced with the acute problem of contaminated fuel in jet aircraft in early 1960. This contamination led to corrosion of Al-alloy fuel tanks in both aerobic (airplane fuel tanks) and anaerobic (stationary storage tanks) systems. Corrosion occurred in the water-phase of fuel-water mixtures and was most common on the bottom of tanks and at the fuel-water interface. The contaminants, viz water, particulate matter, surfactants and microorganisms formed thick slime growths on the bottom and sides of fuel tanks and caused plugging of fuel filters, malfunction of fuel probes and on one occasion, flame out of an engine (60). Under these slimes, degradation of the topcoating material and pitting corrosion of Al wing tanks as a result of microbial activity took place. Areas of exfoliation of the alloy were reported as other manifestations of microbial activity. Apart from the direct financial losses, contamination of fuel tanks can affect the structural integrity and performance of the aircraft. The aircraft industry has taken steps to provide more corrosion resistant alloys in an attempt to provide tanks which are resistant to the environment being handled. Many expensive changes have been made to counter the threat of catastrophic deterioration of aircraft structure by contaminants (61). These include redesigning susceptible components, changing fabrication techniques, use of biocidal polyurethane fuel tank lining and stricter fuel filtering and handling procedures.

2.10.2 Corrosion in fresh- and seawater environments

Fouling of metal surfaces in contact with sea and fresh water is the main cause of several technical problems and economic loss affecting various industrial environments such as cooling water systems. Microbially induced pitting corrosion was experienced on a finned Al-alloy heat exchanger and aluminium screens exposed to ordinary potable water. Since no corrosion inhibitor or microbial control treatment was implemented, a slime deposit formed on the metal, thereby setting up a differential aeration cell (62).

In another case, various metal surfaces (amongst them Al) were exposed to polluted harbour sea water used to supply a heat exchanger system of a thermal power plant. The presence of fouling adversely affected heat transfer, increased frictional resistance in the tubes, and of course increased the overall cost of operating the system (63).

Guillame et al (64) studied conditions of corrosion and immunity of Al in bacterial cultures in fresh and sea water. Pitting corrosion occured when the bacteria died, or when their metabolism was disturbed by decomposition of the nutrient medium, or by the presence of Al^{3+} ions. The action of various Bacillus cultures and a natural living microflora of sea water on Al were examined in sea water by Ulanovskii et al (65). Pitting corrosion was thought to be due to adsorption of proteolytic

bacteria to Al creating alkaline conditions. Willingham and Quinby (66) found that pitting of Al took place in the presence of cultures of SRB in sea water.

2.10.3 Corrosion in mine waters

A project was initiated in order to assess the corrosion performance of Al alloys in the inlet evaporator water circuit at a refrigeration plant in the President Steyn Gold Mine (67). Preliminary results showed that, on removal from the system, yellow-brown tubercular growths had formed on the surfaces of the coupons. On removal of these tubercles an interlinking network of deep pits became evident. The remainder of the coupon was covered with a thin black adherent layer under which the metal remained unattacked. The relationship between these tubercles and pitting has not been positively ascertained. There is, however, some evidence to suggest that the corrosion may have been due to microbial action. Bacteria were found to be present in tubercles produced in the laboratory under similar conditions. The tubercles consisted mainly of Al oxide/hydroxide together with a certain amount of sulphate and silicate. Since very little chloride was detected by both SEM and microprobe analysis, it can only be concluded that the pitting had not been produced by this ion.

2.10.4 Corrosion in other environments

Since Al and its alloys are finding an increasing application for cable sheathings, pipelines and other structures buried in soil, the behaviour of these metals in soils is of considerable interest (Reine et al in 68). Tiller and Booth (68) conducted tests on Al in Butlin medium inoculated with four different SRB, while Brown and coworkers (in 54) tested various Al alloys in different bacterial cultures in organic medium. In both cases, corrosion of all samples was reported to have been accelerated by the presence of bacteria or fungi.

2.11 MAJOR ORGANISMS INVOLVED IN AL CORROSION

Medium	Microorganisms	Type of Al	Type of corrosion	Ref
Bushnell-Haas(B-H) fuel; deionized water-fuel; B-H cystine; seawater med-fuel	*P.aeruginosa* *D.desulfuricans* *C.resinae* *A.niger*	7158-T651	pitting inter-granular blistering exfoliation	69
deionized water; deionized water + Triton X surfactant + Fe_2O_3 + fuel	*Pseudomonas sp.*	2024-T351 7075-T651		70
deionized water-fuel	*P.aeruginosa* *C.resinae* *A.niger* *D.desulfuricans* *Leptothrix* *B.mycoides*	7178-T651 2024-T351 7079-T651 7075-T651	pitting exfoliation intergranular	27, 71
$CaCl_2$, $MgSO_4$, $(NH_4)_2SO_4$ in deion-ized water + fuel	*C.resinae* *Candida spp.* *P.aeruginosa*	2024		55, 72
B-H diluted with distilled water + fuel	*C.resinae* *Penecillium spp.* *Altenaria spp.* *Rhodotorula*	99,7% Al	pitting	63

	bacteria			
water from integral fuel tank	*C.resinae*	7005 T6		73
water + fuel	*P.aeruginosa* possibly DSV	Al fuel tank	pitting	74
Medium A	*Desulfovibrio spp.* *Desulfoto-mac .tum*	Al alloy (Si, Fe, Mn, Cu, Zn, Mg)	severe pitting	68
distilled water; sea water with peptone or succinate or tryphane + phytone + NaCl + glucose	*Pseudomonas spp* *Bacillus spp.* *Achromobacter sp.*	99,99% Al	pitting	64
sea water	*Bacillus spp.* *P. fluorescens*	Al + alloy A Mg 6	pitting	65
B-H + fue	*Pseudomonas sp.* fungi moulds	7075 2024	pitting	75
deionized water + fuel	*P.aeruginosa* *C.resinae* *A.niger* *D.desulfuricans*	7175-T651 2024-T35 7079-T651 7075-T651	pitting intergranular exfoliation	76
potable water	slime growth	Al heat exchanger	pitting	62
aircraft fuel supply	*C.resinae* *Paecilomyces sp*	Al fuel tanks		77

system	*Altenaria* *Penecillium* *Aspegillus* *Fusarium*			
jet fuel	*Paeruginosa* *Aerobacter* *aerogenes* *D.desulfuricans* *Pen. luteum* *A. flavius* *Spahsrotiles nat.* *C resinae* *Clostridium spp.* *Bacillus spp.* *Fusarium spp.* *Micrococcus*	aircraft fuel storage tanks	pitting	78
aviation turbine fuel with anti-icing additive	?*Pseudomonas* S.R.B. *C. resinae*	fuel tanks		79

2.12 MECHANISMS OF MIC OF AL AND AL ALLOYS

Considerable research has been conducted over the past 25 years on the role of microorganisms in various aspects of aluminium corrosion. Most of the results were obtained from studies of aircraft fuel tank corrosion, thus allowing a number of different mechanisms to be postulated for MIC of Al alloys. Each may play a role in the overall biological attack, or may result from different species-environment combinations.

2.12.1 Depletion of natural inhibitors

Blanchard and Goucher (75) investigated the effect of various concentrations of biologically essential ions and ion combinations on Al corrosion and the ability of microorganisms to alter the relative concentration of these ions. They found that nitrates and phosphates acted as inhibitors of corrosion produced by Ca^{2+} ions and $Fe(OH)_3$. They proposed that microbes remove phosphate and nitrate more rapidly than Ca or Fe from the medium by selective and differential utilization of ions, thus making the medium more corrosive. These results were supported by Salvarezza et al

(80) who used pitting potential to assess the aggressiveness of biological species in MIC in relation to the electrolyte composition. They confirmed that in the presence of Cl^- ions, nitrates and phosphates acted as pitting inhibitors, displacing the pitting potential to high values at a low chloride/inhibitor ratio. On the other hand, microbial uptake of those inhibitors, resulted in a fall in pitting potential during microbial growth.

Videla (81), studying the electrochemical behaviour of Al and its alloys in fuel-water systems contaminated by *C.resinae*, concluded that it was due to interaction between the chloride/inhibitor ratio in the medium and the metabolic activity of the microorganisms, leading to inhibitor consumption.

2.12.2 Production of corrosive compounds

Although metabolic products were not identified, de Mele et al (82) found that those produced by *C.resinae* brought about a decrease in pitting potential (Ep) of Al in a jet fuel/water system. Since Ep values were the same in the presence or absence of cells in the growth medium, it was concluded that Ep depended on metabolites. In a corrosion test for determining the quality of maintenance in jet fuel storage, de Maybaum et al (83) found the corrosivity of the medium to be related to the concentration of *C.resinae* metabolites in the aqueous phase of contaminated fuel. A decrease in pitting potential with incubation time was found. In addition, not only living cell metabolites, but also products of decomposition of the fungus were found to increase corrosion rates, a finding supported by Guillaume et al (64) in corrosion tests with bacteria in nutrient medium. They concluded that pitting corrosion occurred only when the bacteria died or when their metabolism was disturbed by decomposition of the nutrient medium. It would thus seem that complexing substances due to cell lysis may aggravate the corrosive problem due to cell metabolites produced by living cells.

Much information has been collected on the microbiological aspects of *C.resinae*, the principal contaminant of jet fuels. It is now well known that these fungi are able to degrade hydrocarbons in the fuel, producing carboxillic acids such as citric, isocitric, and ketoglutaric and succinic, amongst others. The rate of biodegradation is limited by the supply of nitrogen and phosphorous. In tests by Salverezza et al (80), it was found that the acidic metabolites produced by *C.resinae* are able to facilitate the breakdown of the passive oxide film by chloride anions decreasing the pitting potential value. Importantly, in the absence of inhibitors, metabolite production was found to be the most important factor in the corrosivity increase, a view supported by Williams and Lugg (79); de Schiapparelli et al (84) and Videla (81). A strain of *Pseudomonas aeruginosa* was found by Blanchard and Goucher (85) to produce corrosive organic compounds (large molecules with MW = 5000). Salverezza et al (55) and de Mele et al (82) in studying the influence of *C.resinae* and *P.aeroginosa* on the pH and Ep of aluminium, found however, that *P.aeruginosa* had no effect on these parameters. It was concluded that *C.resinae* plays a more relevant role in Al corrosion by the production of corrosive metabolic products.

2.12.3 Creation of oxygen and/or concentration cells

Techniques developed by Miller et al (60) to measure the potential difference between a surface covered with microorganisms and a base surface of aluminium, indicated that electrolytic cells are formed when microbial colonies are in contact with aluminium. Potential differences as high as 60mV were measured and were sufficient to bring about rapid pitting of the anode area, provided the current flow was not interrupted by polarization effects. The effect of microbial proliferation on the electrochemical behaviour of an Al alloy was clearly shown by de Schiapparelli et al (84). Differential aeration caused by the adhesion of biological mats and the accumulated metabolites in these areas were found to maintain potentials necessary for pitting. Research by Videla (81) suggests that the points of attachment of fungal mycelia to the metal surface act as nucleation centres for pitting.

2.12.4 Cathodic depolarization

Considerable research has been carried out on the mechanisms of iron and steel corrosion by microorganisms since von Wolzogen Kuhr and van der Vlugt suggested that microbes act directly as cathodic depolarizing agents. It is now well known that bacteria of the genus *Desulfovibrio* can bring about cathodic depolarisation by virtue of their hydrogenase enzyme. Iverson (74) isolated *Desulfovibrio* in association with other bacteria from tubercles and pits of aluminium alloy fuel tanks. Later, Tiller and Booth (68) compared the actions of Al and steel in cultures of sulphate reducing bacteria. Cathodic behaviour of Al was almost identical to that of steel, with hydrogenase active strains of the bacteria behaving as effective cathodic depolarizing agents.

2.12.5 Extracellular enzyme activity and metabolism of alloy constituents

Hedrick and coworkers (27, 69, 71, 86) formulated the hypothesis that the corrosion of Al alloys by microorganisms, particularly aerobic bacteria, results from the removal of certain metallic atoms (major or minor) from the crystal lattice of the alloy by extracellular enzyme activity.

While observing the progress of corrosion on aluminium alloys by microorganisms, it was noticed that in environments containing low concentrations of nutrients, more corrosion product was formed. This suggested that the microbes were obtaining their metal requirements from the alloys. Aluminium was found to act as a trace element to increase growth of some microbes, but in many cases it was either inhibitory or ineffective (59). Attention was thus turned to Mg - one of the most essential elements for microbial growth. Research was conducted to test the hypothesis. One test consisted of exposing various Al alloys to a deionized water/fuel medium inoculated with a mixed culture of microbes. The aqueous phase was then analyzed for free Al. The results showed 57-73% more Al in the inoculated systems.

A second test determined weight changes in Al alloys (1100, 7079, 2024, 7075 series) containing different percentages of Mg and Zn, exposed to a mixed inoculum of *C.resinae* and *Pseudomonas sp.* Alloy 7075 was found to be most susceptible and alloy 7079 the least susceptible to corrosion. It was proposed that the corrosion resulted from the removal of magnesium and zinc from the basic structure of the alloy since the alloys with a high content of Mg and Zn were subject to more microbial corrosion. In another series of experiments, high purity Mg strips and Al foil were exposed to a mixed culture of *P.aeruginosa* and *C.resinae* in a distilled water/fuel medium. Al foil strips showed little visible corrosive attack in the control specimens and even less in the inoculated system. This was in contrast to the Mg specimen, in which extreme differences between controls and inoculated sets were found. The inoculated Mg samples were completely penetrated at the fuel-water interface. Finally, it was also established that weight changes in Al alloys increased in environments inoculated with microbes under dynamic (agitated) conditions. After reviewing the various postulated mechanisms of microbial corrosion of Al, it can be concluded that each mechanism appears to contribute to a different extent to the phenomenon. Corrosion produced by microorganisms is dependent on the growth phase of the organisms, mineral composition of the water medium, organic composition of the suspending medium, alloy composition and many other variables.

2.13 MINING CONDITIONS

2.13.1 Water distribution

Most of the water found in South African mines is due to infiltration, but varies considerably from one area to another with respect to levels of dissolved and suspended solids, temperature, pH, oxygen content and contamination by microbial organisms.

A large percentage of the water is used for processes (such as dust suppression, water spraying after blasting, as a coolant in rock drills), in machines and as feed for refrigeration units (87).

Mining equipment undergoes rapid and catastrophic corrosion failures in polluted mine waters (88). Pipes and pipe ancillaries constitute the major single source of mining expenditure in the gold mines of South Africa (89), accounting for 3,6% of total working costs in 1980. The expenditure is indicative of the amount of liquid transported - roughly one ton of water per ton of rock broken. It has also been estimated that 3500 l/s is the quantity of mine service water needing refrigeration in the hot gold mines operating at present. Thus there is a massive commitment to water-distribution facilities within the gold mining industry.

2.13.2 Water composition

As mentioned, water composition varies considerably due to various sources and uses of mine water. 10-20% make up water is needed to supplement that lost for various reasons, and this may

come from fissure water, water supply authorities, or from nearby rivers. Because of limited underground water, the high cost of service water and the environmental problems associated with effluent disposal, water is recycled for underground use, often only after simple water-treatment procedures (89). High concentrations of total dissolved solids in the service waters are due to poor-quality underground water, chemicals leached from the rocks, and evaporation in cooling towers and underground areas. In addition, many South African gold mines are plagued with the major problem of acid mine waters formed as a result of oxidation of pyrites. Acid sulphate contaminated waters are formed both underground and at the surface. Underground water may be treated, but surface waters as a result of rainfall and weathering remain largely untouched.

Treatment of mine waters to neutralize the pH and reduce the concentration of suspended solids (which may bring about erosion and erosion-corrosion) is often carried out. Flocculation and settling are used to remove suspended solids, while addition of lime controls the pH.

In South African gold mines there are three general groupings of water type (58). a) The OFS mines which have waters that contain high levels of dissolved salts, mostly chlorides and to a lesser extent sulphates. b) Far West Rand, with medium chlorides and high sulphate ion concentrations. c) Rand, with low chlorides and high sulphates.

2.14 FACTORS AFFECTING CORROSIVITY OF WATERS

The concentrations of various substances in water in the dissolved, colloidal or suspended state vary considerably and all affect corrosion to different degrees. Some important constituents are: - dissolved gases (oxygen, nitrogen, CO_2 , ammonia, sulphurous gases etc); - mineral constituents including hardness salts, sodium salts, salts of heavy metals and silica; - organic matter of plant and animal origin; - microbiological components including bacteria and fungi.

2.14.1 Oxygen and pH

In a survey undertaken by White and Higginson (89) to determine factors affecting the corrosivity of mine waters from a number of South African gold mines, it was found that dissolved oxygen and pH were the major factors controlling corrosion in piping networks.

In these studies it was shown that deaeration in neutral pH ranges reduced the corrosion rate considerably. In neutral waters, the solubility of dissolved oxygen and the relatively low availability of hydrogen ions indicate that the cathodic reaction is the reduction of dissolved oxygen ie.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

In deaerated mine waters, the dominant cathodic reaction is the reduction of hydrogen ions to gaseous hydrogen. In mine waters with pH values less than 5, the reduction in corrosion rate with

deaeration was smaller owing to the greater contribution made by hydrogen ions to the cathodic reaction. Another factor which affects the variation in corrosion rate with dissolved oxygen content is the difference in the protective quality of the scale-corrosion product formed with differing amounts of oxygen available. The formation of protective scale depends on the water's ability to precipitate calcium salts on local cathode surfaces as a result of the production of hydroxide ions from the oxygen reduction reaction.

The pH values of mine waters were found to be in the pH range of 6 to 9, indicating a satisfactory pH control within most mines (89). pH values of 3 or 4, however, are not uncommon. The chief source of acidity in mine waters in South Africa is pyrite which is oxidised both chemically and bacterially (90), yielding waters of low pH with high concentrations of SO_4^{2-} and Fe^{2+}. The acidic water accelerates the breakdown of clay, other silicates and carbonate minerals, thus increasing the concentration of Si, Al, Ca, Mg and Mn ions in solution. The acidic water also tends to maintain a low concentration of bicarbonate ions. Bacteria, such as *Thiobacillus ferrooxidans* greatly accelerate the production of sulphuric acid (87). From a cost consideration, hydrated lime has been found to be the most suitable neutralizing agent (90).

2.14.2 Saturation Index

An indication of the corrosivity of water can be obtained from the Saturation or Langlier Index (LI). This index is given by the difference between the actual pH value and the saturation pH value (pH at which solid calcium carbonate is in equilibrium with its saturated solution). A positive index means that the water is supersaturated with $CaCO_3$, and that deposition of a protective film should occur. When the index is negative, any protective film that is present is stripped, and the base metal exposed to attack (87).

In their study of corrosivity of South African mine waters, White and Higginson (89) found little correlation between corrosion rates for mild steel and the LI values of various mine waters. They attributed this to the fact that impure scale is generally formed, leaving exposed areas and a porous deposit.

2.14.3 Aggressive Ions

Chloride and sulphate ions are aggressive ions in the context of corrosion, and their amounts relative to inhibitors such as carbonates, bicarbonates, and hydroxides are of prime importance in the assessment of the behaviour of water in corrosion. Even with a positive LI, the concentration of chloride above which the scale formed is no longer protective (87). Generally, at lower pH values, the tolerance limits (controlled by alkalinity and Ca concentration) for aggressive ions is lower.

In studies of aluminium corrosion, Blanchard and Goucher (75), amongst others (72, 80) observed that Al corrosion was stimulated by some biologically essential ions and inhibited by others. They

found that in inorganic medium, calcium sulphate, or iron in the form of ferric hydroxide, brought about Al corrosion. Both nitrate and phosphate, however, inhibited corrosion by these two salts, and that caused by NaCl. Phosphate anions, by their buffering action could prevent the localized acidification which takes place at the pit base.

2.14.4 Temperature and Flow rate

As regards temperature, there are two competing effects in the pH region where corrosion is controlled by the rate of oxygen reduction:- rising temperature facilitates the diffusion of oxygen to the metal surface, and the solubility of oxygen in water decreases with increasing temperature. Generally speaking, however, the corrosion rate increases with increasing temperature since the activity of ions is increased. Water temperatures in South African mines vary between a minimum of 4°C and a maximum of 55°C. The virgin rock temperature increases with depth in some areas reaching 60°C. Hydrodynamic factors may be either detrimental or beneficial. In the former case, an increase in flow rate could bring about abrasive effects due to suspended solids such as silicates in the water, thus creating flaws in protective films on the metal surface. It has also been found (91) that the pitting current increases with electrolyte velocity past the pits. In the case of aluminium, Dillon (92) pointed out that oxides formed in flowing water are more porous and thus nonprotective due to the leaching of solution constituents out of the oxide. Flow velocity may also be beneficial, however, especially for active/passive metals. Flowing water facilitates transfer of oxygen to the metal surface in order to maintain the passive layer. In static solutions, however, the transfer rate is too slow and the surface cannot maintain its passivity. Flow velocities in South African mines are generally less than 2 m/s and as such there is a negligible errosive effect due to water alone (58).

2.14.5 Galvanic effects

The presence of metallic ions in solution in mine waters may be deleterious if they tend to plate out of solution onto the surface of a dissimilar metal thereby bringing about a galvanic corrosion effect. Subrahmanyam and Hoey (88) found that corrosion rates of mild steel were significantly increased by Fe^{3+} and Cu^{2+} ions in synthetic acid mine waters. The majority of presently used materials such as mild steel, stainless steel and copper are all cathodic to aluminium alloys and are likely, especially in the case of copper, to bring about galvanic corrosion.

3.0 EXPERIMENTAL PROCEDURE

3.1 MINE SURVEY

Several aluminium alloys were exposed to in situ conditions in a test rig on two South African mines, viz. Free State Geduld (FSG) and Western Deep Levels (WDL) in a project undertaken by Mintek to evaluate corrosion rates of various metals in a heat exchanger circuit (67). These coupons were examined at regular intervals for visible biological growths on the surface as well as for evidence of corrosion. Once these phenomena were visible, the coupons were removed, sealed in sterile plastic bags containing mine water and stored at 4°C. They were then analysed for predominant microbial species.

3.1.1 Analytical Techniques

Biofilm and corrosion product were gently removed from one side of each coupon with a sterile scalpel blade and suspended in mine water which had been filtered through a 0,2µm membrane filter. The biofilm was dispersed through agitation. Aliquots were then plated onto several media:

- Nutrient agar
- Sabouraud dextrose agar
- Pseudomonas selective agar
- Reinforced Clostridial agar

and then incubated at 35°C for 24-48 hours.

Colonies representing the predominant microbial populations in the biofilm, as indicated by the frequency of isolation of these genera, were isolated from the media. Pure cultures of the isolates were obtained by repeated transfer of the colonies onto relevant agar media. These pure cultures were subsequently used in the identification tests.

Bacteria were identified to genus level according to the dichotomous key represented in Fig. 5. Pseudomonads were characterised to species level using the dichotomous key in Fig. 6. Identification of fungi and moulds to genus level was based on differences in gross morphology including colour and morphology of spores.

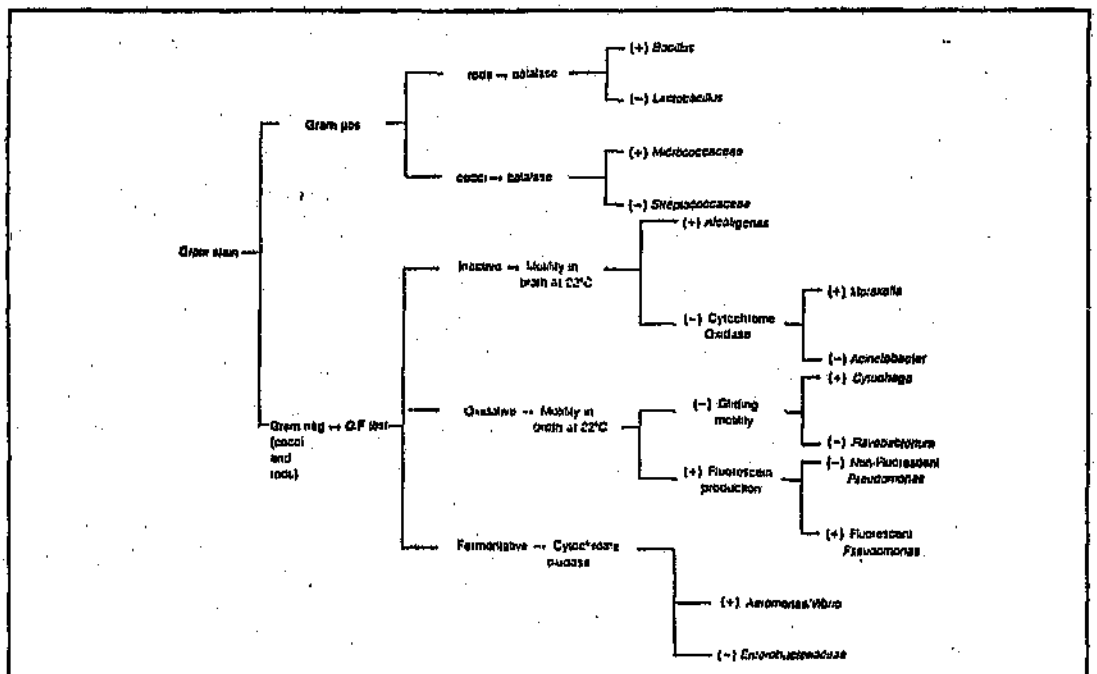

Figure 5. Simplified key for identifying bacterial genera.

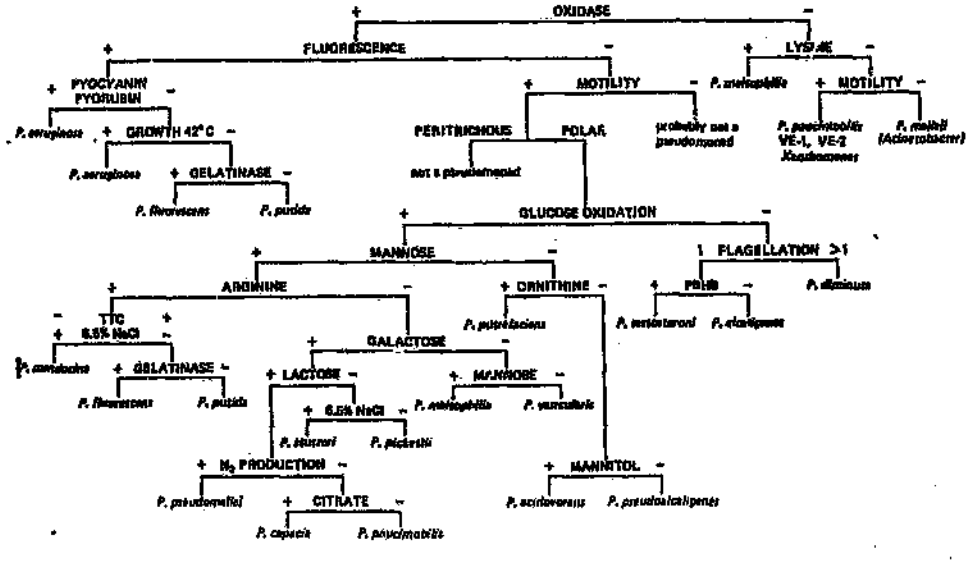

Figure 6. Simple key for identifying Pseudomonas spp.

Samples of biofilm and corrosion product were also placed in sulphate reducing medium (Appendix A) and incubated at 35°C for 7 days, after which growth of SRB was observed as blackening of the medium.

The reverse side of each coupon, containing biofilm was prepared for SEM by fixing in 2% glutaraldehyde for 12 hours, air drying and spatter-coating with carbon. They were then viewed by SEM. Biofilm and corrosion product were subsequently removed ultrasonically using a chromic-phosphoric acid mix (Section 3.8.4.). Specimens were examined once again using SEM to determine the nature and extent of corrosion. EDAX analyses were performed at selected regions.

3.2 SPECIFICATIONS OF FLOW LOOP

A recirculating flow loop system containing facilities for electrochemical and immersion testing, designed by Buchan (58) was used. The total immersion test section was modified slightly to hold 20 immersion specimens. It is constructed from polyvinylchloride pipe with screw couplings to hold the specimen (Fig. 7).

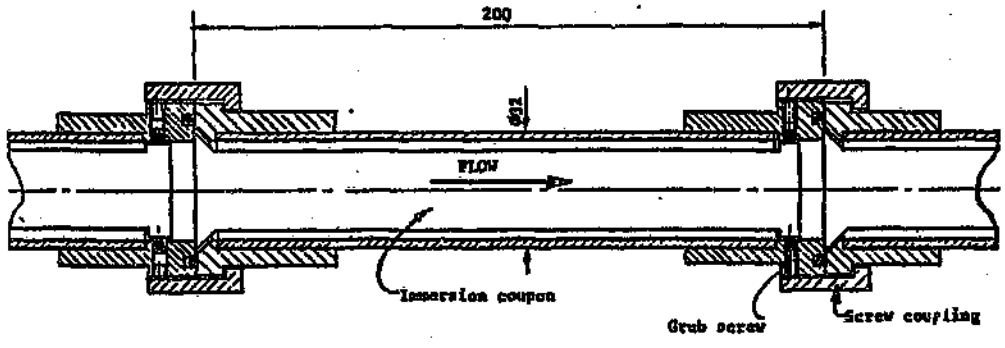

Figure 7. Total immersion coupon holder for flow loop. From (58).

The electrochemical test section consists of a rectangular flow channel capable of accommodating 7 flush mounted electrochemical test specimens (Fig. 8). Reference electrode ports are built into the specimen mounts, while carbon counter electrodes clamp into position in aluminium holders in the perspex cover of the channel.

The temperature of the water in the flow loop was maintained at 35 °C + 1°.

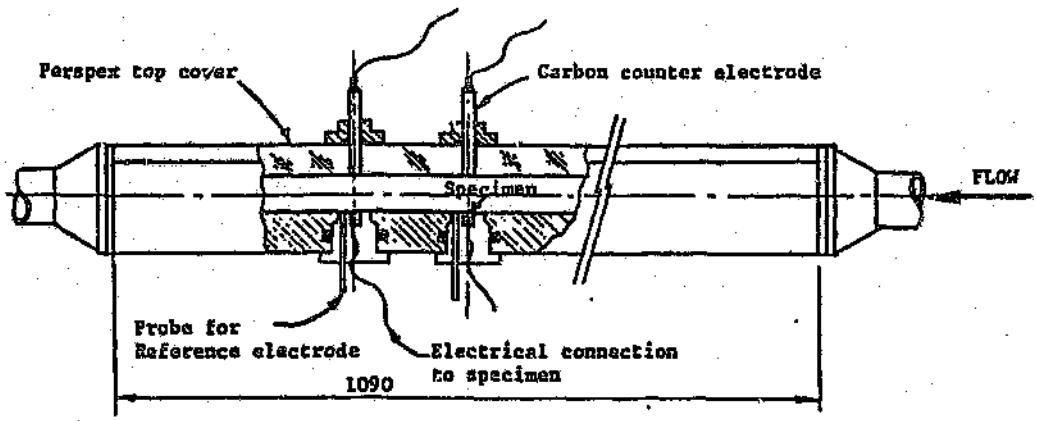

Figure 8. Schematic of electrochemical corrosion test section. From (58).

Figures 9 and 10 illustrate the general layout of the flow loop. A 0,55kW 220VAC pump draws water from the tank, pumps it through the flowmeter and then through the Immersion Test Section or bypasr The water then flows through the electrochemical test section or bypass no.2 before returning to the tank.

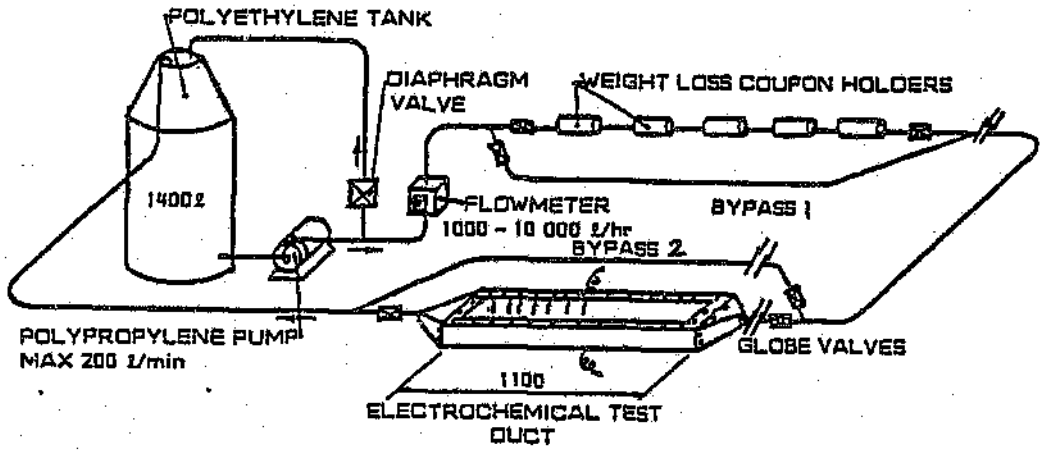

Figure 9. Schematic of layout of flow loop. From (58).

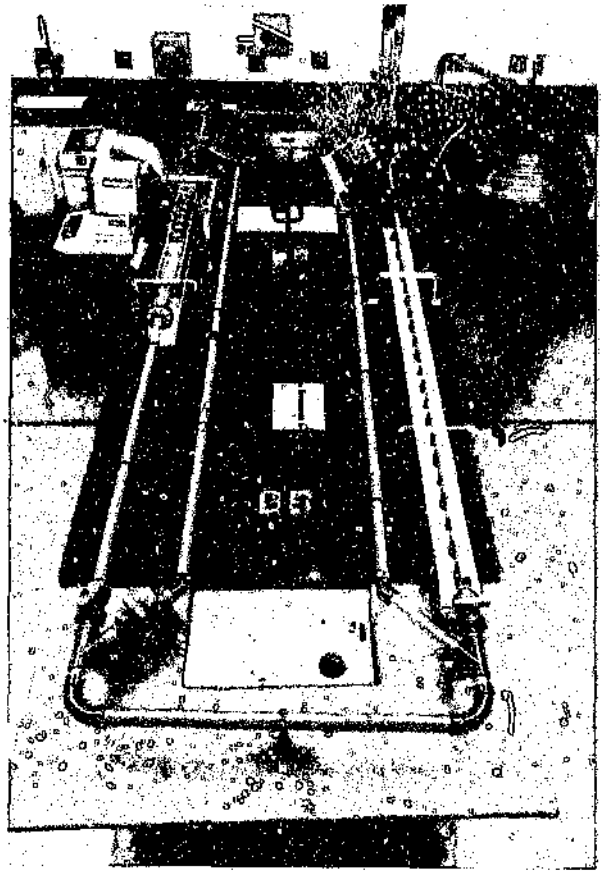

Figure 10. General view of flow loop. From (58).

3.3 TEST MATERIALS

Four aluminium alloys (1070, 5182, 6063 and 6261), a mild steel (MS) and a 3CR12 stainless steel were used in the tests. All alloys were of commercial quality. The actual compositions of the samples used are listed below in Tables 1 and 2.

Table 1. Actual compositions of aluminium alloys used.

ALLOY	%Cu	%Mg	%Si	%Fe	%Mn	%Zn	%Ti	%Al
1070	0.000	0.003	0.075	0.13	0.000	0.007	0.005	99.93
5182	0.032	4.600	0.145	0.32	0.333	0.019	0.017	94.65
6063	0.007	0.460	0.411	0.17	0.060	0.005	0.007	99.00
6261	0.016	0.737	1.080	0.17	0.560	0.006	0.006	97.53

Table 2. Actual composition of steels used.

ALLOY	%C	S	P	Mn	Si	Cu	Zn	Ti	Mn	Cr	Ni
3CR12	,020	,003	,019	1,19	,51	,05	,04	,25	,02	11,2	,60
MS	,03	,014	,016	,20	,01						

All alloys were tested in electrochemical scans and in the static immersion tests. The mild steel (MS) and 3CR12 alloys were not tested under flow conditions.

For the immersion tests under both static and flow conditions, all specimens were exposed in the "mill-finish" state in order to approximate actual mining conditions. For tests under flow conditions, anodized and conversion coated specimens were also tested.

3.4 BACTERIA USED IN TESTS

Both a pure and a mixed culture of SRB were utilized. The pure strain, purchased from the National Collection of Marine and Industrial Bacteria (Scotland), was *Desulfovibrio desulfuricans* strain Teddington R. The mixed strain was that isolated from the mine survey samples. A pure strain of *Pseudomonas aeruginosa* isolated from the mine samples was also used.

3.5 CULTIVATION OF BACTERIA

Bacteria were cultured both in a nutritive medium and in mine water. The use of nutritive medium ensures microbial growth under optimal conditions thus providing an aggressive, rapid test, representing the worst conditions. The mine water, however, simulates actual conditions.

3.5.1 Sulphate Reducing Medium

This medium used by Ringas (93), was utilized in these tests for both SRB and *Pseudomonas cultures*. The recipe for the base medium can be found in Appendix A. The base medium was prepared in 1L Schott bottles, autoclaved at 121°C for 20 mins and stored air-tight at 4°C until required. Pseudomonads were cultured in aerated base medium. For SRB cultures, filter-sterilized redox poising chemicals were added to the base medium just before culturing. These consisted of a 2% solution of sodium ascorbate and either a 7,8% solution of ferrous ammonium sulphate or a 2,6% solution of ammonium sulphate, each added at a rate of 5 ml/litre of base medium.

3.5.2 Mine Water

Water was collected from Durban Roodepoort Deep Mine Shaft 5 in a 1000L galvanized mild steel tanker trailer. The water was left to stand for 3 days to allow any solids to settle, before being transferred to the laboratory. The water had been treated with flocculants and lime. The composition of the water is listed in table 3.

Table 3. Composition of mine water.

	Bacteria*	Sterile*
Chloride, Cl	61	58
Sulphate, SO_4	2390	2126
Nitrate, NO_3	14,9	20
Magnesium hardness as $CaCO_3$	125	75
Calcium hardness as $CaCO_3$	651	750
Total alkalinity as $CaCO_3$	32	20
Total Hardness as $CaCO_3$	2140	2182
Langlier Index	0,23	0,26
pH value	7,9	7,6
Conductivity in mS/m at 25°C	283	334
Total dissolved solids	3814	3756
Loss on Ignition of TDS at 500°C	458	1152 (5000 °C)
Total suspended solids	23	11
Sodium, Na	159	115
pH of saturation at 21°C	7,67	7,44
Copper	0,2	

Results are expressed in mg/L where applicable.

* see 3.2 below

Mine water for use in growing bacterial cultures was sterilized by autoclaving in IL Schott bottles at 121°C for 20 mins. Before adding the SRB, it was aseptically deaerated with 0,2µm membrane-filtered nitrogen and redox poising chemicals and sodium lactate were added.

3.5.3 Preparation of Bacterial Cultures

Pure cultures of *P.aeruginosa* were stored on agar slopes at 4°C. When required, a few isolated colonies were suspended in 30 ml medium (or mine water) and incubated at 35°C for 24 hours. This culture was then passaged to 1 L of medium (or mine water) incubated at 35°C and allowed to proliferate. Four day old cultures were used for electrochemical tests. Plate counts were performed to enumerate the organisms in cultures before use.

The culture of *D. desulfuricans* was revived from a freeze dried ampoule in 50 ml of SRB medium with reducing agents. Aliquots were passaged onto solid agar medium, allowed to proliferate and then stored at 4°C as stock cultures. When required, aliquots were passaged from stock cultures to 30 ml bottles of medium and finally to 1 L Schott bottles of medium and cultivated at 35°C. Four

day old cultures were used in electrochemical tests and enumerated using the Most Probable Number (MPN) test. Stock cultures of the mixed SRB were also stored on solid medium and passaged and cultivated as for the SRB above.

3.6 ELECTROCHEMICAL TESTS

3.7 Specimen Preparation

Cylindrically shaped aluminium specimens (10 x 15 mm long) were prepared from extruded aluminium rod. They were set in a polyester resin block with electrical connections made through a self-tapping screw in the back onto which a wire was soldered. For specimens in the flow loop, a 4mm diameter perspex tube was placed against and parallel to the specimen in the mould, so that the reference electrode could be as close as possible to the corroding surface.

Mild steel specimens (15mm x 10mm diam.) were cut from rod and the electrical connection made by soldering the wire onto the surface. 3CR12 specimens were machined from 3mm plate and used in the form of discs of 15mm diameter, onto which a wire was soldered. As with the aluminium samples, the steel samples were set in resin.

All specimens were wet ground to a final grit size of 1000µm on silicon carbide paper, rinsed in water and finally degreased in acetone. The specimen/resin interface was masked with masking lacquer (Mowat 45 Stop-off lacquer) to prevent crevice formation.

3.7.1 Experimental Arrangement

For static electrochemical testing a one litre flask, with apertures for insertion of a Standard Calomel reference electrode, carbon counter electrodes, gas inlet and outlet pipes and specimen holder, was used.

Four day old bacterial cultures were used. These were poured into the corrosion flask which was then sealed. Since direct deaeration of the solution produced a pH change (93), the headspace only was deaerated with ultra-high purity nitrogen passed through a 0,2 µm membrane. The solution itself was anaerobic due to the presence of the redox poising chemicals. The H_2S gas was bled into a NaOH trap before being discharged to the atmosphere. In the case of *Pseudomonas* cultures, aeration was achieved by bubbling compressed membrane-filtered air through the solution.

Both mine water and nutritive medium were used for electrochemical tests. Either ferrous ammonium sulphate or ammonium sulphate were added with the sodium ascorbate to SRB medium or mine water. Use of the former leads to the formation of iron sulphide which was not desirable in all cases.

The experimental set up for electrochemical tests in the flow loop was described in Section 3.2. Electrochemical tests were conducted using a Princeton Applied Research Potentiostat/Galvanostat Model 273 interfaced with an Apple II Computer and a Solartron Schlumberger 1286 Electrochemical Interface connected to a Cullinan Computer.

3.7.2 Potentiodynamic Scans

A stabilization period of one hour was allowed before scanning commenced. This was found to be sufficient time for a stable Ecorr value to be reached Under flow conditions, scans were only commenced once the free corrosion potential had stabilized. Scans were run from 150mV below Ecorr to a final potential of 1000 mV above Ecorr at a scan rate of 1 mV/s.

Scans were conducted in duplicate under the following conditions:

- static tests in *Pseudomonas* cultures in medium and in sterile medium as a control;
- static tests in *D.desulfuricans* cultures in medium containing ferrous ammonium sulphate and in sterile medium containing the same redox poising chemical as the control;
- static tests in the mixed SRB culture under the same culture conditions as *D. desulfuricans*.

3.7.3 Cyclic Polarization Scans

Specimen preparation and stabilization times were the same as for the potentiostatic scans. Scans were started at the free-corroding potential, Ecorr at a rate of 1 mV/s and then reversed at a current density of 100μA/cm. Scans were performed in duplicate and sometimes in triplicate.

Scans were carried out under the following conditions:

- *Pseudomonas* cultures in both medium and mine waters.
- Sterile, aerated mine water and nutritive medium.
- *D.desulfuricans* cultures in both medium and mine water each containing either ferrous ammonium sulphate or ammonium sulphate.
- Mixed SRB cultures in nutritive medium and mine water as above.
- Sterile deaerated nutritive medium and mine water with the same redox poising chemicals as above.
- A mixed culture of *Pseudomonas* and SRB in mine water under flow conditions.
- Sterile mine water under flow conditions.

Plots from the scans were examined to determine the effect of bacteria on:

- the free corrosion potential Ecorr;
- the passivation range;
- the size of the hysteresis loop formed by the reverse scan.

3.7.4 Tafel Extrapolation

Specimen preparation and stabilization times were the same as for the potentiostatic scans. The Tafel plots were obtained over a range of 100mV at a sweep speed of 1mV/s starting from an initial potential of -50mV from the rest potential. The cathodic and anodic slopes for tests in bacterial cultures were compared with those in sterile medium in order to determine whether bacteria in fact altered either the cathodic or anodic processes. Scans were conducted under the same conditions as for cyclic polarization scans.

3.8 STATIC IMMERSION TESTS

3.8.1 Specimen Preparation

Coupons, 45 x 20 mm and ranging in thickness from 1,2 - 3,5 mm were machined from the six different alloys. A 5 mm hole was drilled in the centre at one end. The edges of each specimen were rounded and the holes chamfered to minimize edge corrosion effects. The dimensions of each coupon were measured to an accuracy of 0,01 mm. They were then degreased ultrasonically in acetone for 20 minutes and finally weighed to 0,1 mg. The edges and suspension holes were masked with 45 Stop-off Lacquer.

3.8.2 Experimental Arrangement

Triplicate specimens of each alloy were suspended on glass hangers in a random fashion in 2L flasks. The lid and lip of each flask were greased and closed by means of a clamp. The lid of the flask contained ports for:

- aeration/deaeration
- fluid removal and addition
- NaOH trap for H_2S bleed off.

Flasks with attached lengths of tubing and the specimens were autoclaved at 121°C for 20 minutes.

Four day old bacterial cultures in nutritive medium and in mine water and sterile controls were aseptically added to each flask which was then incubated in a water bath at 35°C. SRB cultures and corresponding controls were deaerated with ultra-high purity nitrogen gas which was passed through a 0,2µm membrane filter. *Pseudomonas* cultures and controls were aerated with compressed air passed through a similar filter.

A semi-continuous culture technique was used ie periodic removal of exhausted medium and cells followed by addition of fresh medium. This involved removal of 100-200 ml fluid twice a week with replacement of the same amount of fresh medium. This technique maintains the cells in a state of active growth. Strict aseptic conditions were maintained throughout the duration of the tests.

Figures 11 and 12 show the specimen jar and the lid with various attachments.

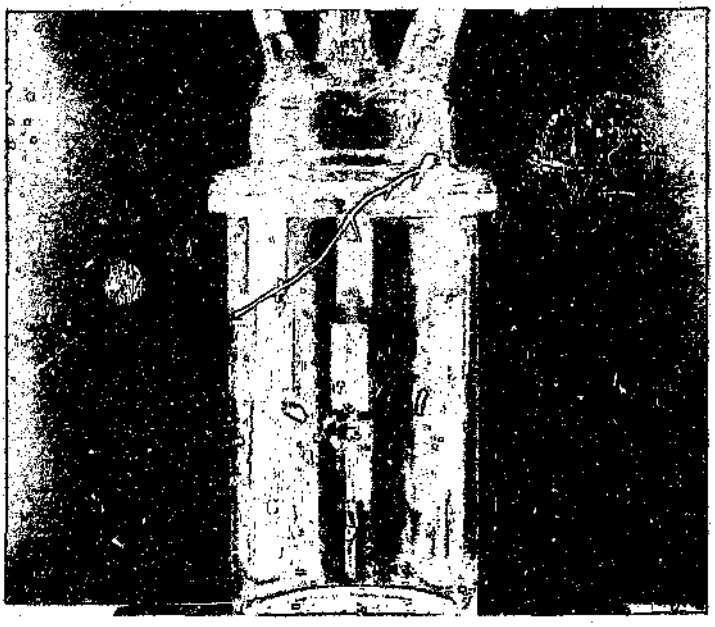

Figure 11. Corrosion flask with immersion specimens.

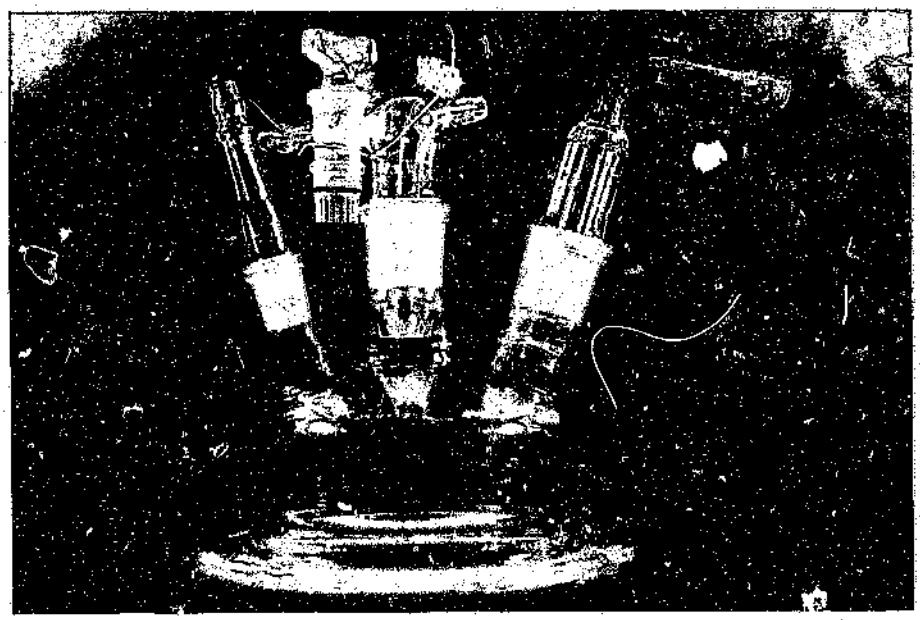

Figure 12. Lid of corrosion flask used in immersion tests showing ports: A - Inlet for fresh medium joined to a reservoir; B - Nitrogen gas bubbler and outlet port for H_2S
C - Outlet for exhausted medium

Medium was extracted by clamping off port A and the H_2S outlet port, and bubbling gas through the medium. The pressure build up forced the fluid through port C. The gas was then turned off and fresh medium allowed to flow through A. Tygon tubing was used throughout. The tubing can be autoclaved for sterility and is impervious to oxygen.

The water bath was housed in a wooden cabinet illuminated by a germicidal UV lamp in order to decrease chances of contamination from the atmosphere.

3.8.3 Specimen Examination

After an exposure period of 7 weeks, the samples were removed from the flasks and photographed immediately. One sample from each set was prepared for SEM by fixing in 2% glutaraldehyde for 12 hours and then drying in a desiccator. These samples were then coated with carbon and the attached biofilm and corrosion product viewed. Qualitative EDAX was used to analyse corrosion products. Some samples were then gold coated for improved visualization of the biofilm.

The surfaces of the coupons were then cleaned (see below) and re-examined by SEM for corrosive attack.

Optical microscopy was also used to examine cleaned specimens. The cleaned specimens were re-weighed and weight losses calculated.

3.8.4 Specimen Cleaning

The cleaning procedure involved scrubbing of the specimens with a nylon brush under running tap water and then immersion for half an hour in a chromic acid/phosphoric acid mixture (Appendix B) at 25 °C. During immersion in the acid, the specimens were scrubbed twice with a nylon brush. They were then rinsed in tap water and finally in acetone. They were then dried on paper towels and stored in a desiccator.

3.9 FLOW LOOP IMMERSION TESTS

3.9.1 Specimen Preparation

Test specimens cut to size were prepared in the same way as for static immersion tests.

3.9.2 Experimental Arrangement

Specimens were inserted into the immersion section of the flow loop. Tests were run in sterile mine water which was treated with biocide (Chemserve Bioshock) at a dosage of 50 mg/l/week. Weekly bacteriological plate counts were carried out to ensure sterility of the water. The flow rate was set at 1,5 m/s. The temperature reached a maximum of 35°C without cooling. Samples were exposed for 7 weeks.

Due to breakdown of the pump seal after the sterile immersion tests, this water was lost. Additional mine water was collected from the same spot as before and analysis showed it to be of very similar composition to the first water (Table 3).

This water was left unsterilized. Five litres of 4 day old cultures of *P.aeruginosa* were added to the water and allowed to proliferate for 1 week before insertion of new specimens. After 1 week's exposure to the Pseudomonads, during which time it was hoped that a slime layer had formed on the specimens, 5 litres of 4 day old *D. desulfuricans* culture were added to the tank. The total exposure time of the specimens was 7 weeks.

3.9.3 Specimen Evaluation

This was carried out as for the static immersion tests.

3.9.4 Specimen Cleaning

As for static immersion tests.

4.0 RESULTS

4.1 MINE SURVEY RESULTS

4.1.1 Microbial isolation and identification

FSG samples

All FSG test specimens were covered with thick slimy growths together with fungal and mould species. The condition of some of the coupons on removal from the test rig can be seen in Figs. 13 - 16.

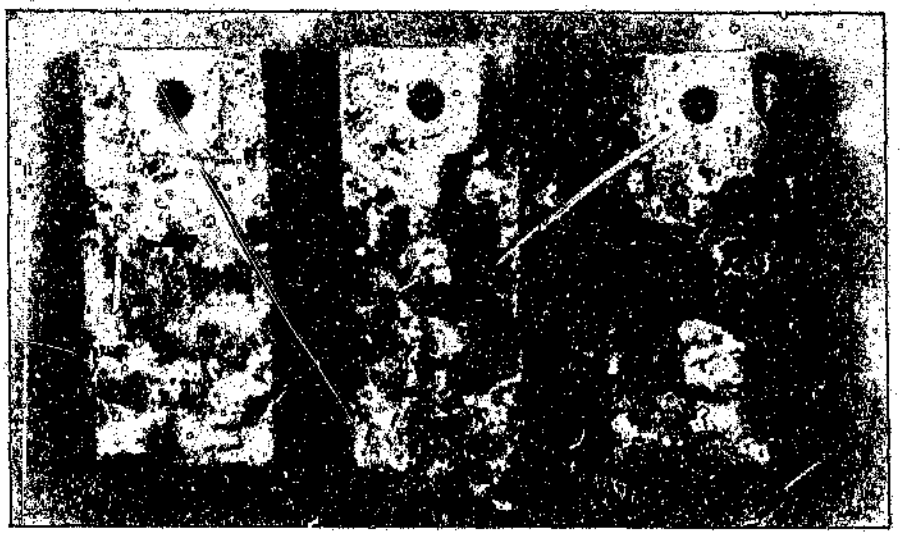

Figure 13. Alloy 1200 in the condition as removed from the system.

Figure 14. Alclad coupons in the condition as removed from the system.

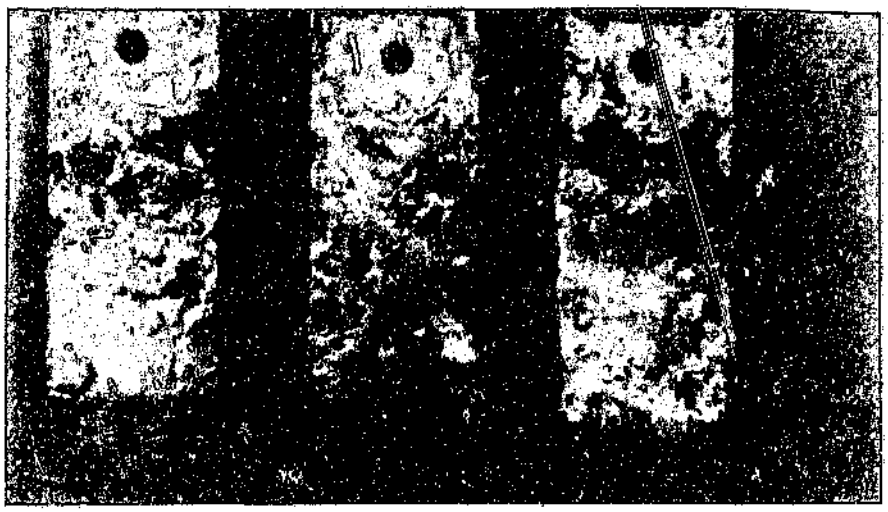

Figure 15. Alloy 5251 in the condition as removed from the system.

Figure 16. Alloy 6261 in the condition as removed from the system.

Some fungi were identified as belonging to the following genera:

- *Altenaria*
- *Curvularia*
- *Rhizopus*
- *Cladosporium* (possibly)

Colony and spore morphologies are illustrated in Figs. 17 - 21.

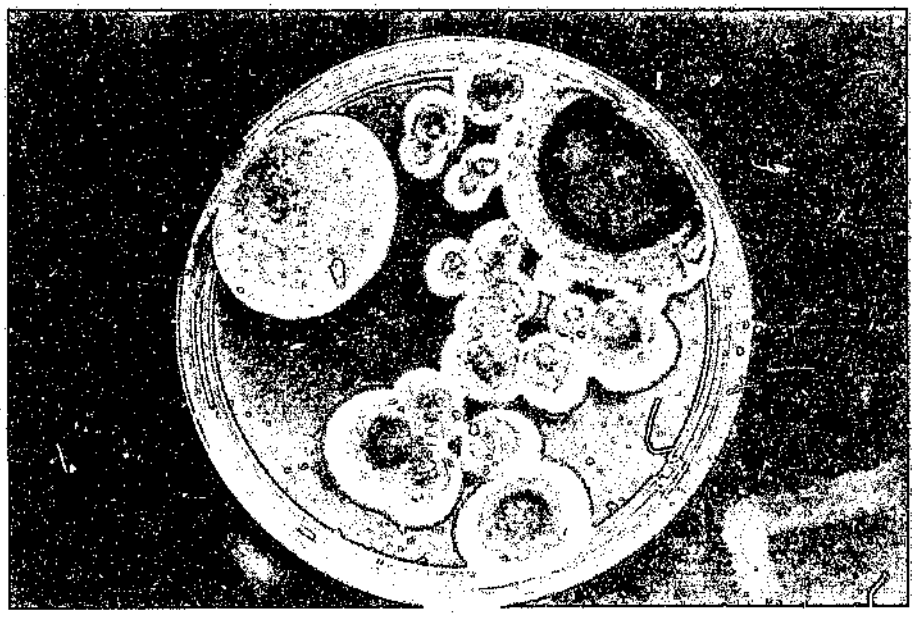

Figure 17. Possible Cladosporium colonies.

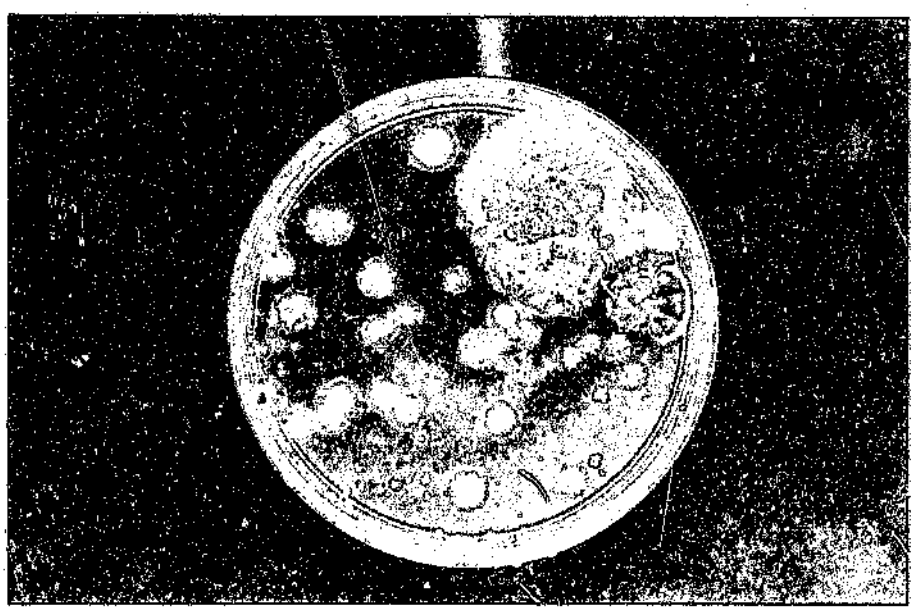

Figure 18. Fungal, mould and yeast colonies on Sabouraud Dextrose agar.

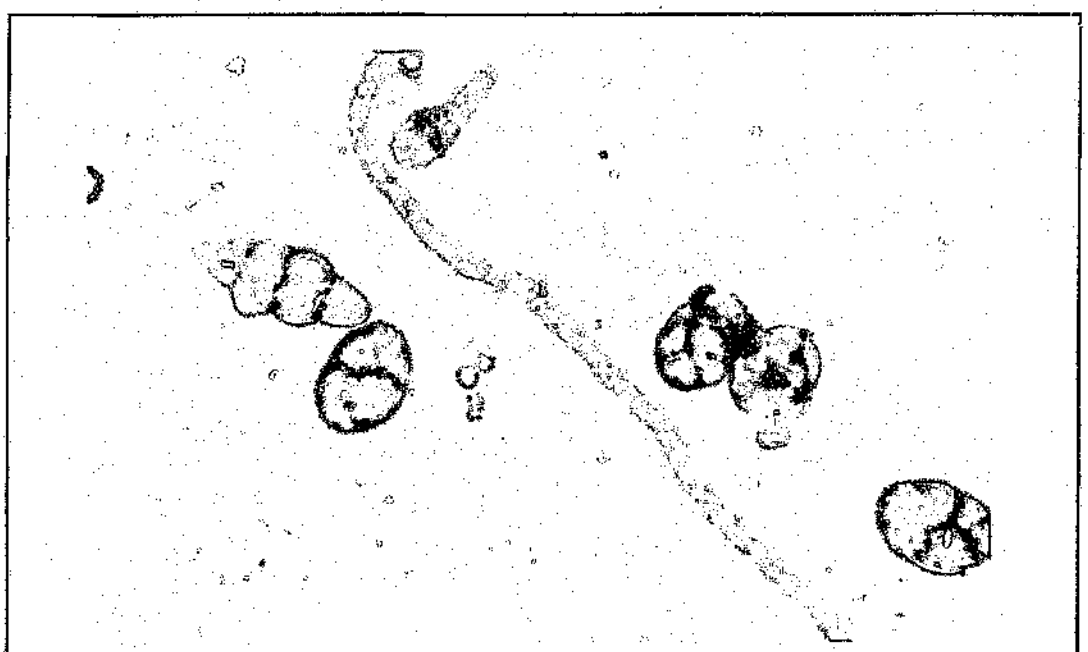

Figure 19. Spores of the fungus Altenaria (Mag. 100 x).

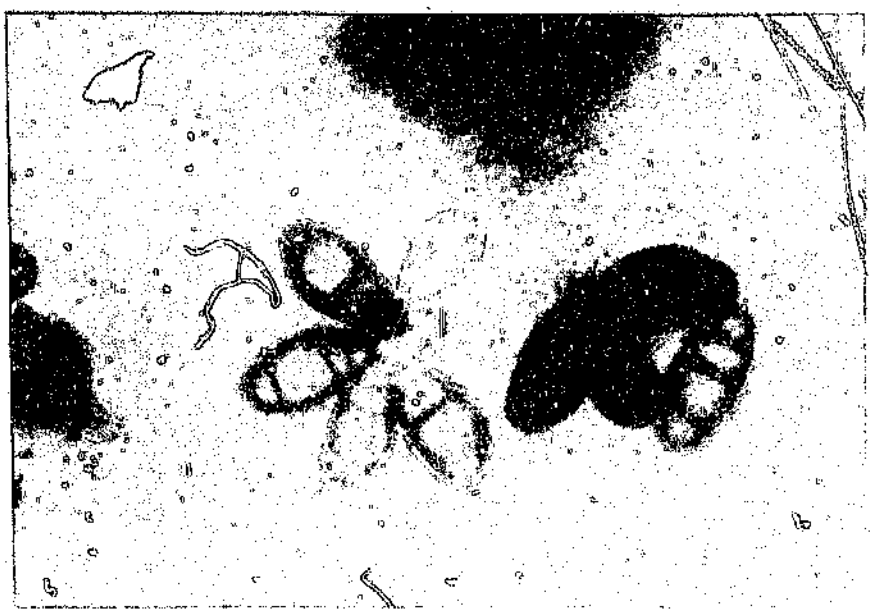

Figure 20. Spores of the fungus Curvularia (Mag. 1000 x).

Figure 21. Possible spores of the fungus Cladosporium (Mag. 400 x)..

SRB were positively identified on all alloys tested viz. 1200, 5251, 6261 and Alclad. The 1200 alloy seemed to be more heavily colonized by these organisms, as indicated by a more rapid positive result for the SRB test.

Pseudomonas species were found on all alloys, but were more prolific on the Alclad specimens. The presence of *Pseudomonas* was merely confirmed but not all isolates were identified to species level. *P.aeruginosa* and *P.fluorescence* were identified and frequently isolated.

Other bacterial genera isolated with less frequency included:

- *Chromobacter spp.*
- *Alcaligenes spp.*

The appearance of the samples as viewed by SEM are illustrated in Figs. 22 - 27. Thick sessile biofilms and corrosion product were observed on some specimens before cleaning (Figs. 22 and 23). Individual cells were not observed in these cases due to the presence of large amounts of extracellular polysaccharide. In other cases (Fig. 24) single cells were clearly visible. Fungal hypae were also observed (Fig. 25).

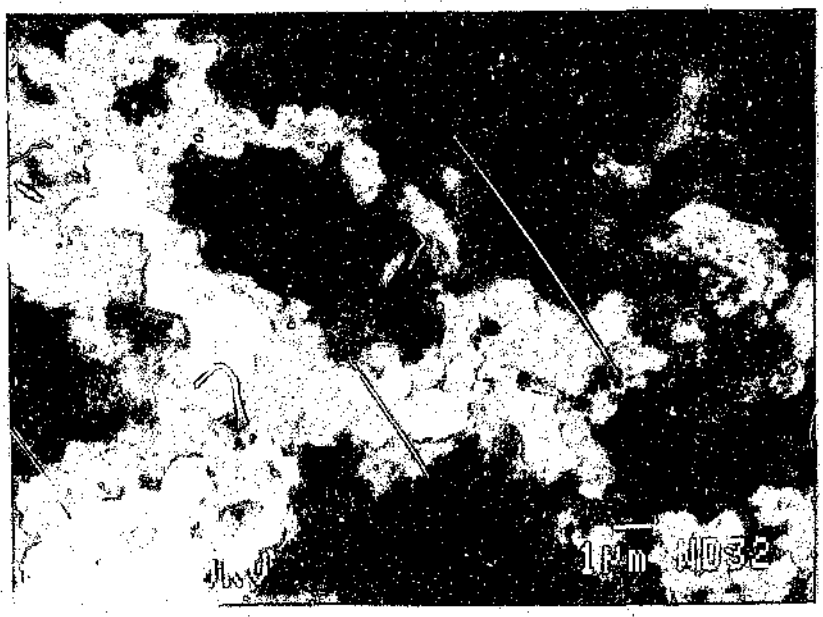

Figure 22. Biofilm on Alclad specimen before cleaning.

Figure 23. Biofilm on alloy 6261 before cleaning.

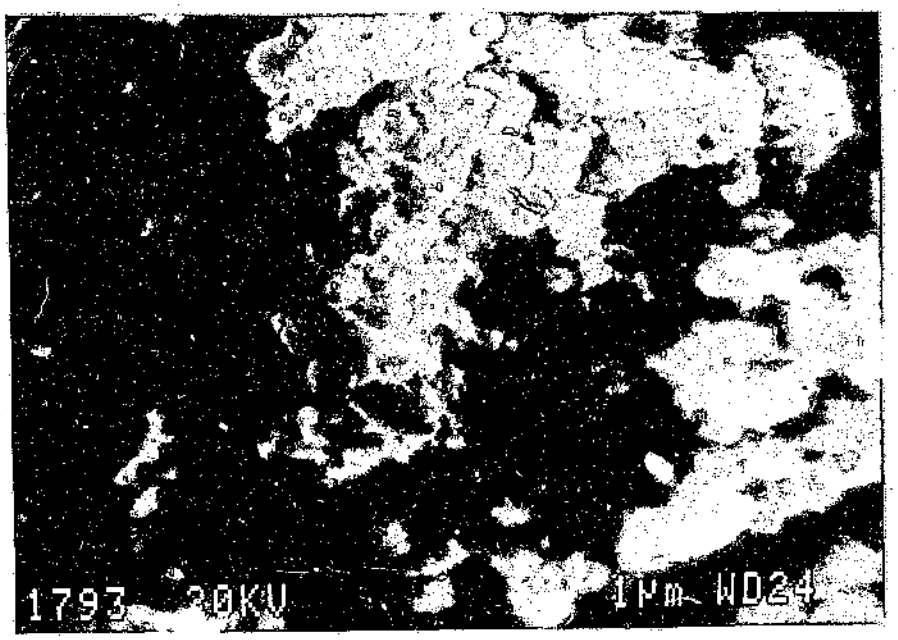

Figure 24. Alloy 6261 before cleaning - note individual cells clumped together.

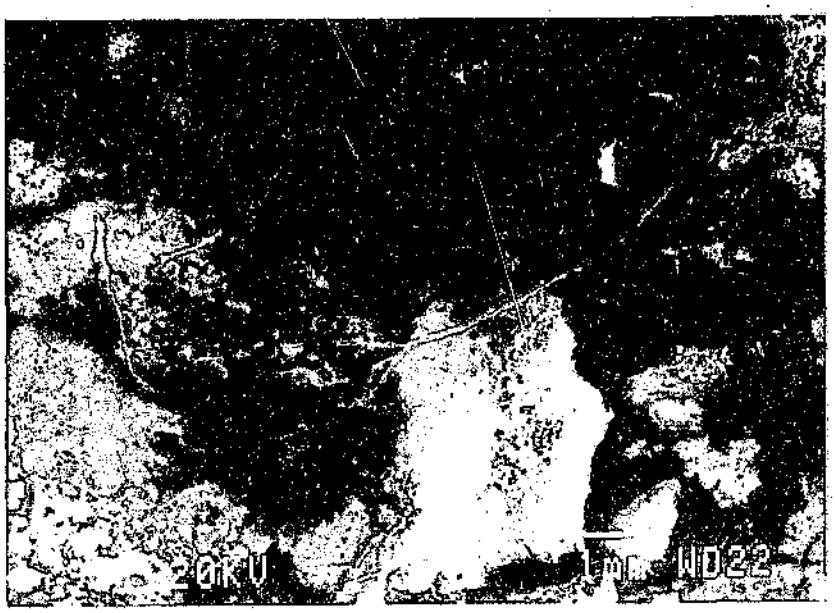

Figure 25. Alloy 6261 with fungal hyphae and corrosion product.

WDL samples

In contrast to FSG samples, WDL samples (viz. 1200, 5251, 6261, Alclad, painted, conversion coated, anodized) were not as heavily colonized by microorganisms.

The 1200 and Alclad alloys exhibited the most biological growth, whilst the 6261 alloys were heavily encrusted with scale. The conversion coated and painted coupons were covered by a thin, easily removable brown film. The 5251 and anodized alloys appeared to have remained uncolonized.

Fungal and mould species were isolated from all coupons, but these were not identified to species level.

Pseudomonas spp. were isolated from 1200, 6261 and the conversion coated alloys.

SRB were positively identified on 1200, 6261 and Alclad specimens.

SEM revealed that all specimens were covered with biofilm (Fig. 26). Tubercles covered with bacteria were also observed (Fig. 27).

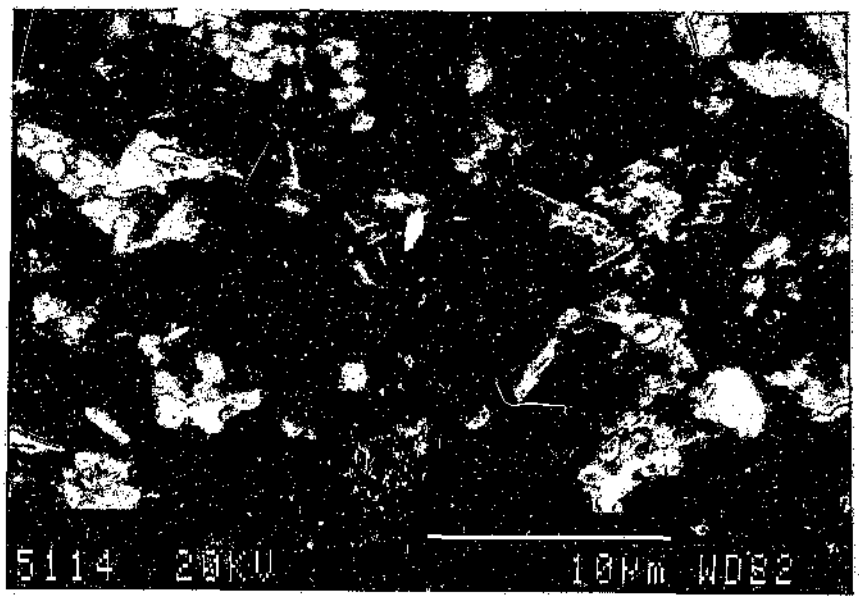

Figure 26. Biofilm on conversion coated specimen.

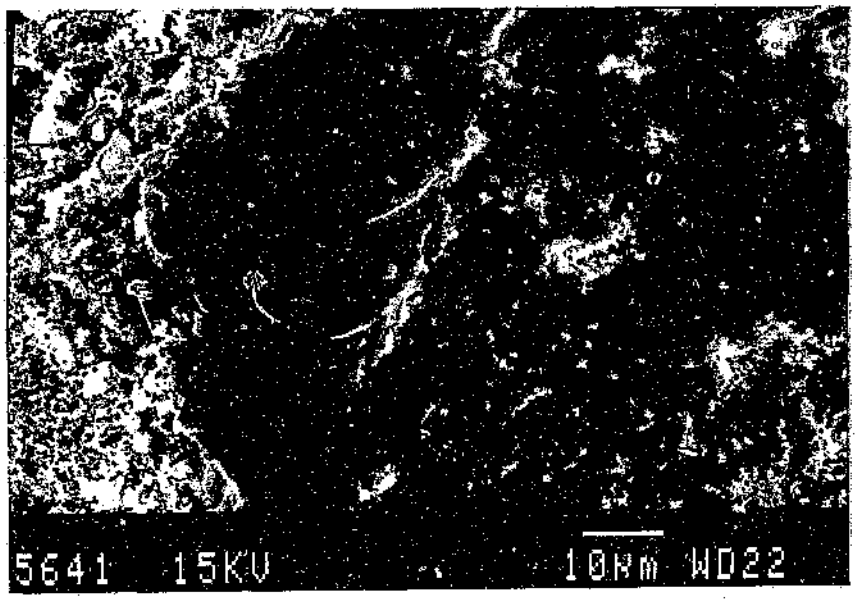

Figure 27. Tubercle on specimen 6261.

4.1.2 Examination of corroded surfaces.

Samples exposed to FSG waters

On removal of the biofilm, the surfaces were found to have undergone noticeable corrosion and showed evidence of exfoliation and pitting. Figs. 28 - 31 show the condition of some alloys in the acid cleaned condition.

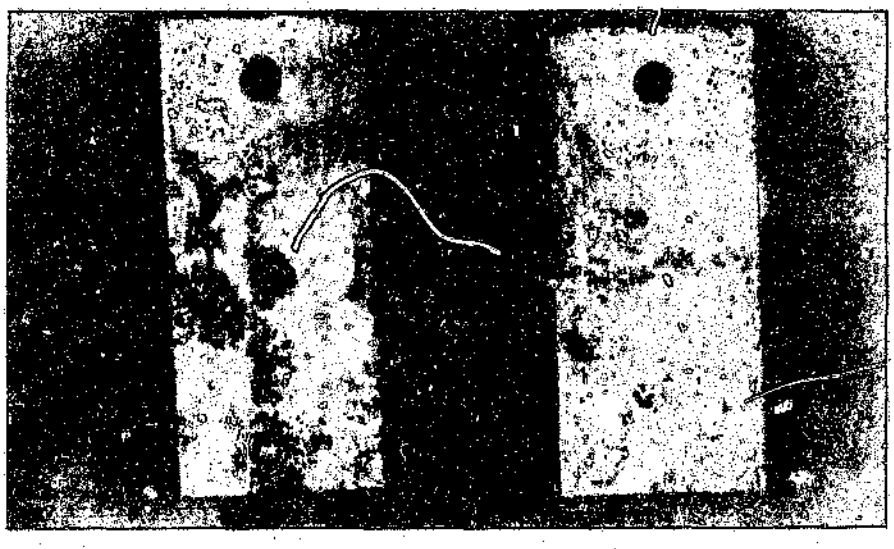

Figure 28. Alloy 1200 in the acid cleaned condition.

Figure 29. Alloy 5251 in the acid cleaned condition.

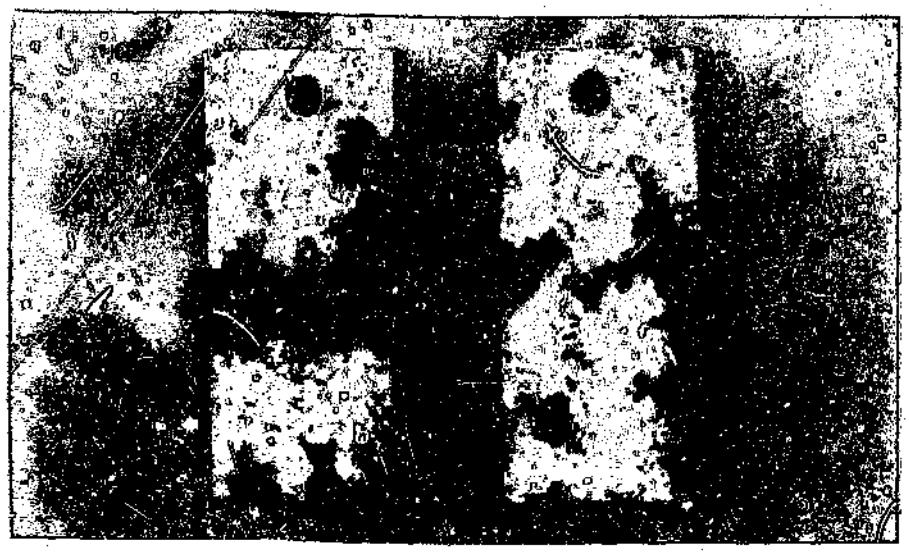

Figure 30. Alclad in the acid cleaned condition.

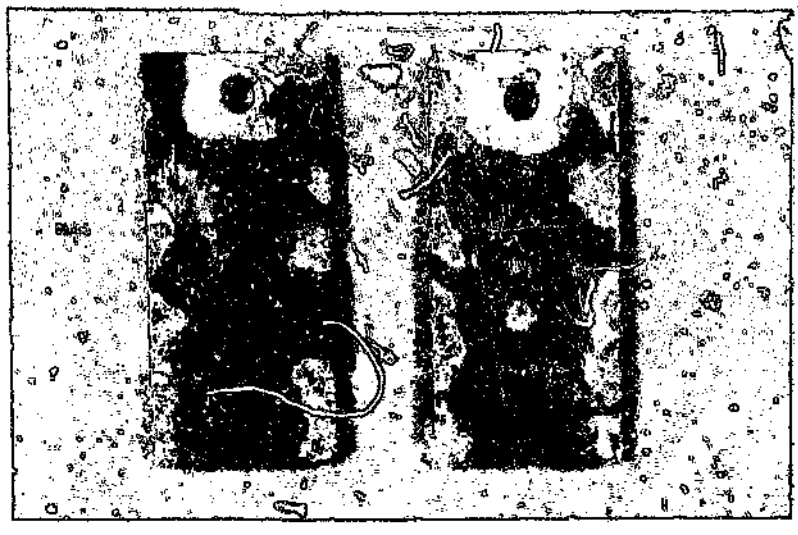

Figure 31. View of alloy 6261 after cleaning.

The acid cleaned specimens examined by SEM revealed pitting attack of all alloys (Figs. 32 - 34). Intergranular attack was present in alloy 1200 (Fig. 35), in which the triple points of corrosion initiation are clearly visible.

EDAX analysis showed that sulphide precipitates were present in abundance, often at the bottom of pits (Fig. 36). An EDAX trace is shown in Fig. 37. Newman et al (94) in a study of the effects of sulphur compounds on the pitting behaviour of 304L stainless steel in near neutral chloride solutions, found metal sulphides at the bottom of pits formed in the presence of sulphide, thiosulphate or tetrathionate. They suggested that the active sulphur species enhance corrosion by impeding the repassivation of the bare metal surface following chloride induced film breakdown. This mode of sulphide pitting could well apply to the aluminium alloy samples.

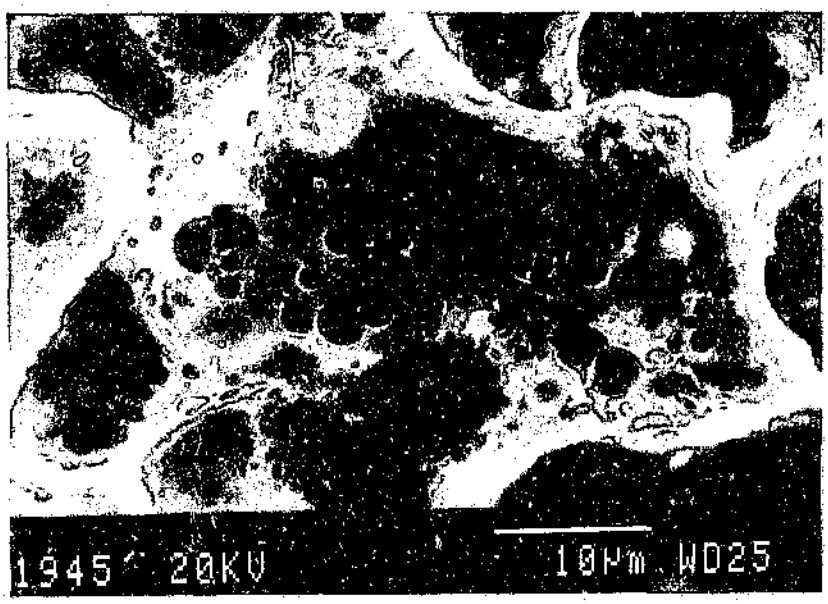

Figure 32. Pitting attack on Alclad.

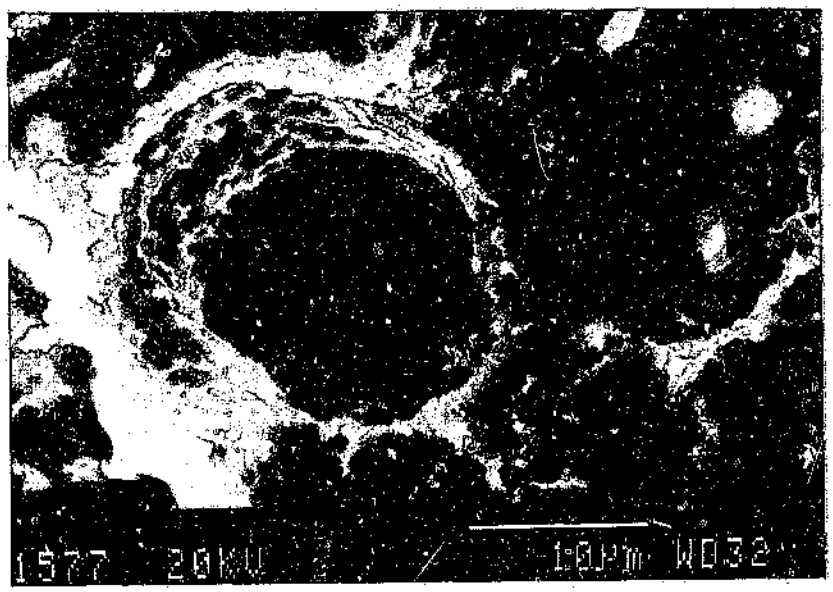

Figure 33. Pitting attack in 5251.

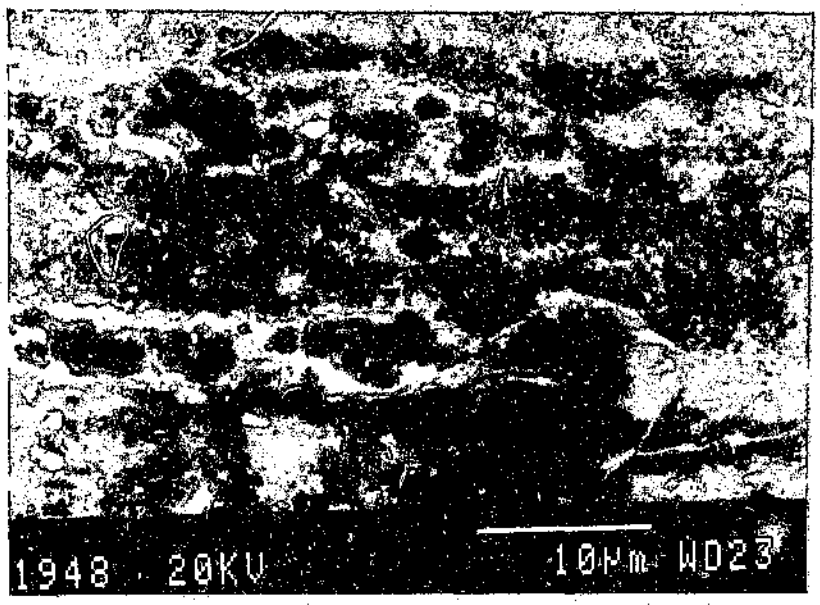

Figure 34. Pitting attack in 1200.

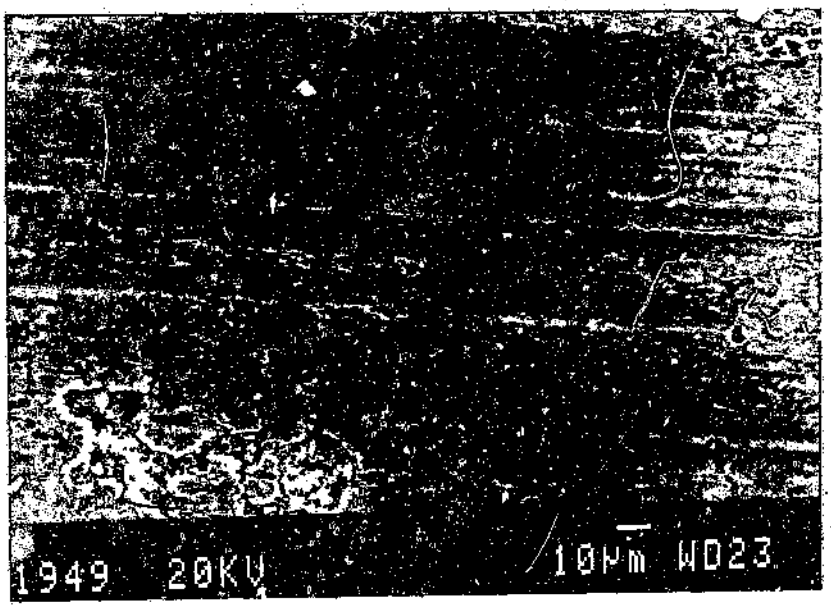

Figure 35. Intergranular attack in 1200.

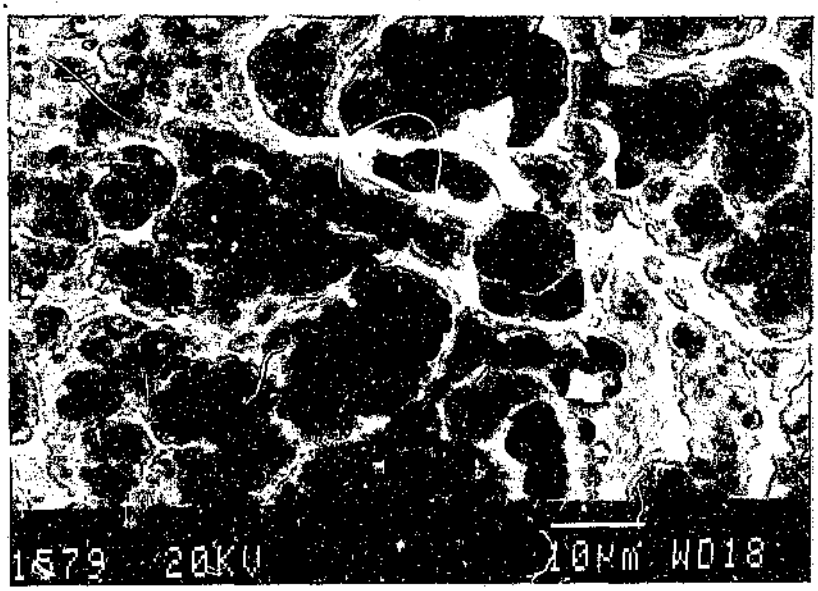

Figure 36. Sulphide precipitates in pits.

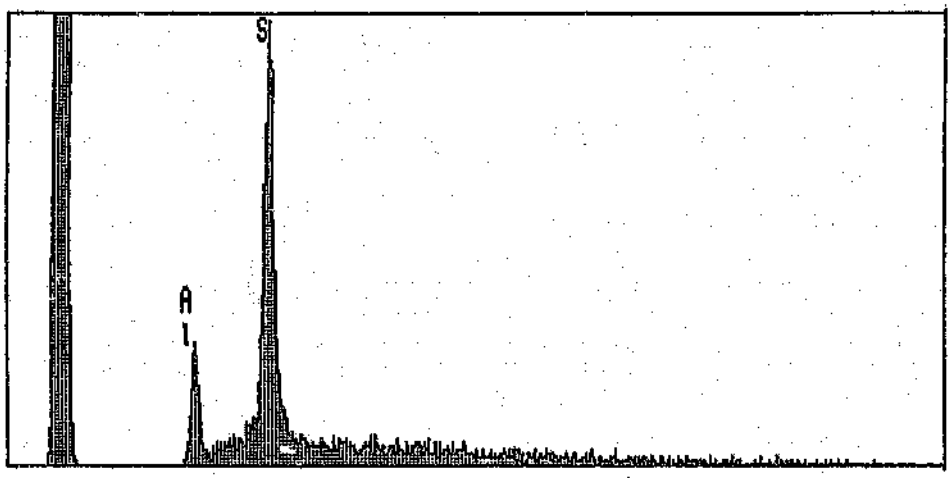

Figure 37. EDAX trace of precipitates in Fig. 36.

Samples exposed to WDL water

The condition of the surfaces on removal of the biofilm can be seen in Figs. 38 - 40. Pitting attack was present in 1200, 5251, 6261, Alclad and conversion coated specimens (Figs. 41 and 42). Although the conversion coated specimen seemed undamaged macroscopically, at the SEM level of examination, it showed damage in the form of intergranular attack and pitting (Fig. 43). The 1200 coupon also showed signs of intergranular attack (Fig. 44). The 5251 specimen showed microscopic damage in the form of interlinking pits in the direction of the extrusion lines (Figs. 45 and 46).

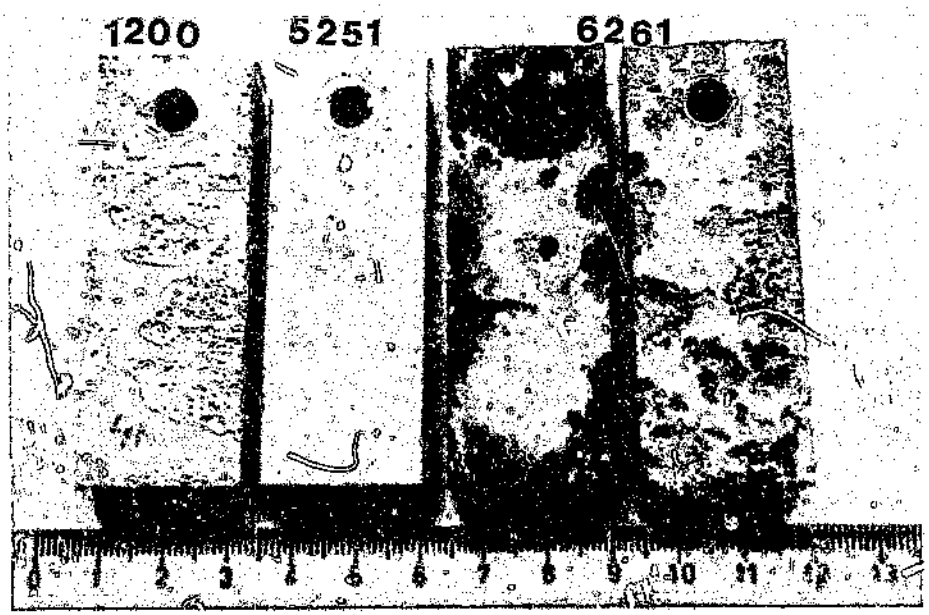

Figure 38. Condition of coupons after biofilm removal.

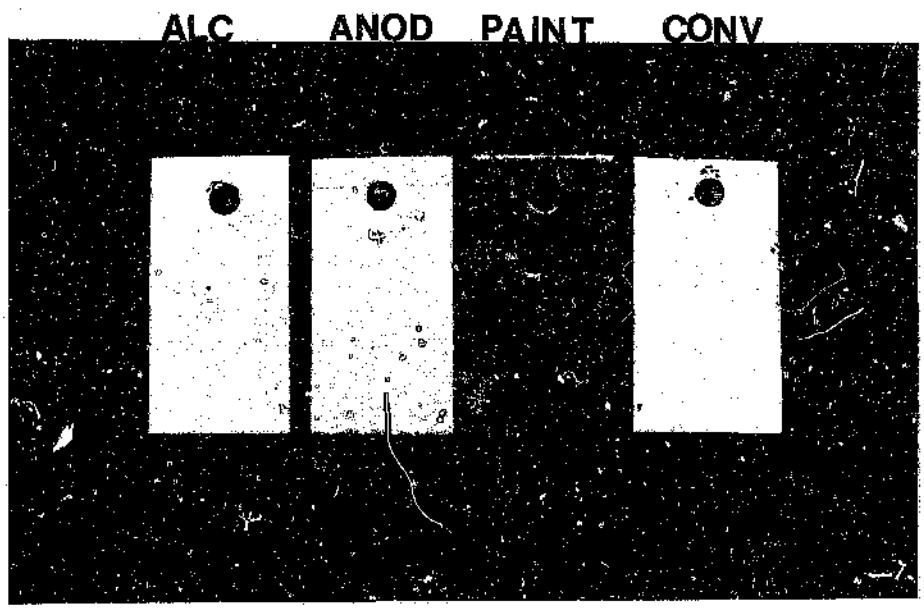

Figure 39. Condition of coupons after biofilm removal.

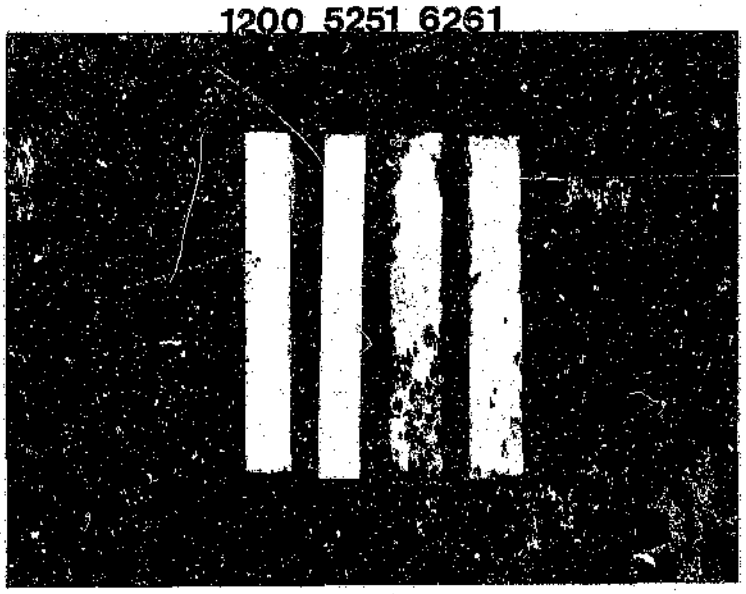

Figure 40. Condition of coupons after biofilm removal.

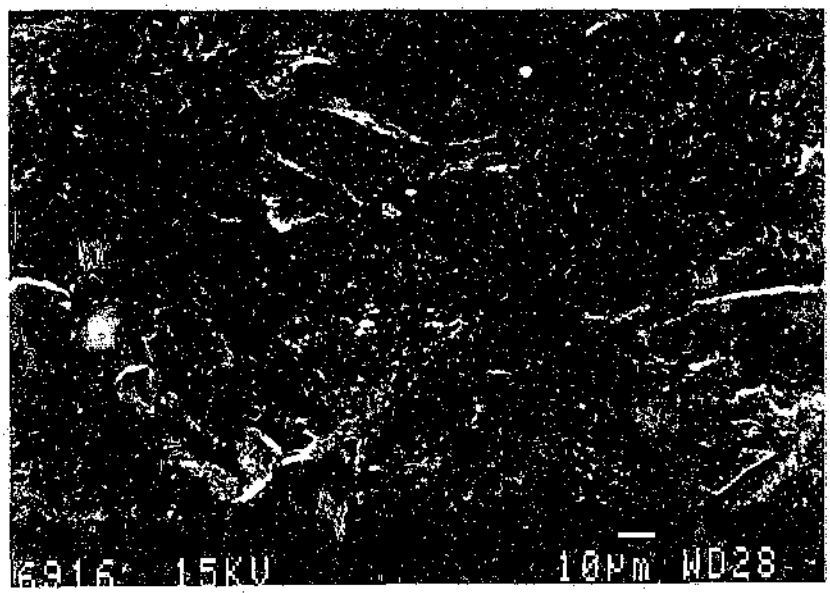

Figure 41. Pitting on the surface of a 6261 specimen.

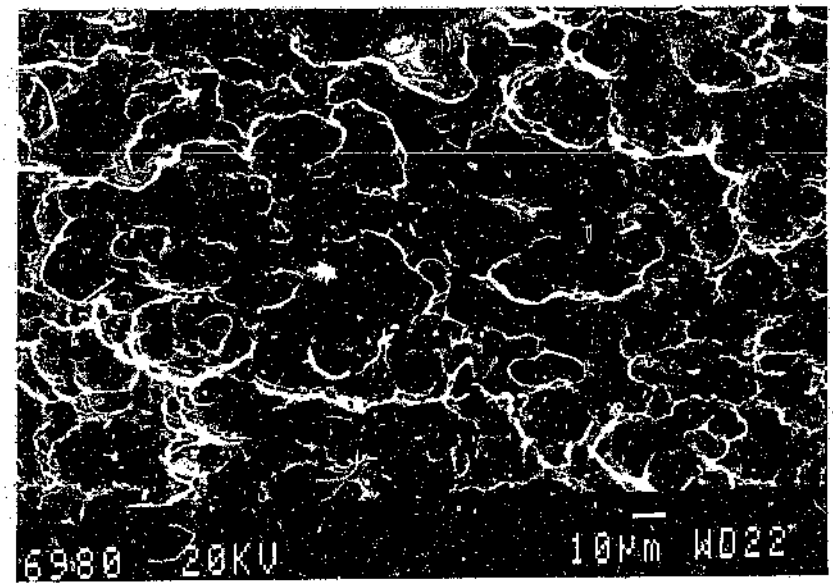

Figure 42. Pitting in Alclad specimen.

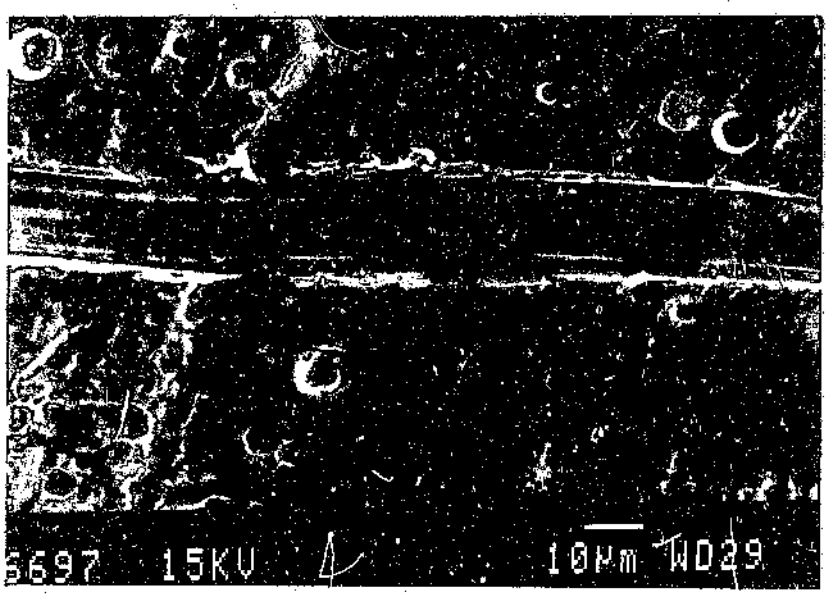

Figure 43. Pitting and intergranular attack on the conversion coated specimen.

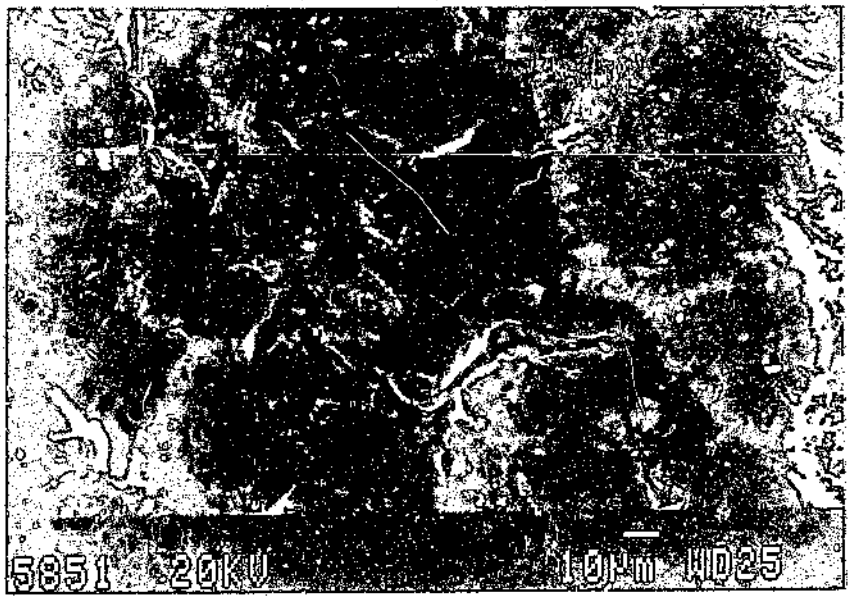

Figure 44. Intergranular attack on alloy 1200.

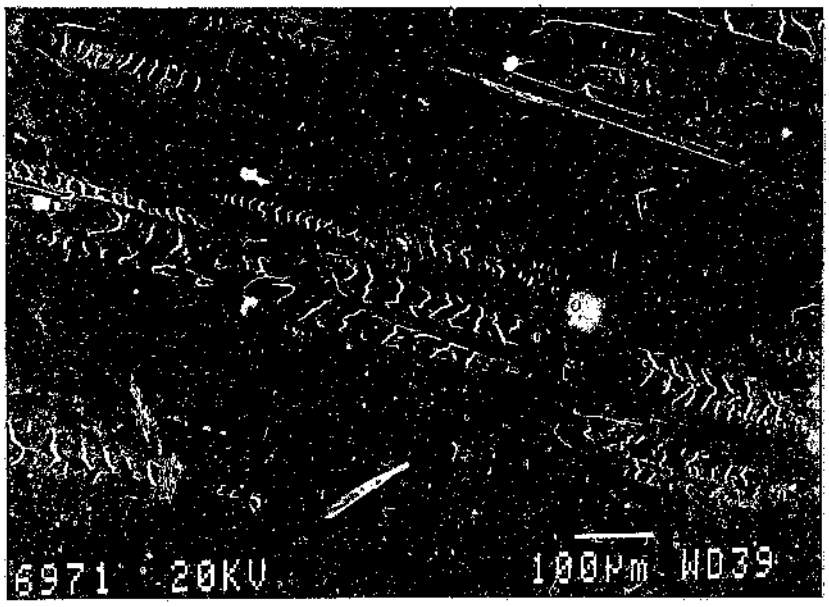

Figure 45. Pits in the direction of extrusion lines in alloy 5251.

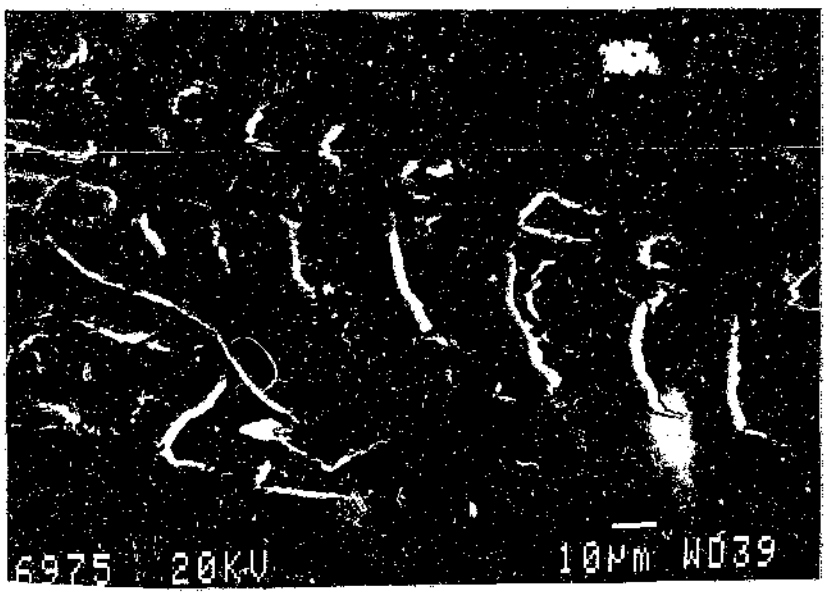

Figure 46. Close up of Fig. 45 showing pits.

4.2 IMMERSION TESTS - STATIC

The condition of the alloys on removal from the flasks can be seen in Figs. 47 - 56.

The aluminium alloys immersed for seven weeks in the SRB cultures in medium were covered by a thin greyish film and discrete black patches, all of which were easily scraped away. The mild steel coupons were covered by a thick black adherent layer which could not be scraped away. Tubercles were visible over the entire surface. The 3CR12 coupons revealed a few black tubercles, but otherwise were covered by a thin grey film.

In mine water tests, the aluminium alloys were covered by a thin easily removable brown corrosion product layer. Discrete black patches were found on the 6-series alloy specimens. The corresponding mild steel coupons were covered by a thick black corrosion product and tubercles. Discrete black patches covered the 3CR12 coupons.

Coupons immersed in sterile deaerated medium were covered by a thin off-white film which was easily removed. The mild steel coupons exhibited a typical reddish-brown corrosion product.

All coupons in the deaerated mine water were covered by a thick film of aluminium hydroxide. Coupons in the *Pseudomonas* cultures, both in medium and in mine water, were covered by a bulky, brown coloured corrosion product which was easily removed. Control coupons in sterile

mine water and medium were covered by a thin white film and a yellow-brown film respectively. The films adhered loosely.

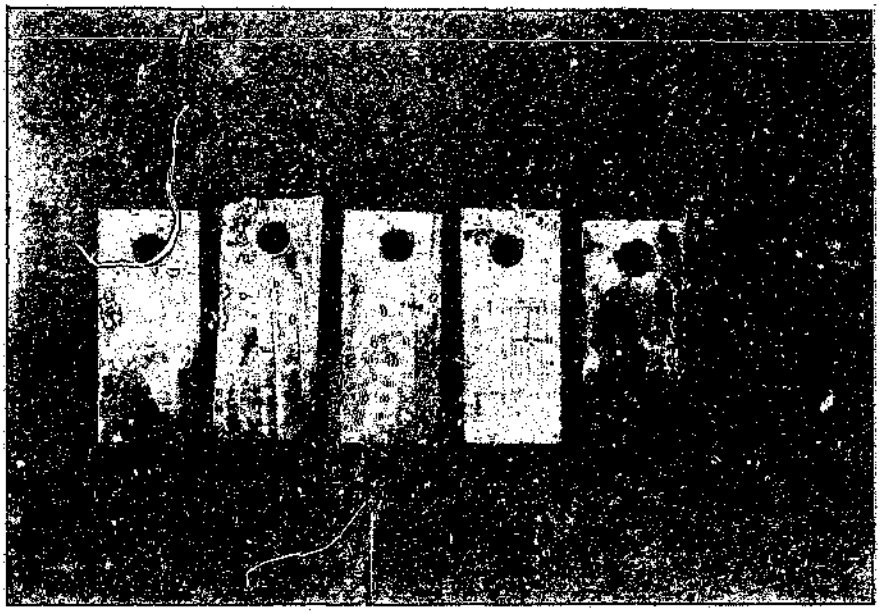

Figure 47. Condition of coupons on removal from the static immersion tests: in a mixed SRB culture in medium

The samples shall be referred to as follows:-

1 - 1070

2 - 5182

3 - 6063

4 - 6261

5 - 3CR12

6 - mild steel

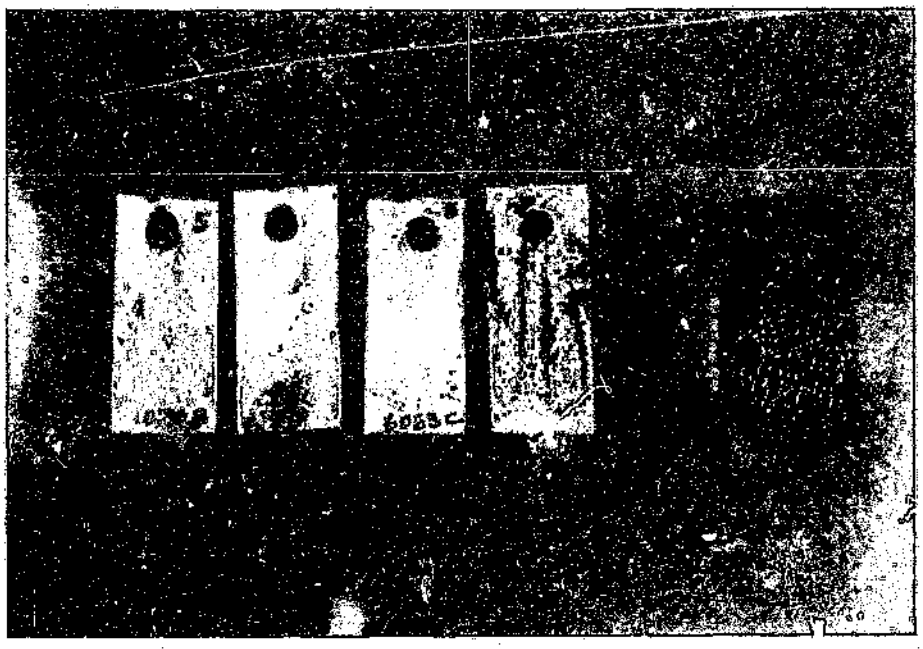

Figure 48. Condition of coupons on removal from the static immersion tests: in *D.desulfuricans* culture in medium.

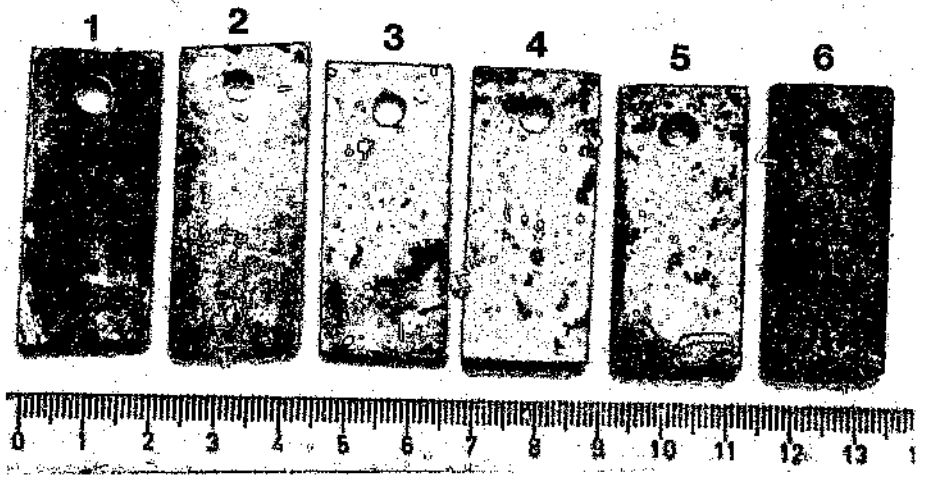

Figure 49. Condition of coupons on removal from Pseudomonas culture in medium.

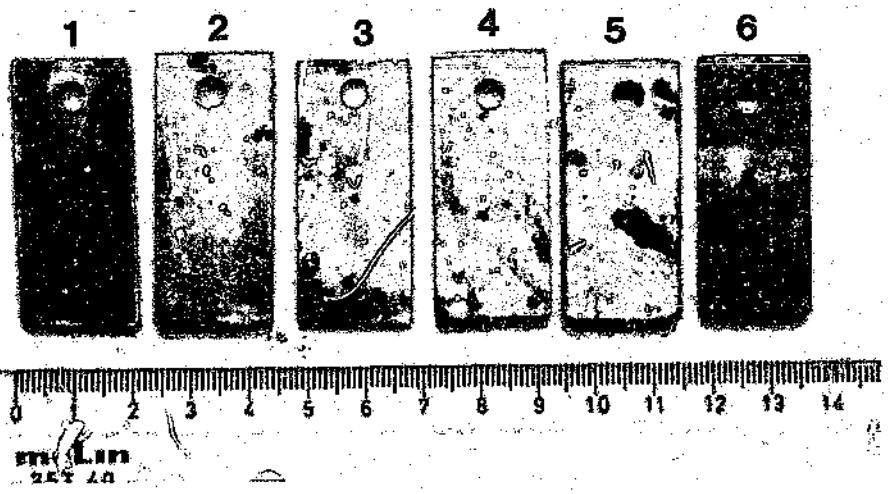

Figure 50. Condition of coupons on removal from aerated Pseudomonas medium (control).

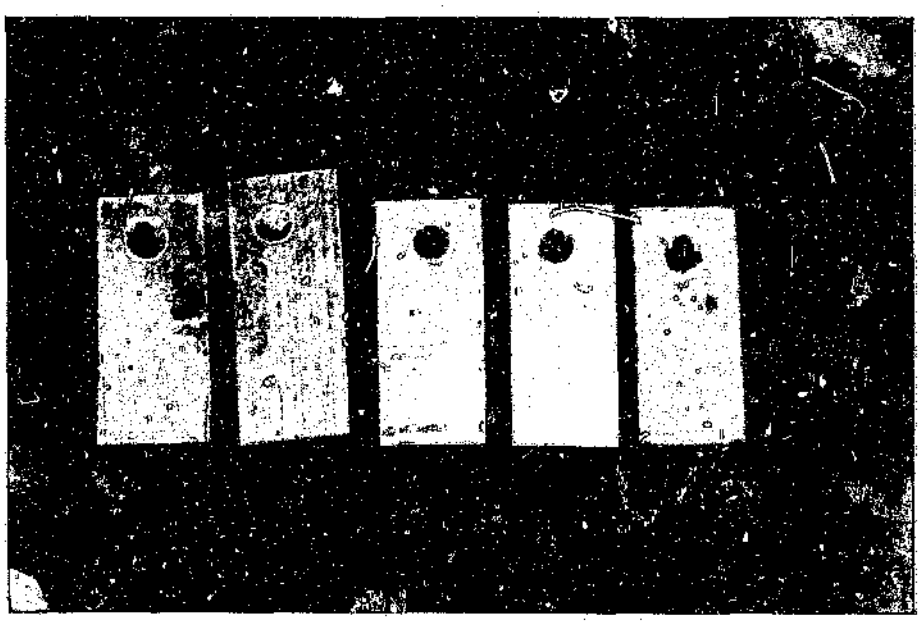

Figure 51. Condition of coupons on removal from deaerated SRB medium (control)

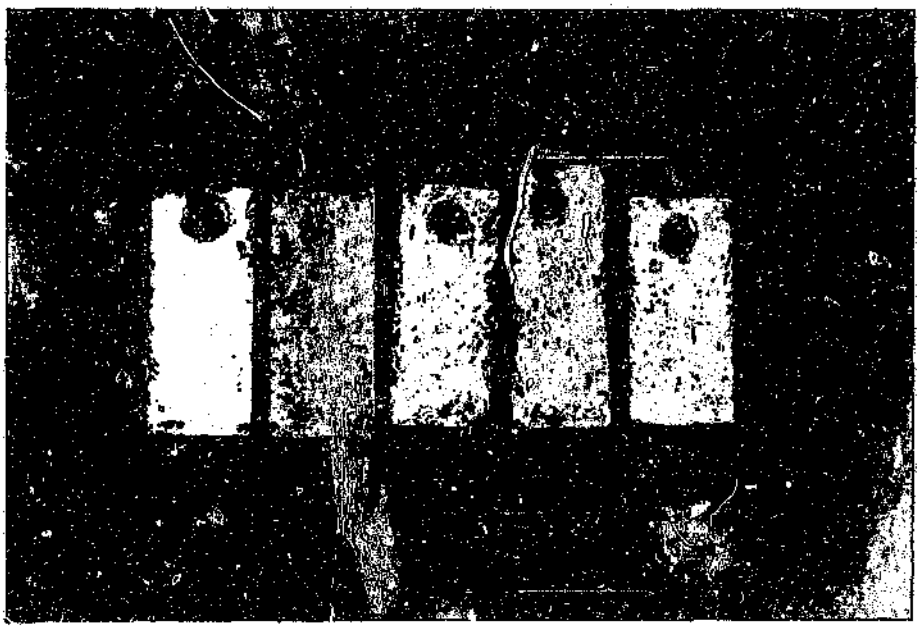

Figure 52. Condition of coupons on removal from D.desulfuricans culture in mine water.

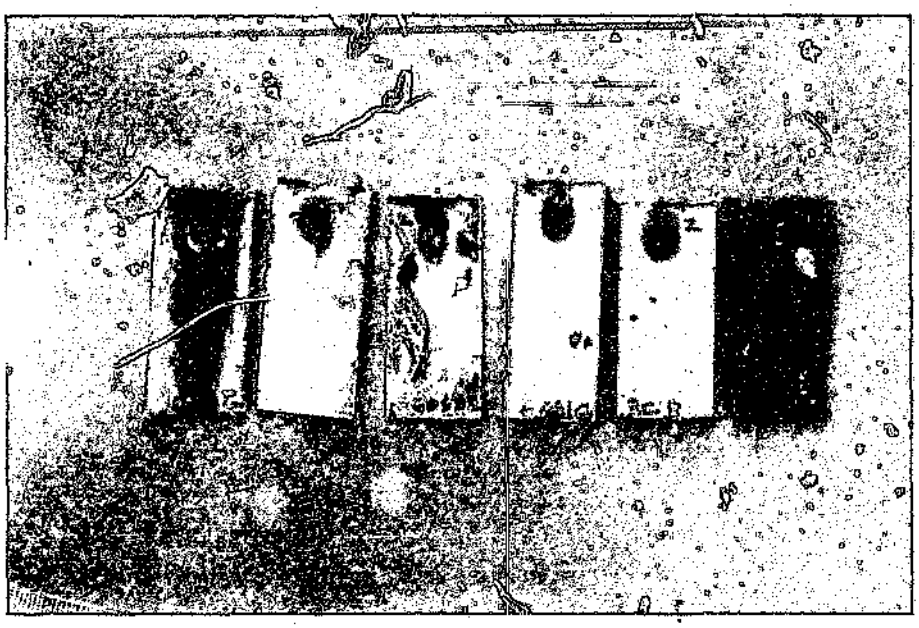

Figure 53. Condition of coupons on removal from the mixed SRB culture in mine water.

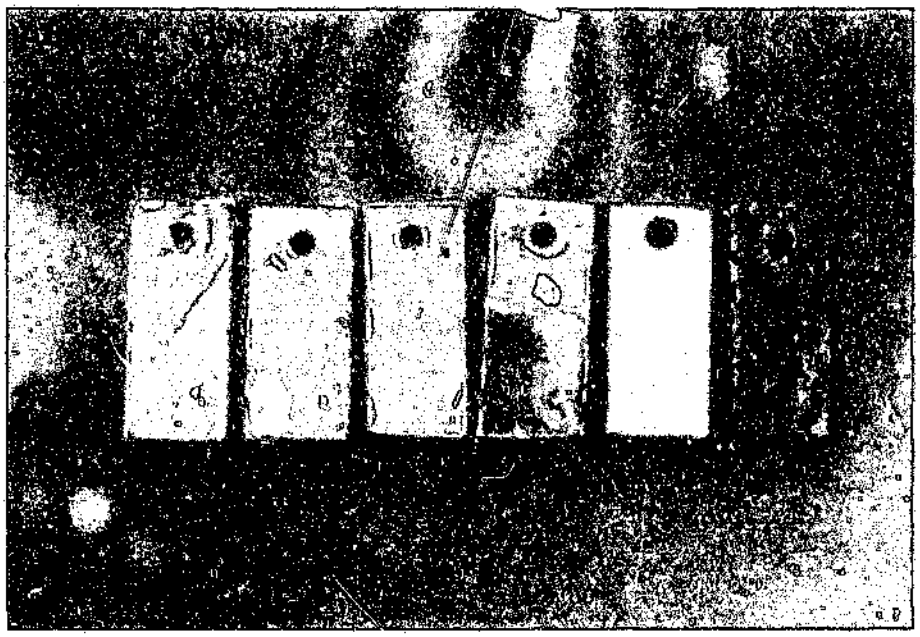

Figure 54. Condition of coupons on removal from the Pseudomonas culture in mine water.

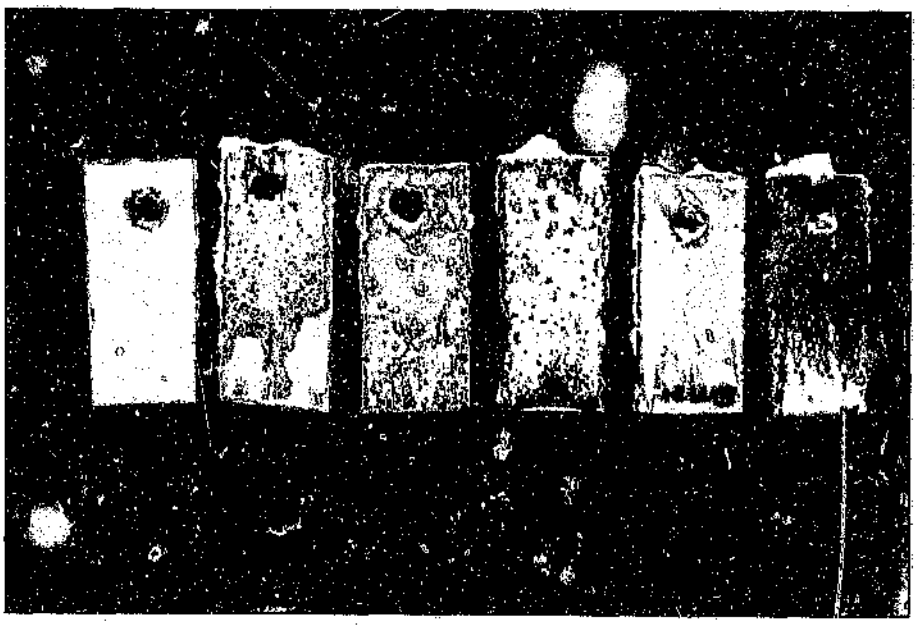

Figure 55. Condition of coupons on removal from sterile deaerated mine water

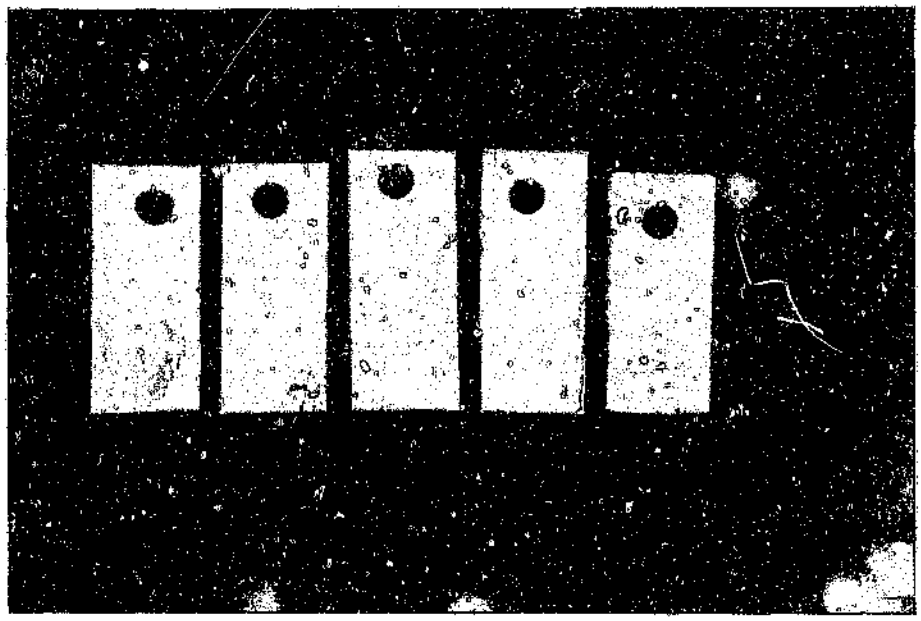

Figure 56. Condition of coupons on removal from sterile aerated mine water.

Coupons from each set were examined by SEM for evidence of microbial colonization and the corrosion product analysed by EDAX. After removal of the biofilm and corrosion product, the coupons were re-examined by SEM to identify both the type and extent of corrosive attack.

4.2.1 Tests in nutritive medium

All aluminium alloys exposed to both pure and mixed SRB cultures in medium were colonized by thick sessile biofilms (Fig. 57). Fig. 58 shows a typical mature biofilm whose surface organisms are often elongated to produce long branching filaments that form tufts of cells projecting into the flowing phase and exerting frictional resistance (14). In alloys where the extrusion lines and roll marks were well defined, the biofilm grew even more thickly (Fig. 59). In many cases, tubercles of corrosion product covered by bacteria were observed (Fig. 60). On some areas of the coupons where the biofilm was not fully developed when the coupons were removed, the mode of colonization could be observed. Fig. 61 shows the beginning of colonization by individual cells, while Fig. 62 shows a colony of bacteria on the alloy surface. The 3CR12 and mild steel coupons were heavily colonized, the latter containing typical tubercles covered with bacteria (Fig. 63).

Patches of FeS (see EDAX trace in Fig. 64) were observed on the surface of all aluminium alloys (Fig. 65). Corrosion product on aluminium consisted mainly of S, P, Fe, Si, Mg, Al, Ca (see EDAX traces in Fig. 66). On the ferrous metals, the corrosion product consisted mainly of Fe, S and P.

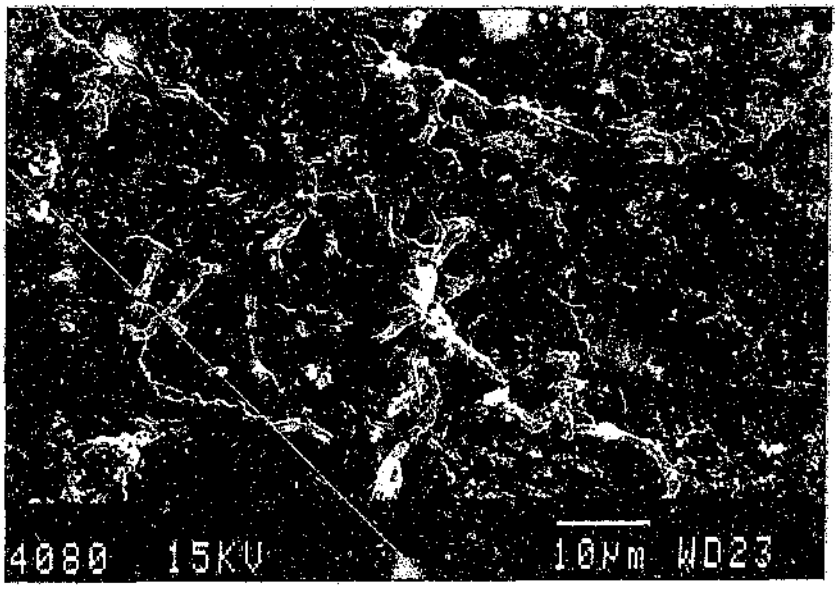

Figure 57. Biofilm on alloy 6261 in mixed SRB culture in medium: Note remnants of glycocalyx.

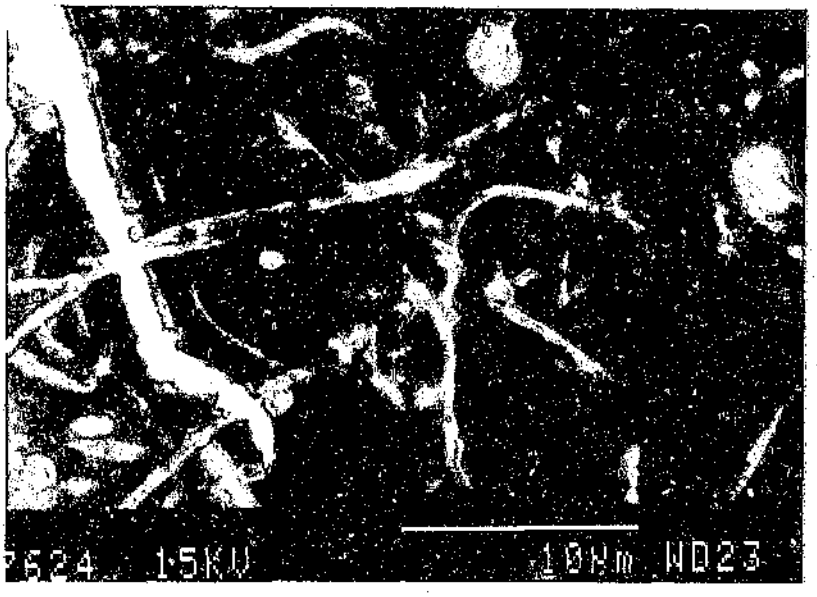

Figure 58. Alloy 1070 in D.desulfuricans culture in medium: Note branching of cells.

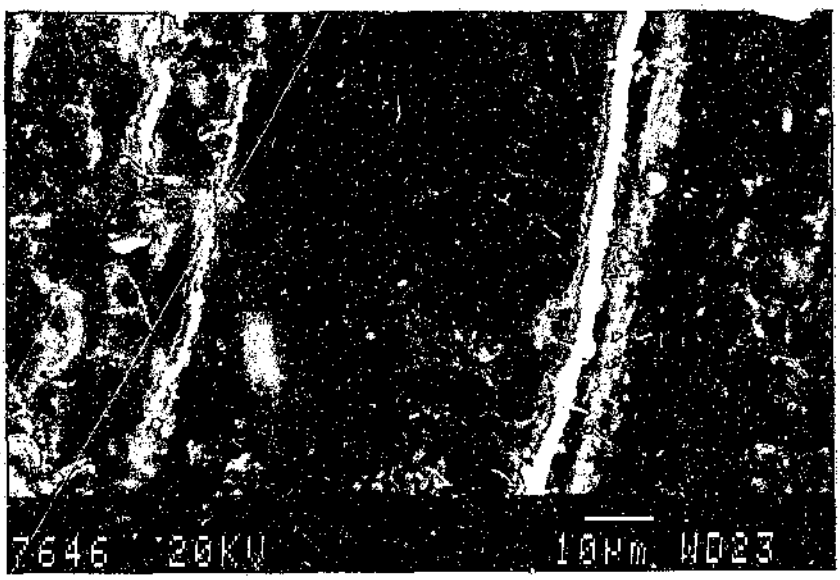

Figure 59. Thick biofilm between extrusion lines of alloy 6261: in *D.desulfuricans* culture.

Figure 60. Tubercle covered with bacteria: Alloy 6261 in *D.desulfuricans* culture.

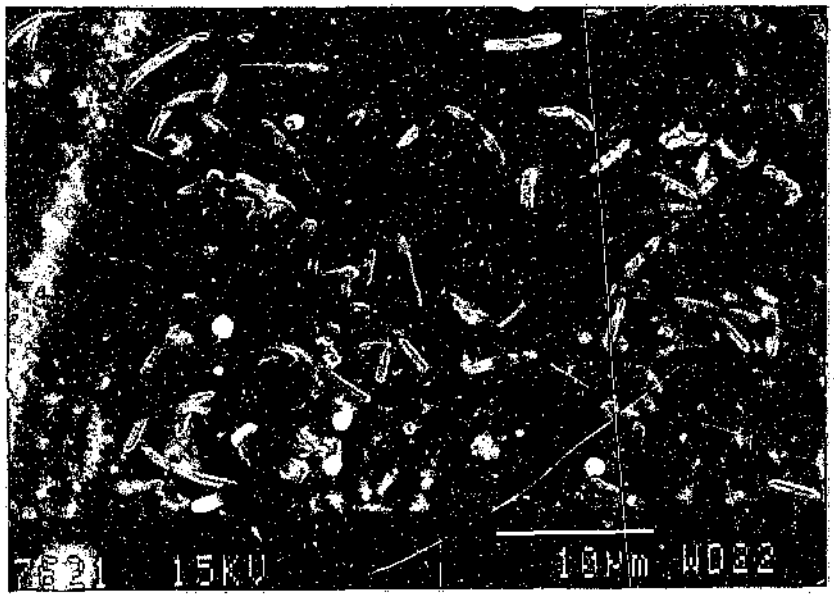

Figure 61. Initial colonization by Desulfovibrio on alloy 5182.

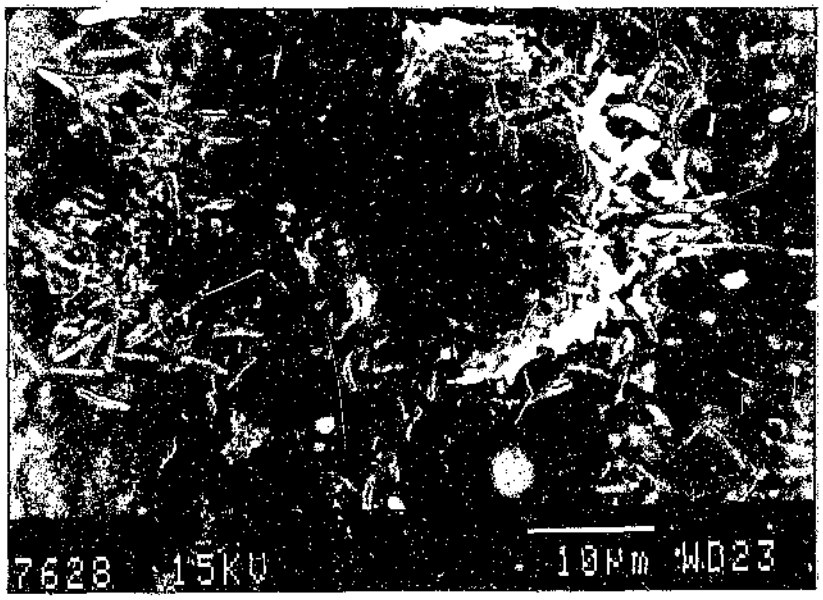

Figure 62. Later development of a colony of Desulfovibrio cells.

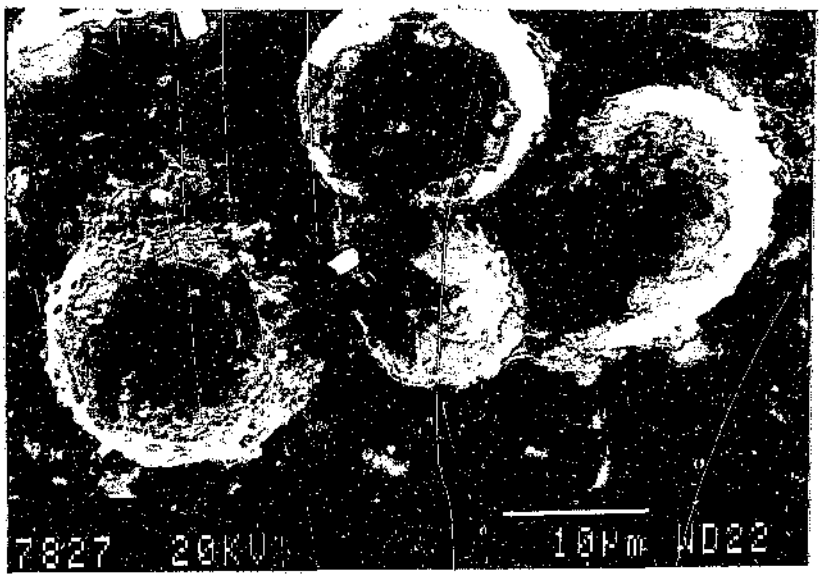

Figure 63. Tubercles covered with bacteria on mild steel: in *D.desulfuricans* culture in medium.

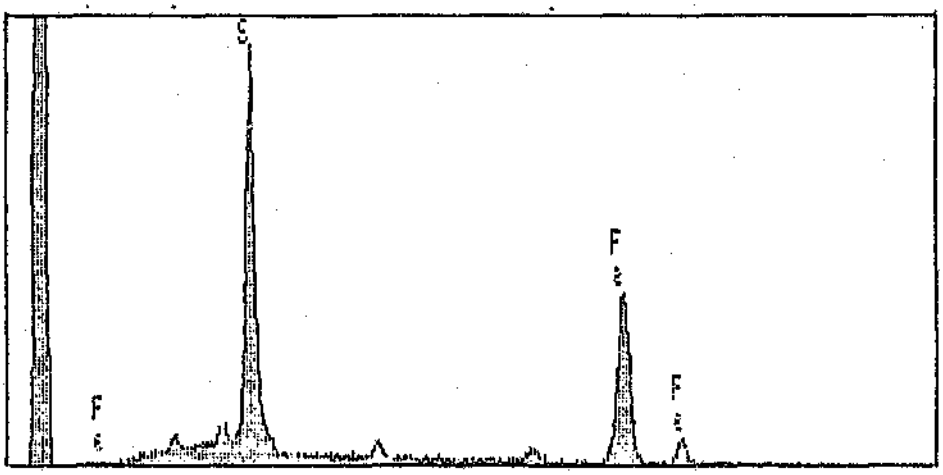

Figure 64. EDAX trace of FeS patches on alloys.

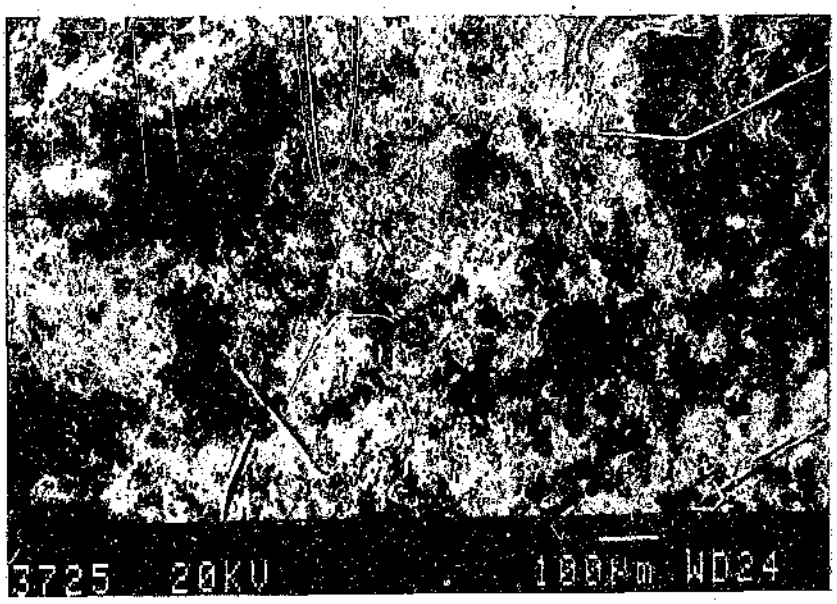

Figure 65. Patches of FeS corrosion product on the surface of 1070: in *D.desulfuricans* culture.

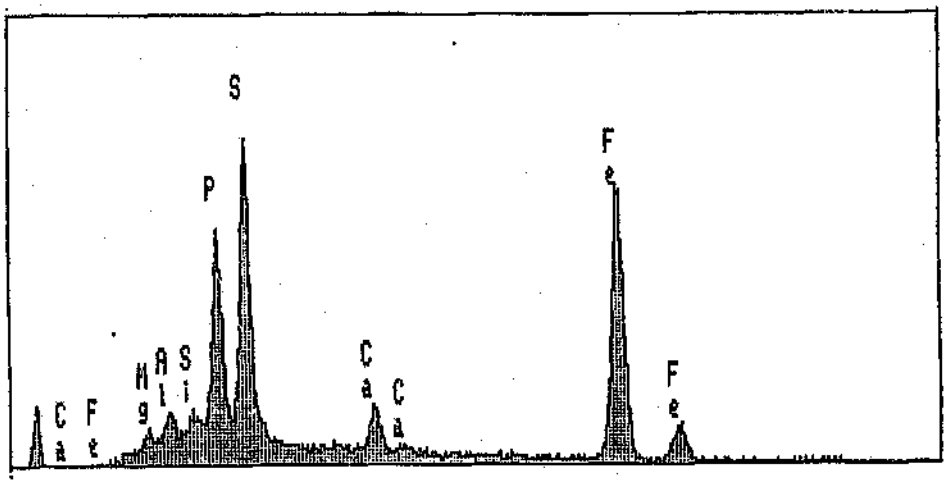

Figure 66. Typical EDAX trace of corrosion product.

Aluminium samples exposed to *Pseudomonas* cultures were heavily colonized (Fig. 67). Mild steel and 3CR12 also exhibited thick biofilms. Corrosion product on aluminium alloys consisted mainly of Al with small amounts of Si and P.

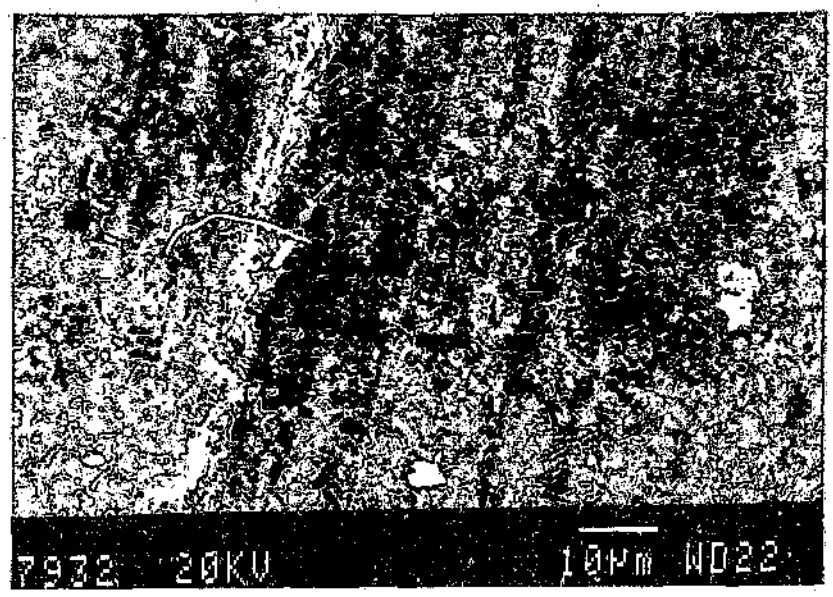

Figure 67. Alloy 5182 in Pseudomonas culture

All samples exposed to SRB showed severe pitting attack once the biofilm had been removed (Figs. 68 - 70). In the 5182 alloy, pitting was also noted at inclusions along the grain boundaries (Fig. 71). An EDAX analysis of the pits revealed the presence of Mg, Mn and Fe, suggesting preferential pitting at these inclusions. There was also evidence of intergranular attack on all the alloys (Fig. 72).

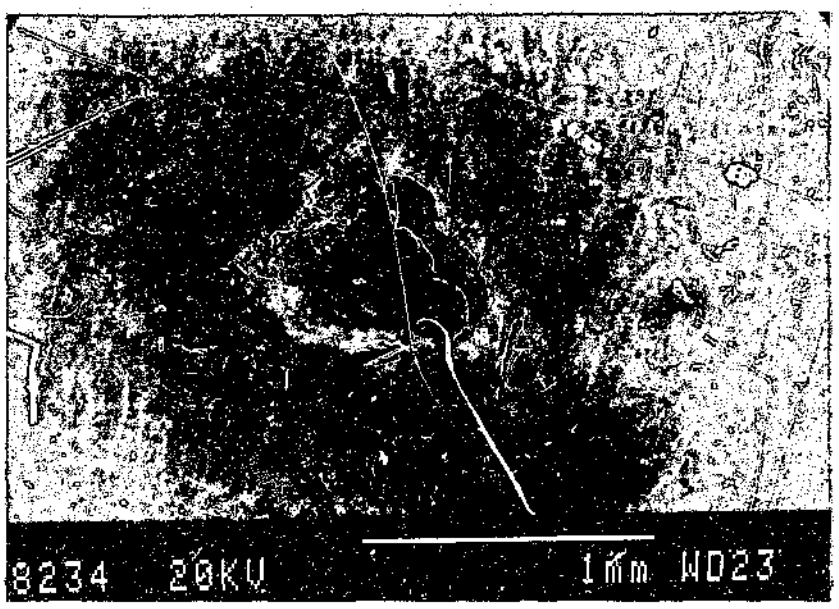

Figure 68. Start of a pit under a tubercle: Alloy 1070 in mixed SRB culture.

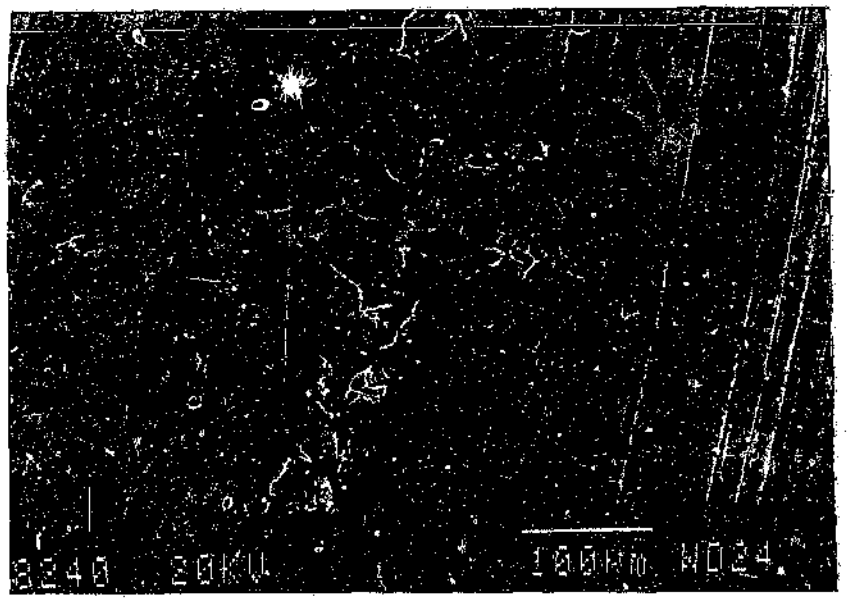

Figure 69. Alloy 6063 after immersion in a mixed SRB culture.

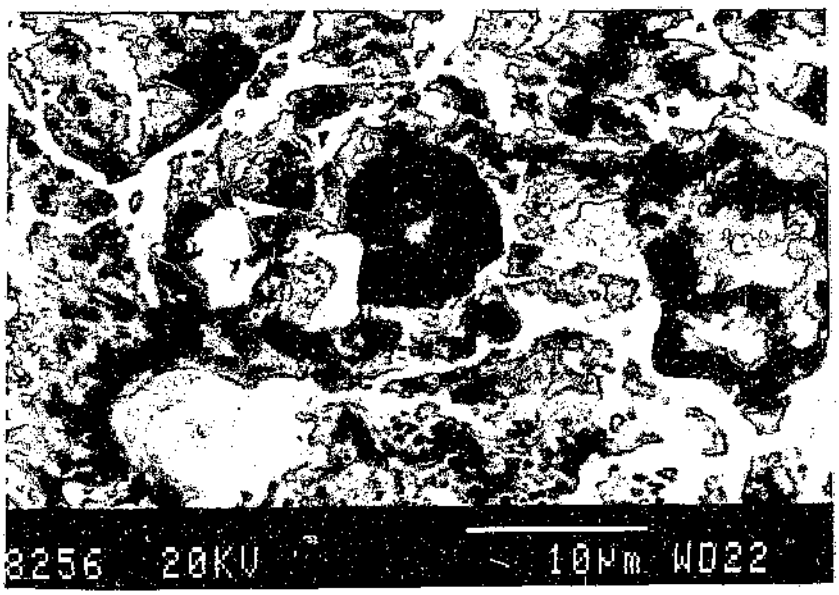

Figure 70. Pitting in mild steel.

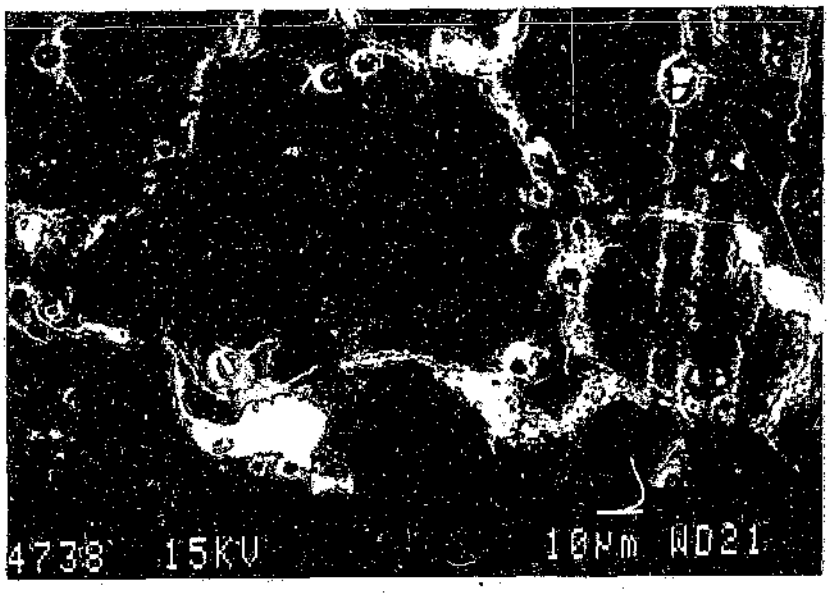

Figure 71. Pitting in alloy 5182: after immersion in *D.desulfuricans* culture.

Figure 72. Pitting and intergranular attack in alloy 6261.

Alloys exposed to *Pseudomonas* cultures were also pitted (Fig. 73), often along the grain boundaries (Fig. 74).

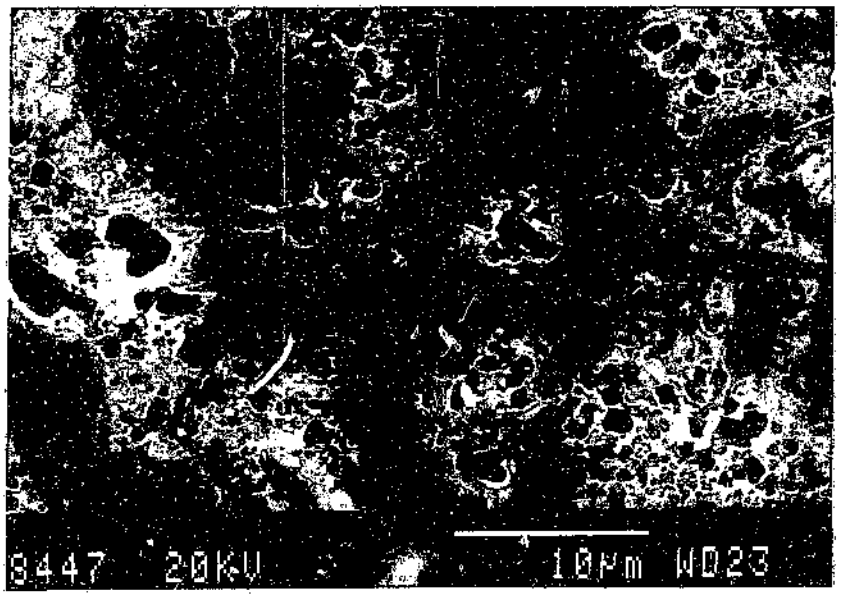

Figure 73. Alloy 6261 in Pseudomonas culture in medium: Cleaned condition.

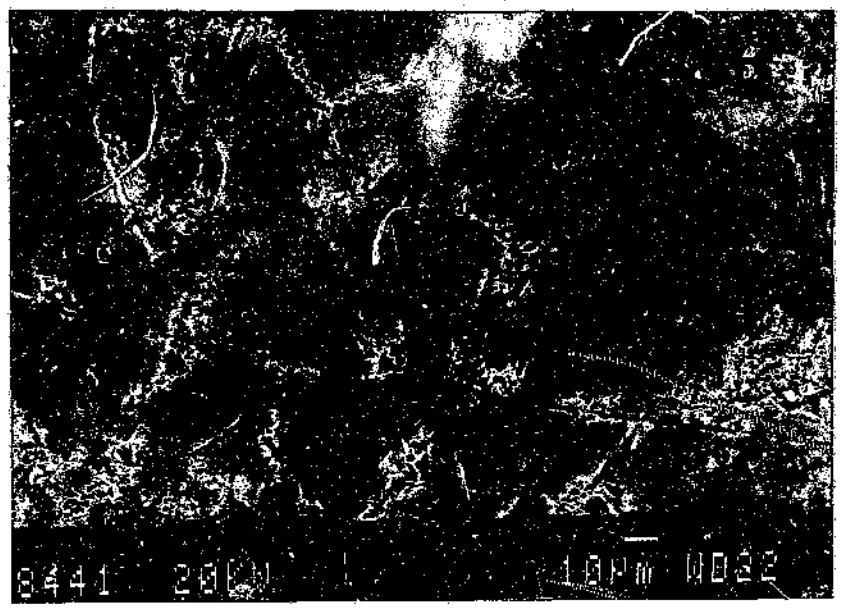

Figure 74. Alloy 1070 in Pseudomonas culture in medium.: Cleaned condition.

The control samples in sterile medium also exhibited some pitting, but this was not as severe as those exposed to bacteria and was possibly due to attack by chloride ions in the medium (Fig. 75). Some pitting was also seen to initiate at intermetallic compounds in the 5182 alloy (Fig. 76). The EDAX trace is shown in the following figure (Fig. 77), suggesting that the alloy is particularly susceptible to pit initiation at Fe- and Mn-rich inclusions. A generalized type of attack was also evident on aluminium samples (Fig. 78). Fig. 79 shows chloride type pitting attack on mild steel.

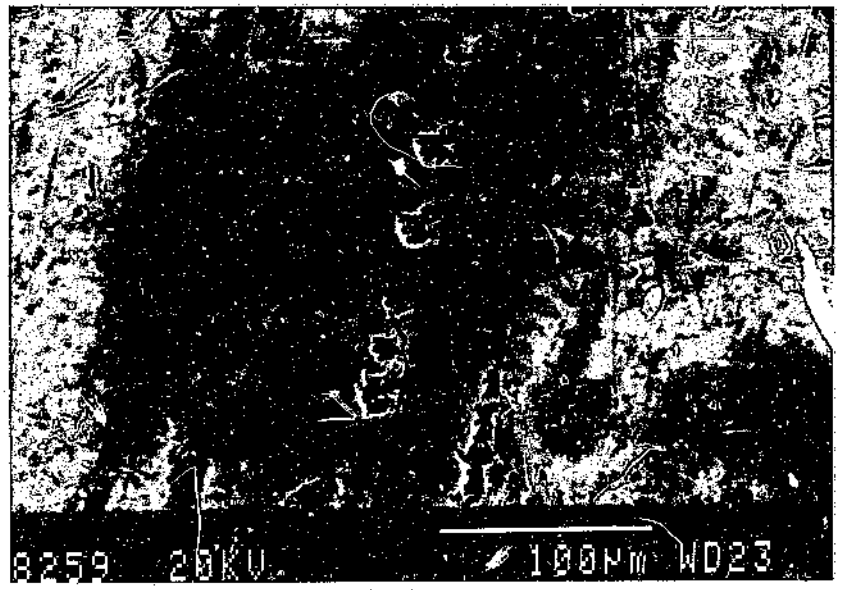

Figure 75. Pitting in alloy 1070 in sterile SRB medium.

Figure 76. Pit at inclusion in 5182 in sterile SRB medium.

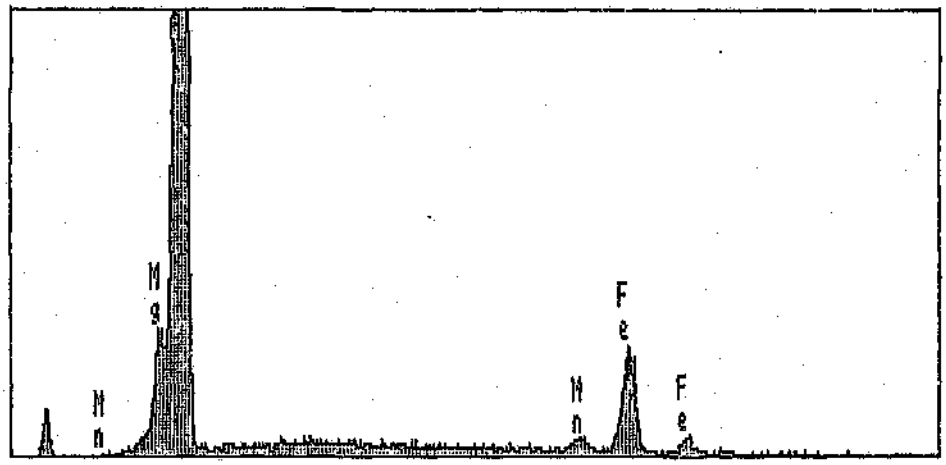

Figure 77. EDAX of intermetallic compounds in 5182 alloy.

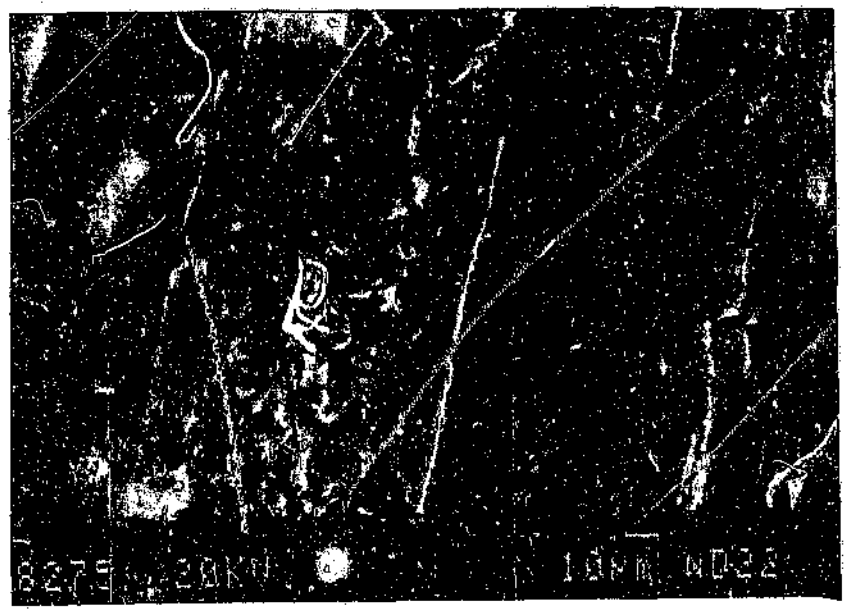

Figure 78. Alloy 6261 in sterile SRB medium.

Figure 79. Chloride pitting in mild steel in sterile SRB medium.

4.2.2 Tests in mine water.

The mixed SRB culture in mine water colonized the aluminium alloys showing the typical elongated filaments with tufts of cells (Fig. 80). Individual colonies in the process of dividing to form coherent biofilm were observed (Fig. 81). Masses of bacteria and corrosion product were common on the surface (Fig. 82).

3CR12 and mild steel specimens were more heavily colonized (Fig. 83). Tubercles covered with bacteria were common (Fig. 84).

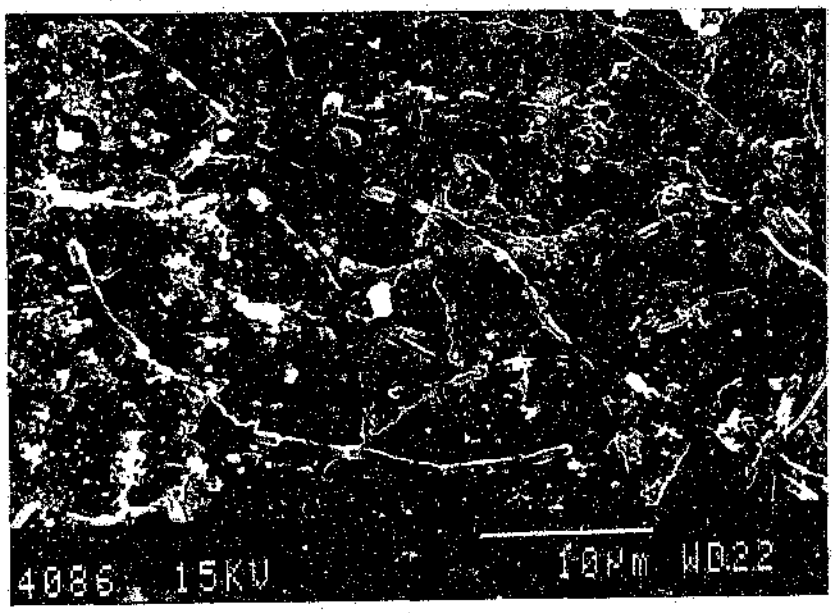

Figure 80. Alloy 6261 in a culture of mixed SRB in mine water.

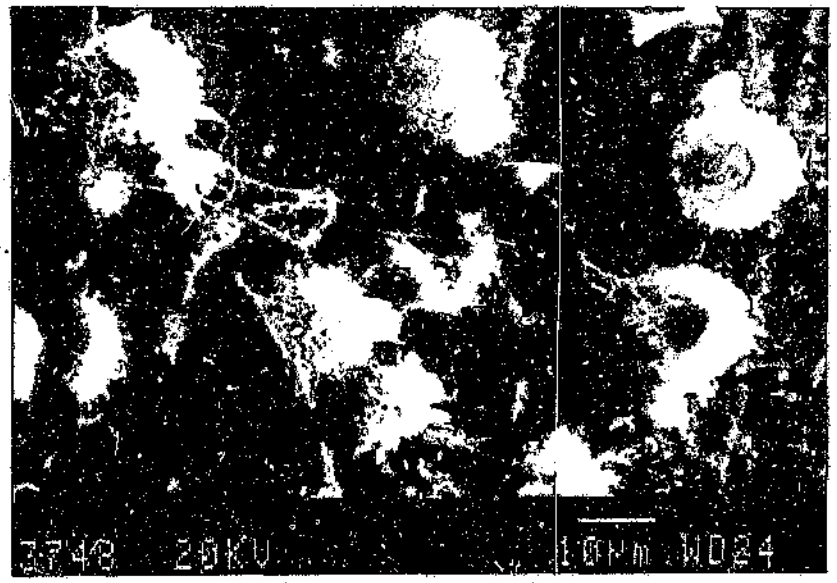

Figure 81. Individual bacterial colonies on 6063 in mixed SRB culture in mine water. Note interlinking by glycocalyx strands.

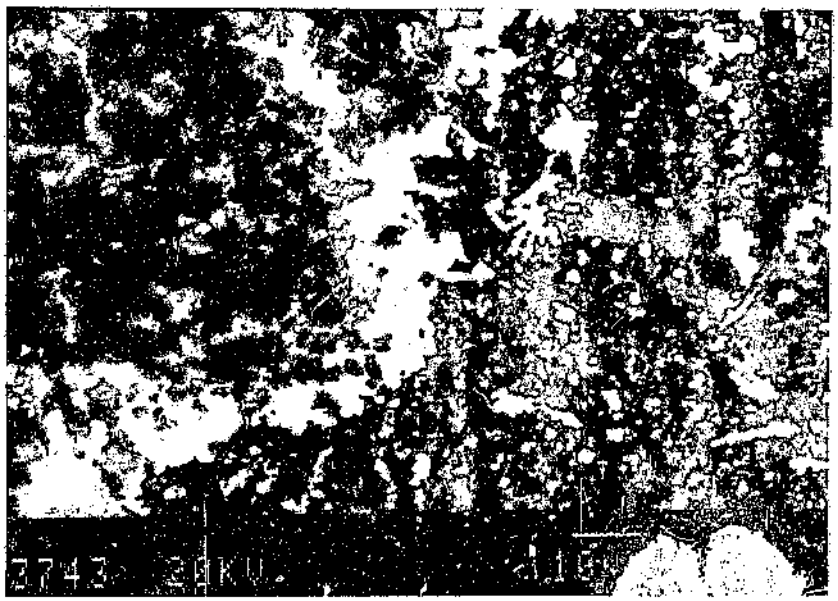

Figure 82. Tubercle and bacteria on alloy 5182: in mixed SRB culture mine water.

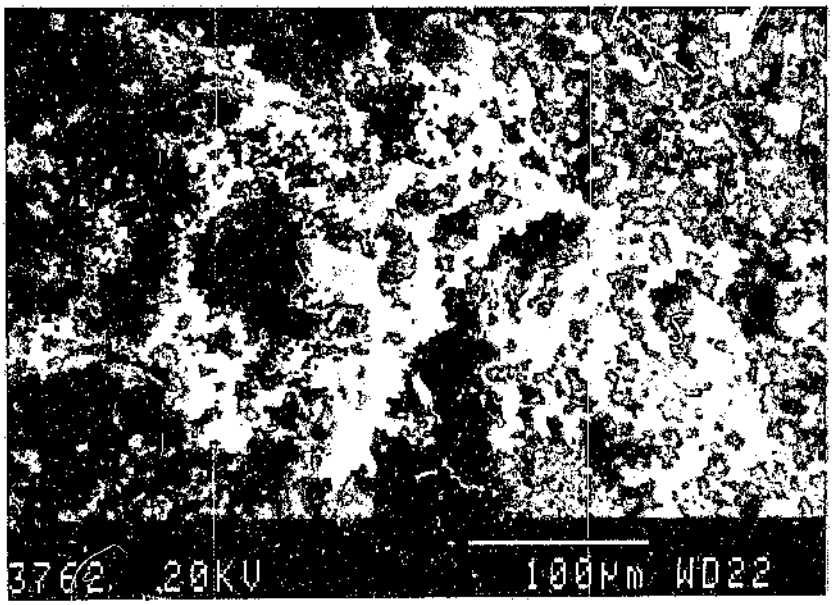

Figure 83. Biofilm on 3CR12 in mixed SRB culture in mine water.

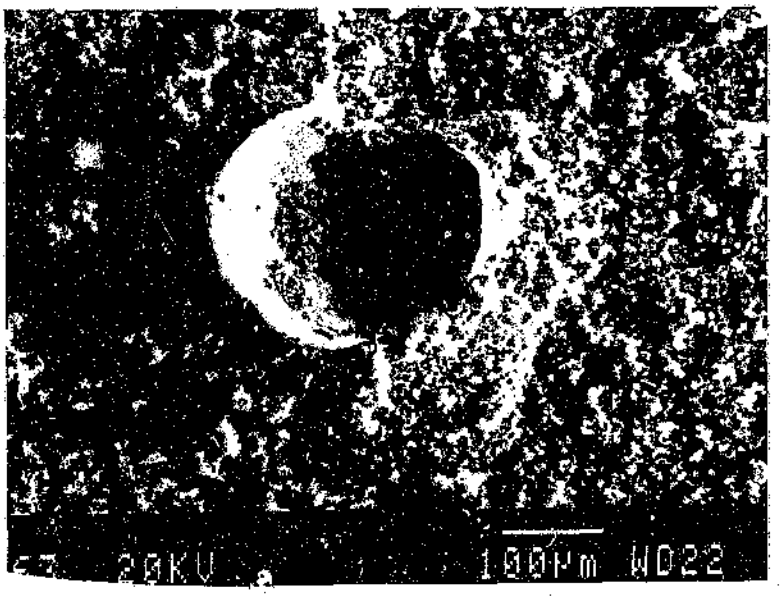

Figure 84. Hollow tubercle on mild steel in mixed SRB culture in mine water.

In the *D.desulfuricans* culture, colonization of the aluminium alloy surfaces was sparser than in the mixed SRB culture. This was especially so on the 1070 and 5182 alloy surfaces where few to no cells were observed. Biofilm did, however, develop on the 6-series alloys (Fig. 85).

Colonization of 3CR12 and mild steel was well developed as shown by the thick biofilm development (Fig. 86). Tubercles on the mild steel surface are depicted in Fig. 87.

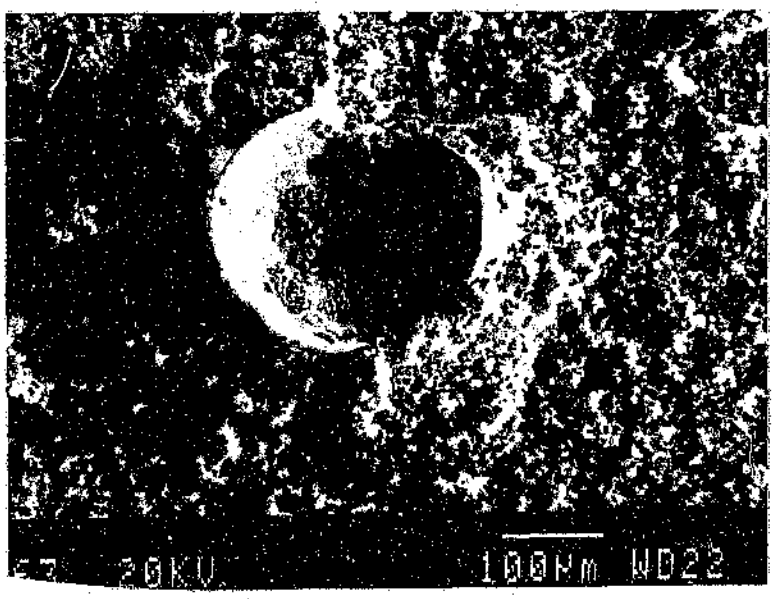

Figure 84. Hollow tubercle on mild steel: in mixed SRB culture in mine water.

In the *D.desulfuricans* culture, colonization of the aluminium alloy surfaces was sparser than in the mixed SRB culture. This was especially so on the 1070 and 5182 alloy surfaces where few to no cells were observed. Biofilm did, however, develop on the 6-series alloys (Fig. 85).

Colonization of 3CR12 and mild steel was well developed as shown by the thick biofilm development (Fig. 86). Tubercles on the mild steel surface are depicted in Fig. 87.

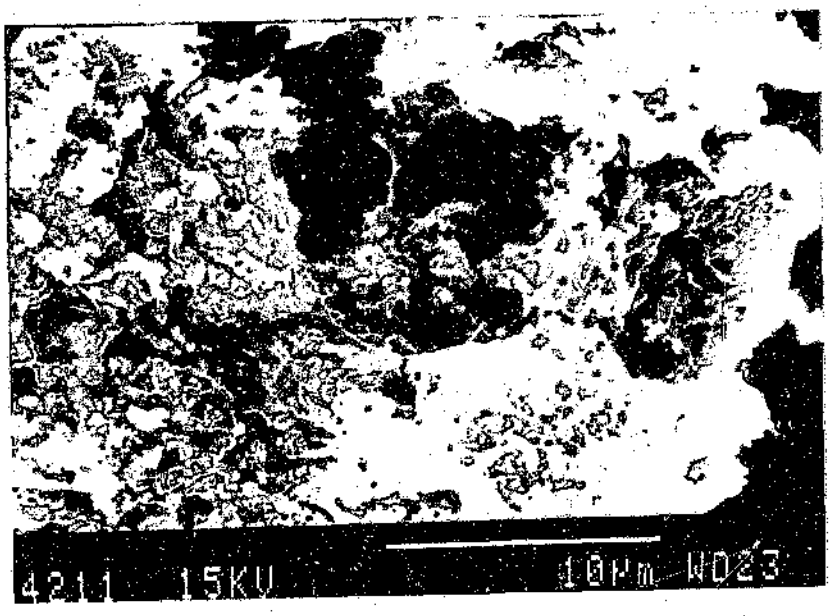

Figure 85. Biofilm on 6063 in D.desulfuricans culture in mine water.

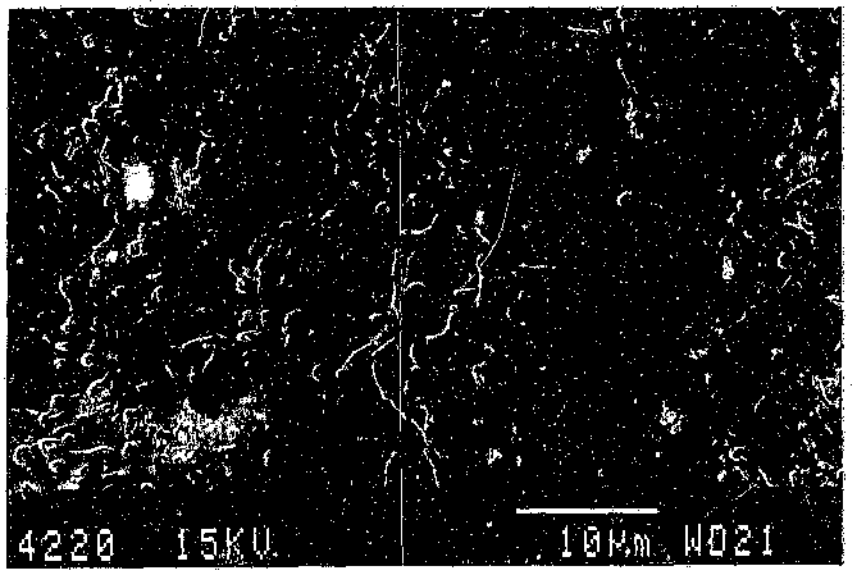

Figure 86. Surface of 3CR12 after immersion in D.desulfuricans culture in mine water.

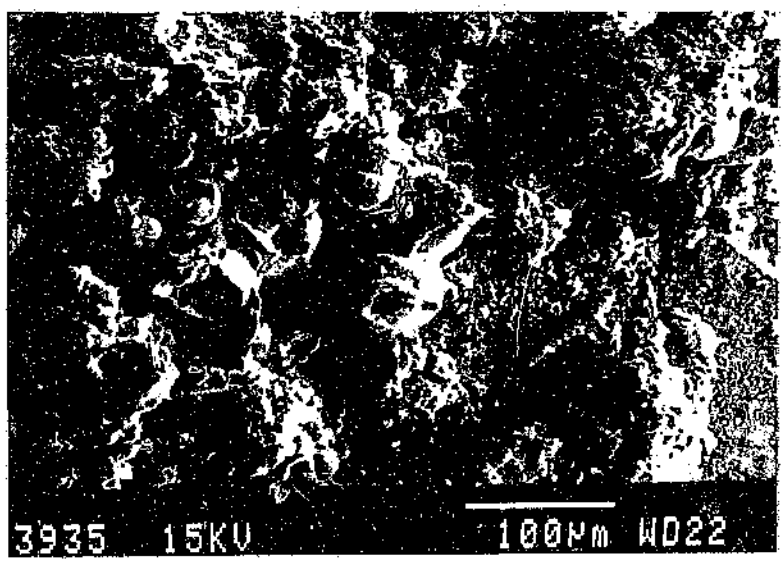

Figure 87. Tubercles on mild steel in D.desulfuricans culture in mine water.

Corrosion product on aluminium alloys contained mainly Al, P, S, Ca, Fe (EDAX traces in Fig. 88). FeS was the main corrosion product on the ferrous metals.

Both aluminium and ferrous coupons were well colonized by Pseudomonads. The surfaces were typically covered by mounds of bacteria and large amounts of corrosion product (Fig. 89). The EDAX trace of corrosion product from Fig. 89 appears in Fig. 90.

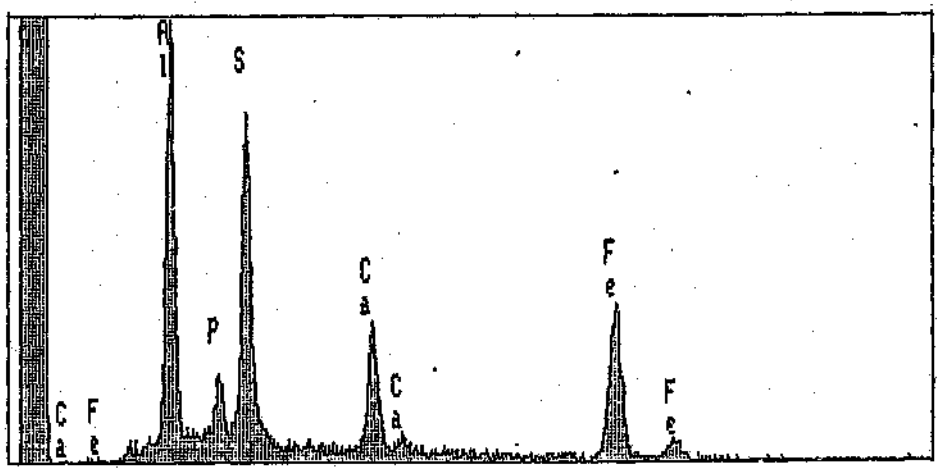

Figure 88. EDAX of corrosion product on aluminium alloys.

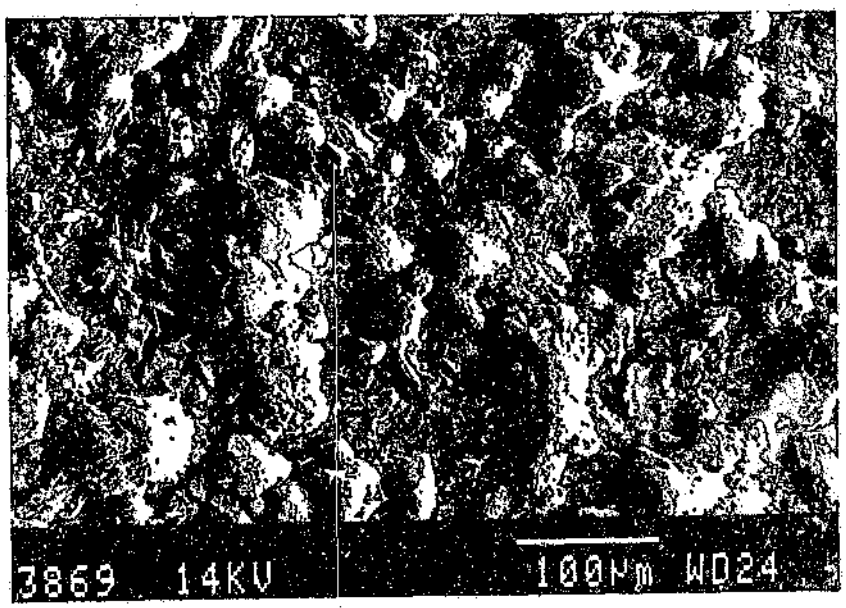

Figure 89. Mounds of bacterial growth and corrosion product on 5182 in *Pseudomonas* culture in mine water.

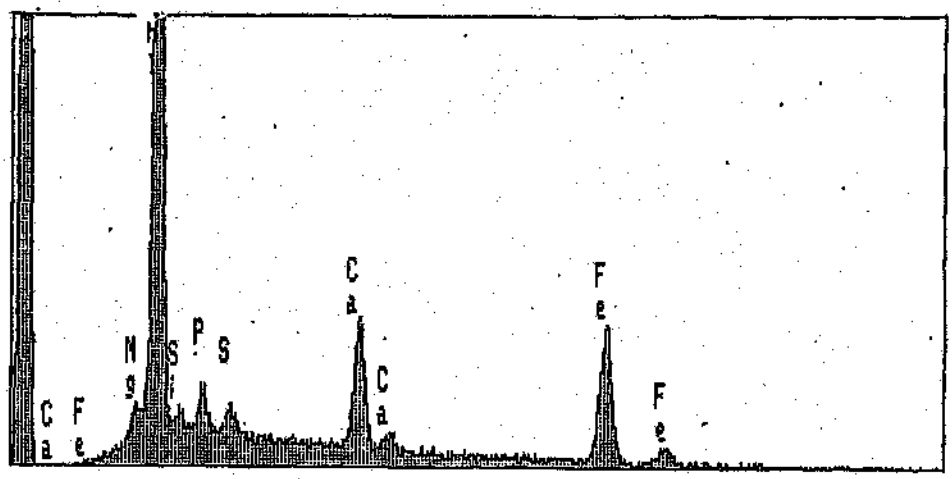

Figure 90. EDAX of corrosion product.

It was difficult to compare the type of corrosion damage on aluminium coupons in the deaerated mine water. This was due to the fact that the control coupons also underwent severe corrosion. This seemed to be mainly in the form of selective dissolution of a certain phase and severe pitting of the remaining phase (Figs. 91 and 92). Minimal damage was observed on the ferrous samples.

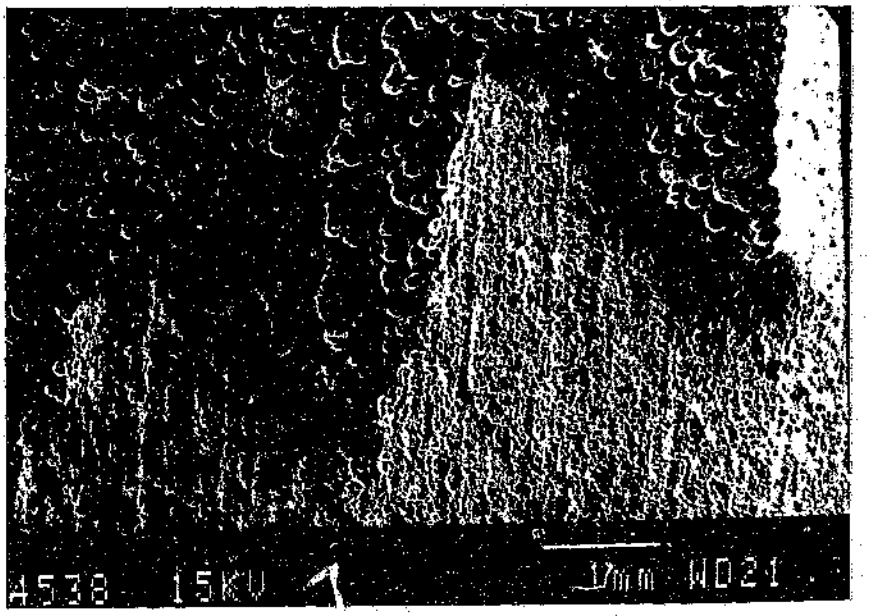

Figure 91. Alloy 5182 in sterile deaerated mine water.

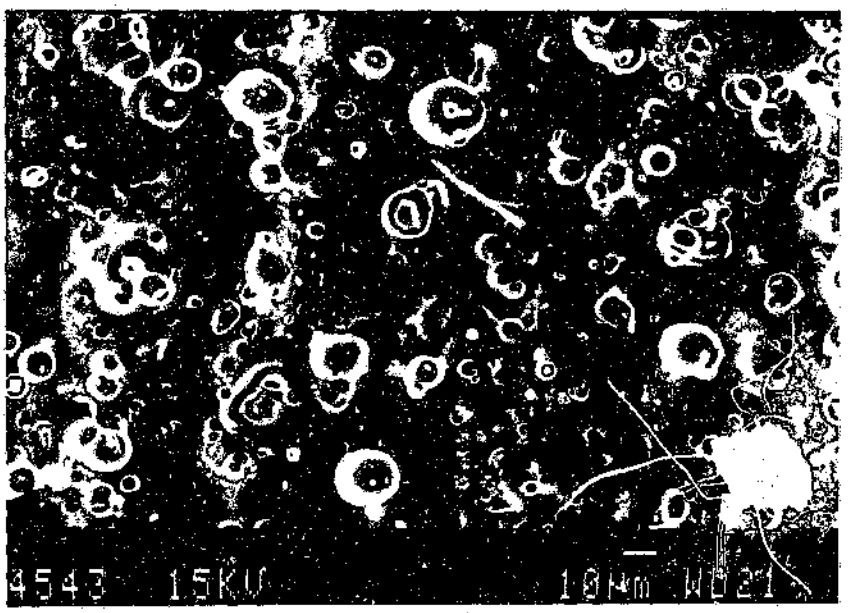

Figure 92. Alloy 6261 in sterile deaerated mine water showing pitting attack.

Coupons exposed to *D.desulfuricans* cultures were damaged by pitting attack especially in the case of the 6-series alloys (Fig. 93). In some cases, this was seen to follow the grain boundaries (Fig. 94). The 1070 and 5182 alloys tended to show selective phase attack as in the controls (Fig. 95).

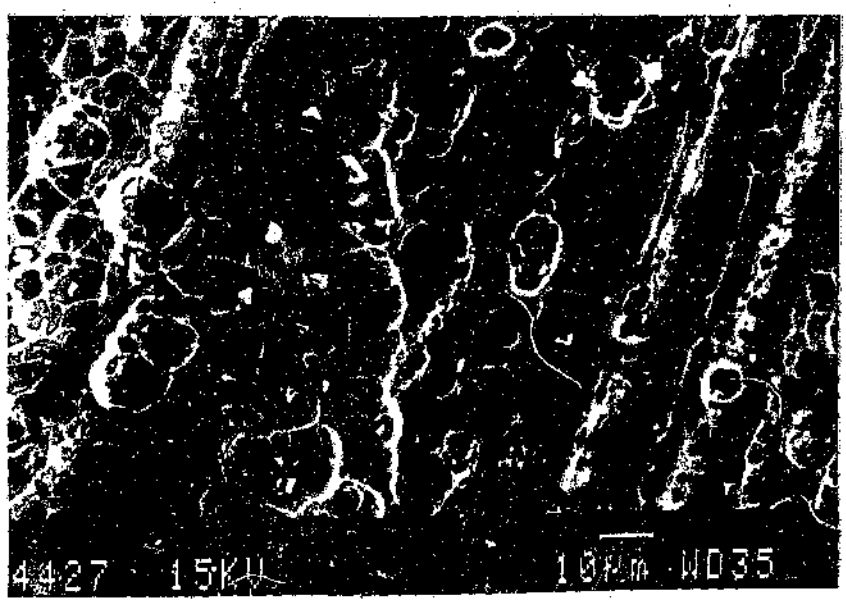

Figure 93. Pitting in alloy 6261: after immersion in *D.desulfuricans* culture in mine water.

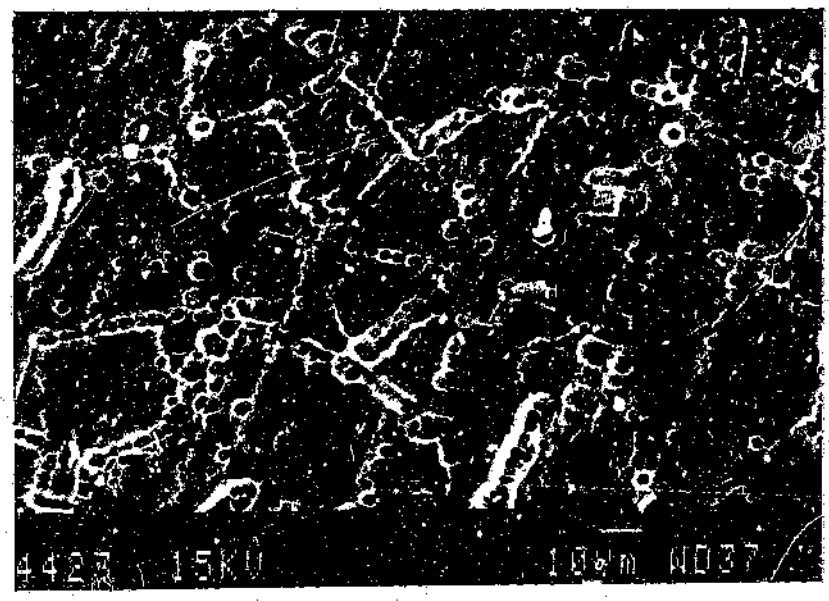

Figure 94. Pitting along grain boundaries: Alloy 6063 in *D.desulfuricans* culture in mine water.

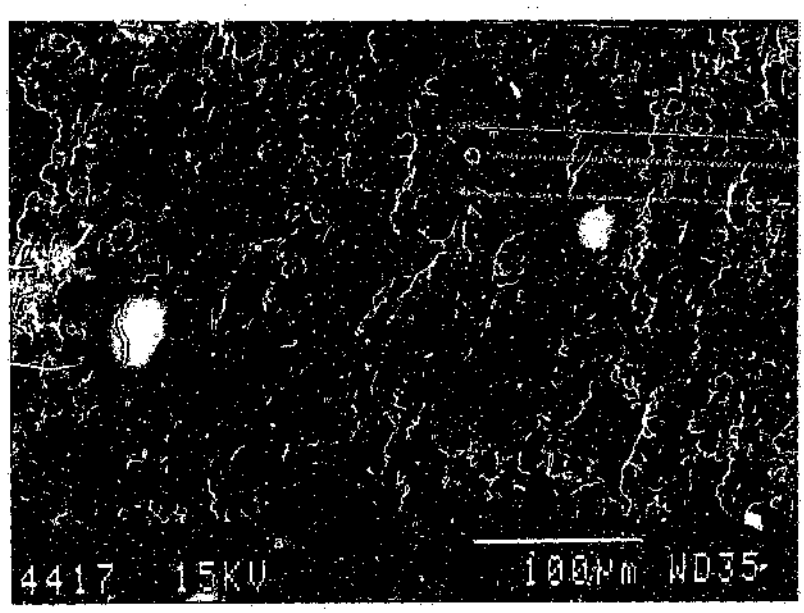

Figure 95. Alloy 6063 in D.desulfuricans culture in mine water.

Damage to coupons in the mixed SRB culture was more severe and presented itself as pitting (Figs. 96 and 97) and intergranular attack. The ferrous metals also underwent these types of attack (Fig. 98). Selective phase dissolution was also evident (Fig. 99).

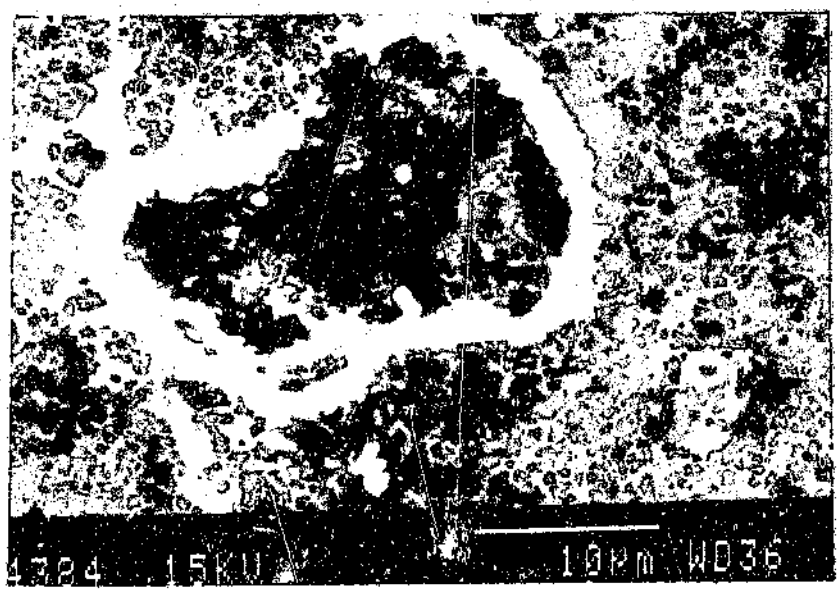

Figure 96. Alloy 1070 in mixed SRB culture in mine water.

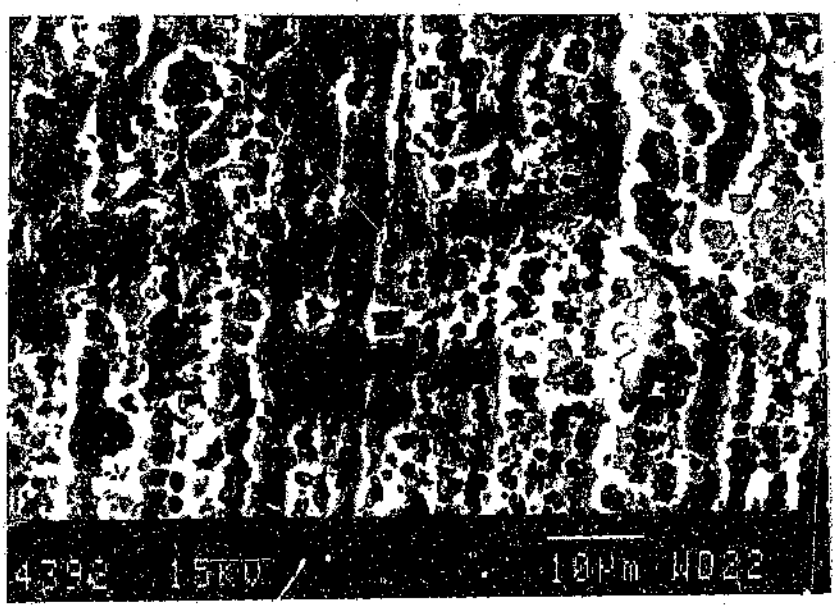

Figure 97. Pitting in alloy 6063 in mixed SRB culture in mine water.

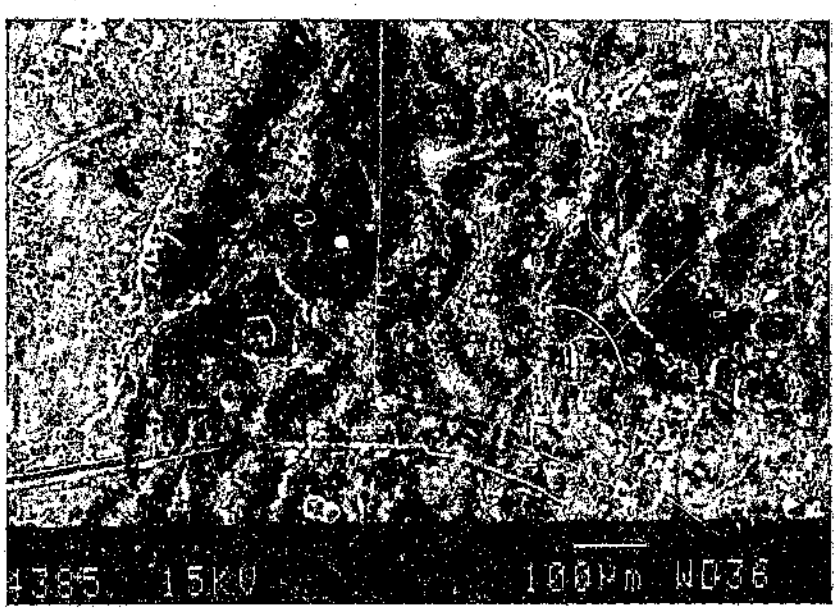

Figure 98. Intergranular corrosion of mild steel: in mixed SRB culture in mine water.

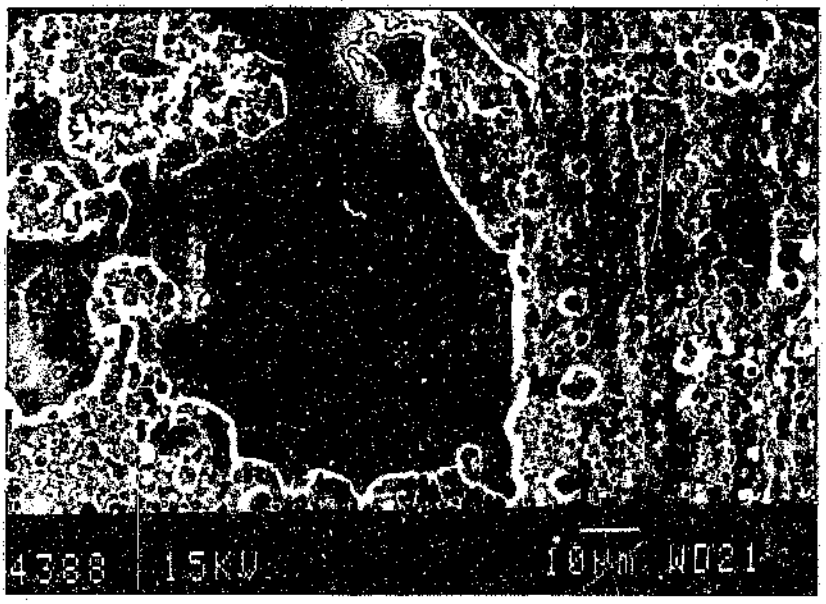

Figure 99. Selective corrosion of phases and pitting in 5182 in mixed SRB culture in mine water.

Pitting was found on samples exposed to *Pseudomonas* cultures in mine water. This seemed to initiate at inclusions especially, in the 5182 alloy (Figs. 100 and 101). Fig. 102 is the EDAX trace of the inclusion in this alloy and shows a small amount of Mg and preferential pit initiation at Fe- and Mn-rich intermetallic compounds. Intergranular attack (Fig. 103) and selective phase attack (Fig. 104) were also observed.

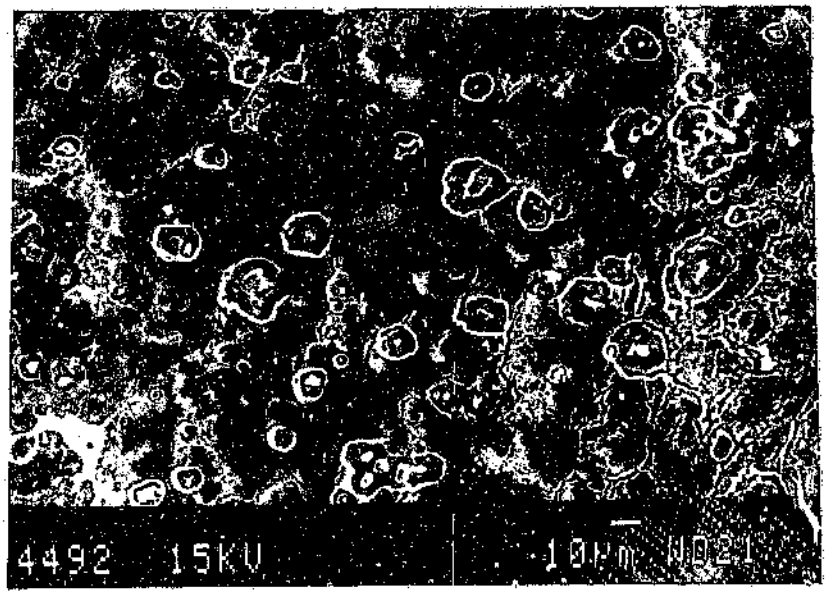

Figure 100. Pitting at inclusions in alloy 5182: in *Pseudomonas* culture in mine water.

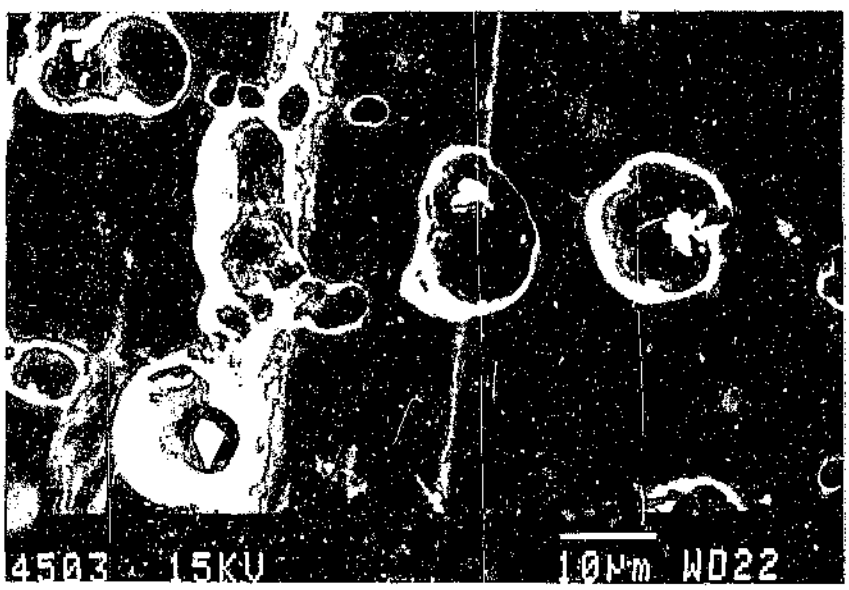

Figure 101. Pitting of alloy 6261 after immersion in Pseudomonas culture in mine water.

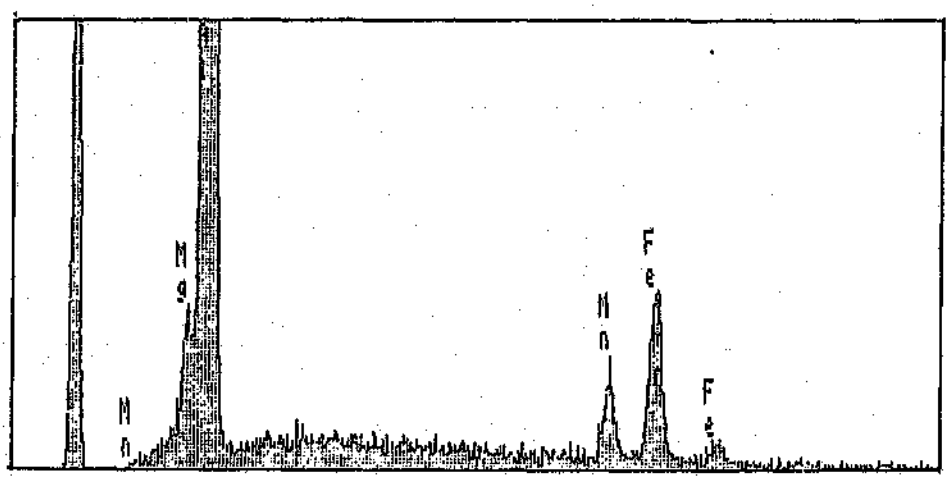

Figure 102. EDAX trace of inclusion in 5182 alloy.

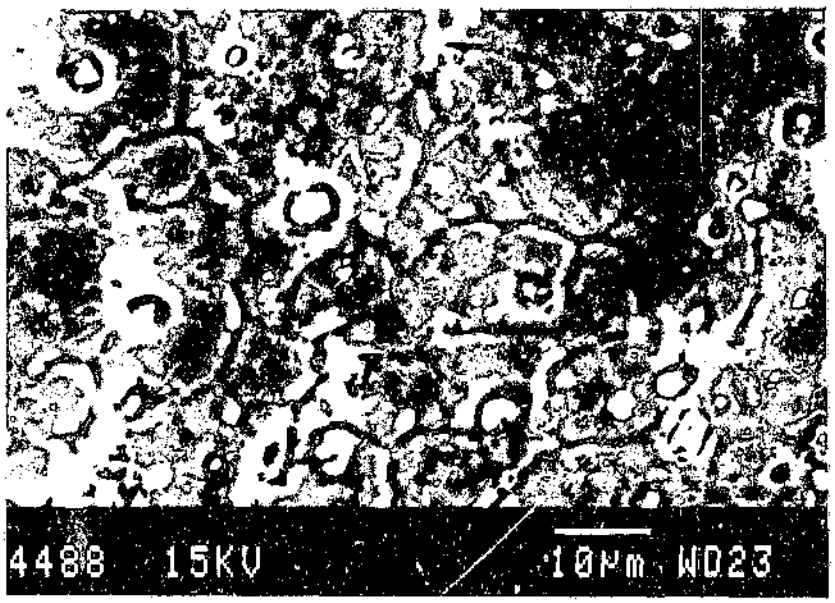

Figure 103. Alloy 6063 in Pseudomonas culture in mine water.

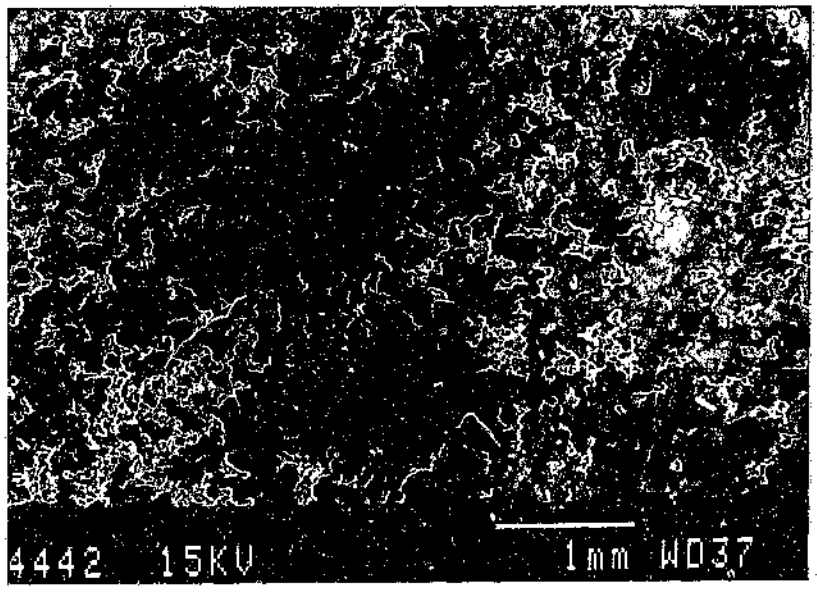

Figure 104. Selective attack of phases in 1070: in *Pseudomonas* culture in mine water.

Pitting attack was observed in the control samples, though not as severe as in the bacterial cultures (Fig. 105). This also seemed to nucleate at inclusions.

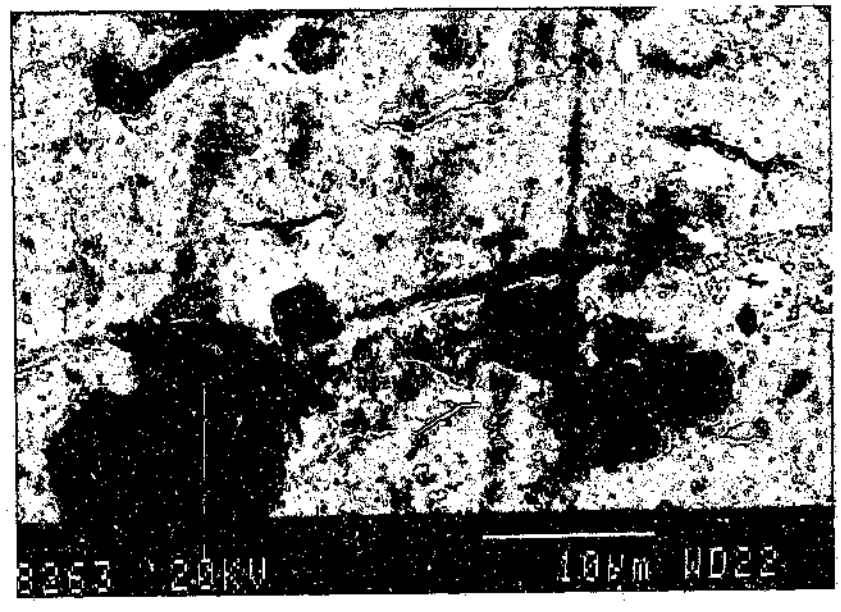

Figure 105. Alloy 1070 in sterile aerated mine water.

4.2.3 Weight Loss test results.

Weight loss test results for the alloys exposed under different conditions are depicted in the diagrams below (Figs. 106 and 107). Actual values may be found in the table in Appendix C.

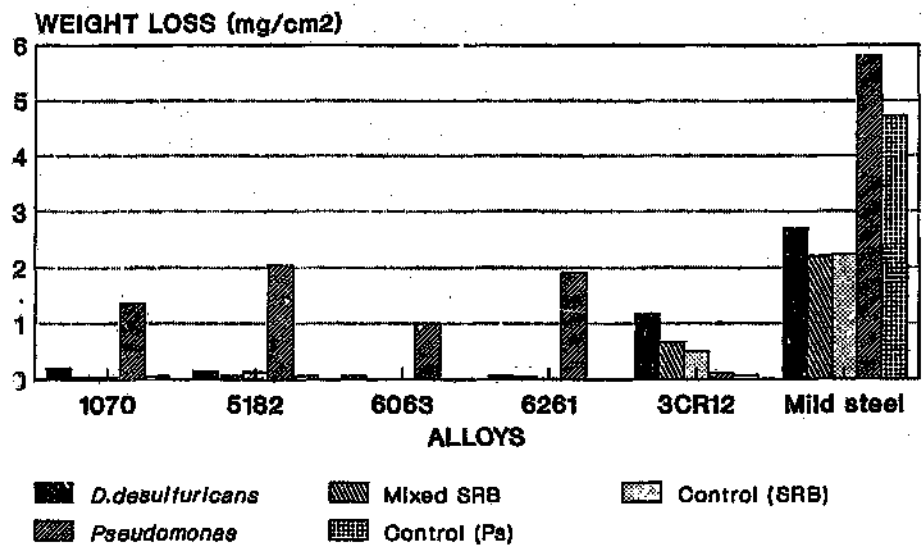

Figure 107

4.2.3 Weight Loss test results.

Weight loss test results for the alloys exposed under different conditions are depicted in the diagrams below (Figs. 106 and 107). Actual values may be found in the table in Appendix C.

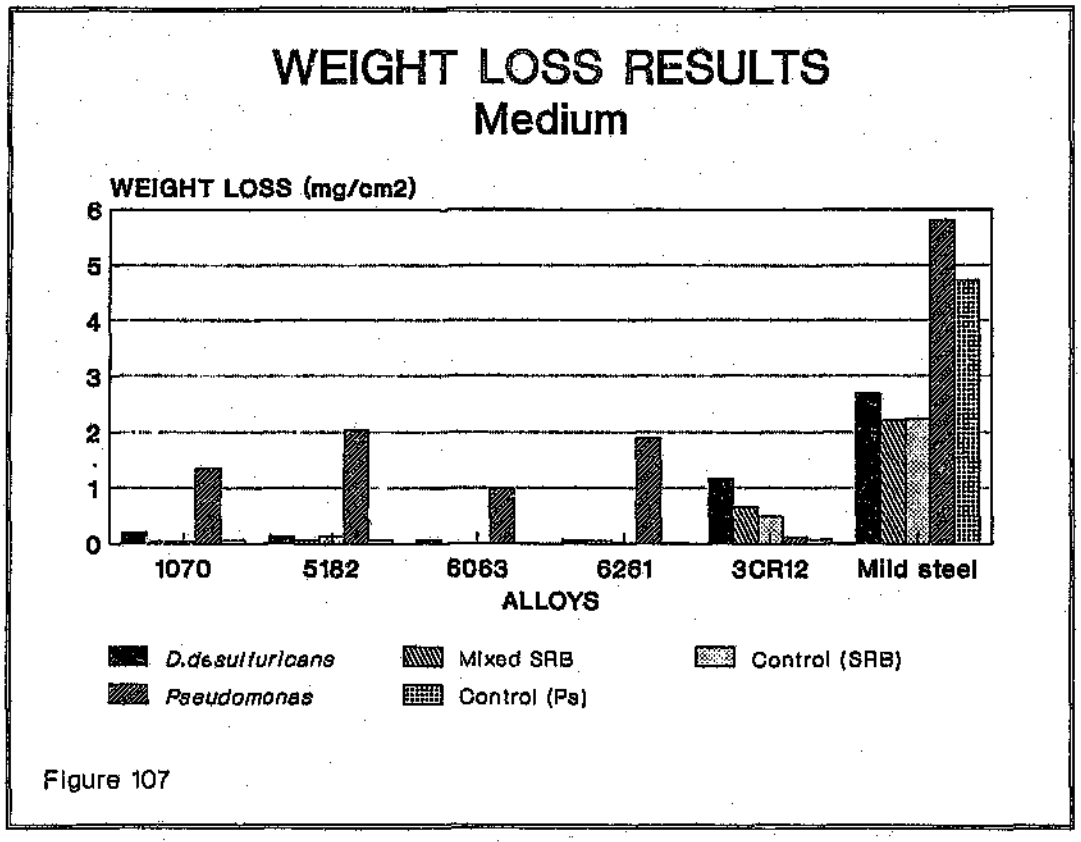

Figure 107

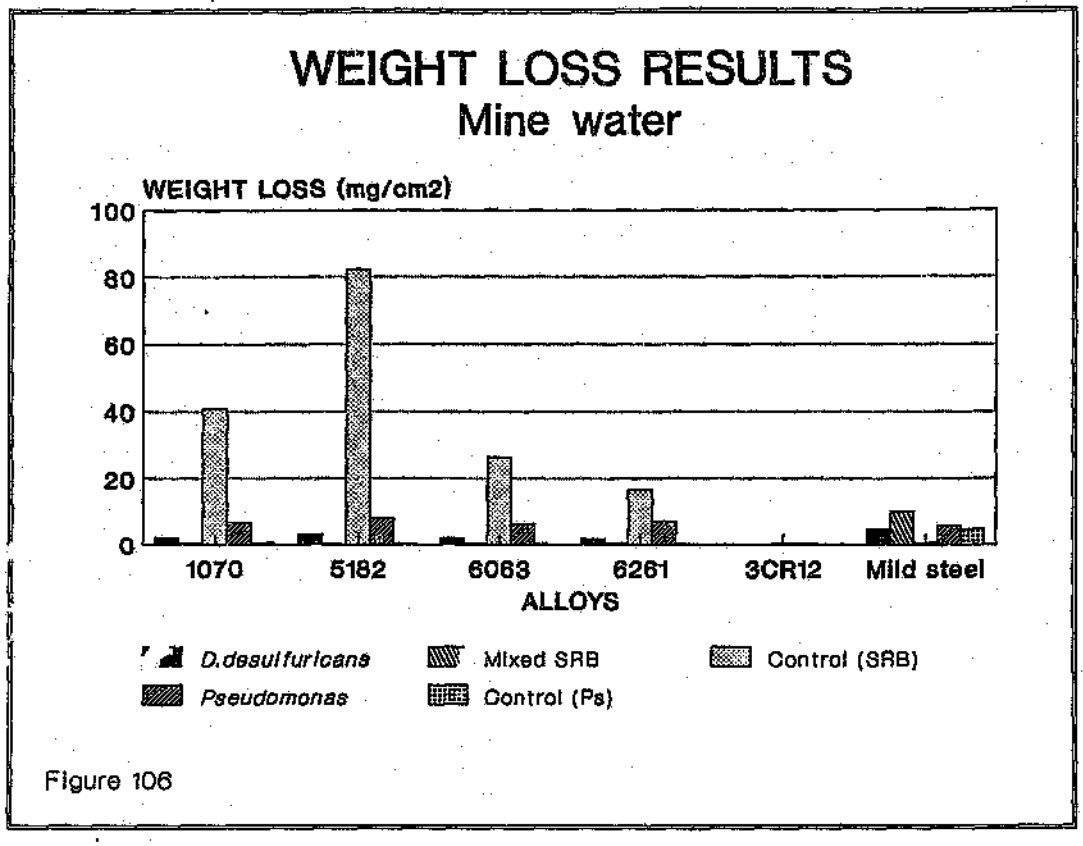

Figure 106

4.3 IMMERSION TESTS - FLOW CONDITIONS

The condition of the samples on removal from the flow loop after exposure to both sterile mine water and mine water containing bacteria are shown in Figs. 108 and 109. Under both exposure conditions, the samples appeared to be visually largely undamaged. In both cases the 6261 alloy was covered with an adherent dark brown film, though in the mine water containing bacteria, this alloy was also encrusted with a scale-like deposit in places.

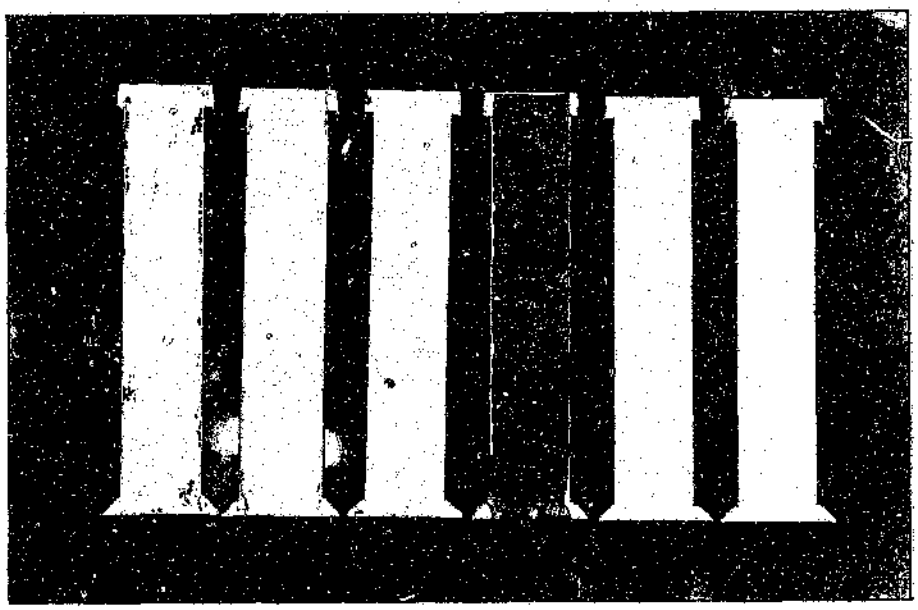

Figure 108. Condition of coupons on removal from sterile flow loop.

Figure 109. Condition of coupons on removal from flow loop with bacteria.

Figure 108. Condition of coupons on removal from sterile flow loop.

Figure 109. Condition of coupons on removal from flow loop with bacteria.

Using SEM, it was observed that the alloys were in fact sparsely populated by clumps of cells covered with corrosion product comprising mainly Al, S, P and Ca. (Figs. 110 and 111). Most of the surface was covered by a layer of 'mud-cracked' corrosion product (Fig. 112), which was also present on the control samples. The dark surface deposit on alloy 6261 was shown by the EDAX analysis to contain Al, Si, S, Ca and Cu (Fig. 113). This was for both the control and test samples. The scale deposit on 6261 was identified by EDAX as containing Al, Si, S and Ca. There was no colonization on either the anodized or conversion coated specimens.

Figure 110. Alloy 1070 from flow loop with bacteria.

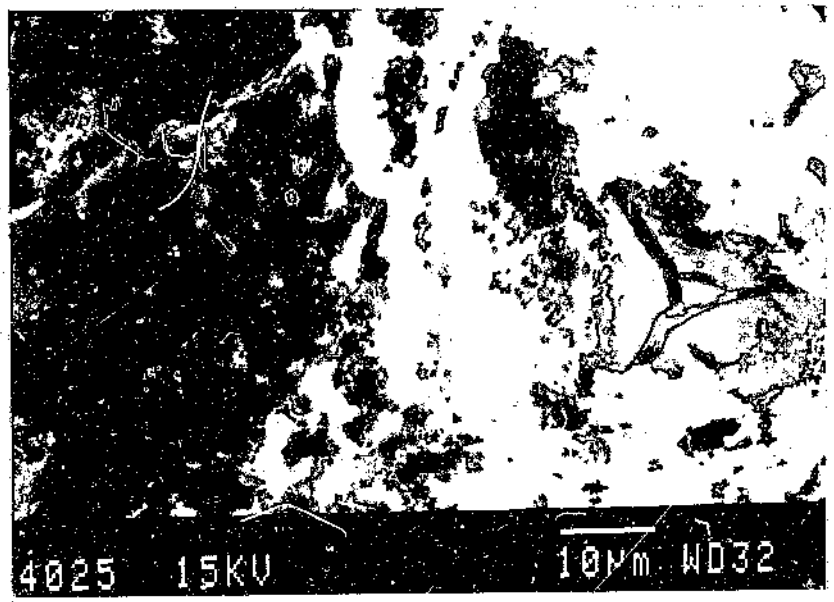

Figure 111. Alloy 5182 from flow loop with bacteria.

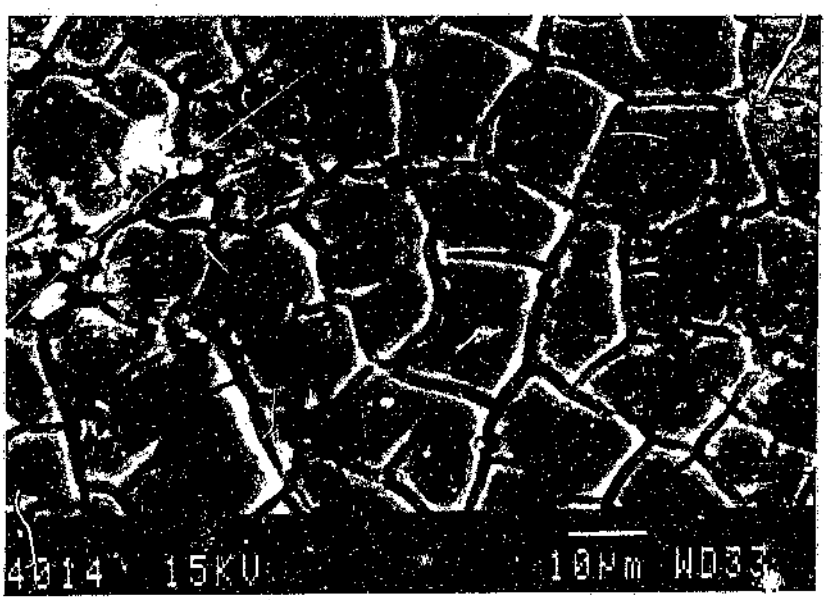

Figure 112. Alloy 1070 from flow loop with bacteria.

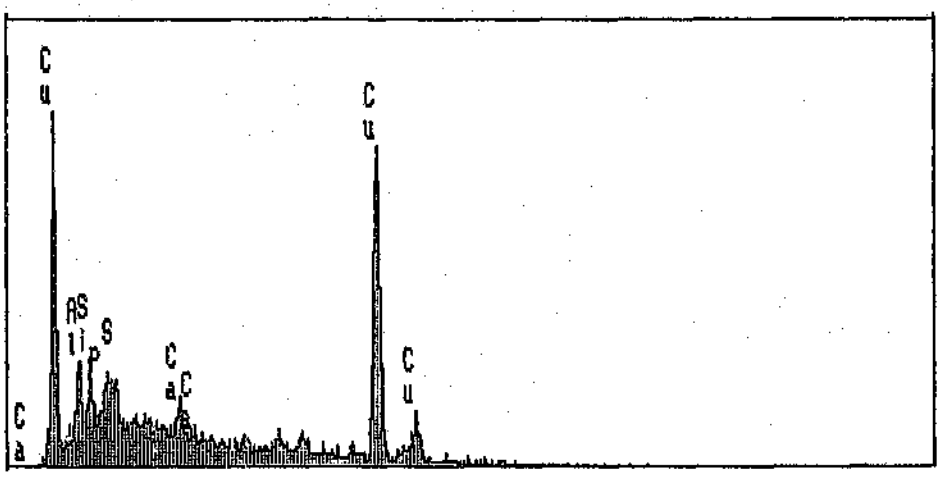

Figure 113. EDAX trace of surface deposit on alloy 6261.

Damage to the samples was minimal, both for control and test coupons. This was the case for all alloys except 6261 which exhibited severe pitting under the scale deposit (Fig. 114).

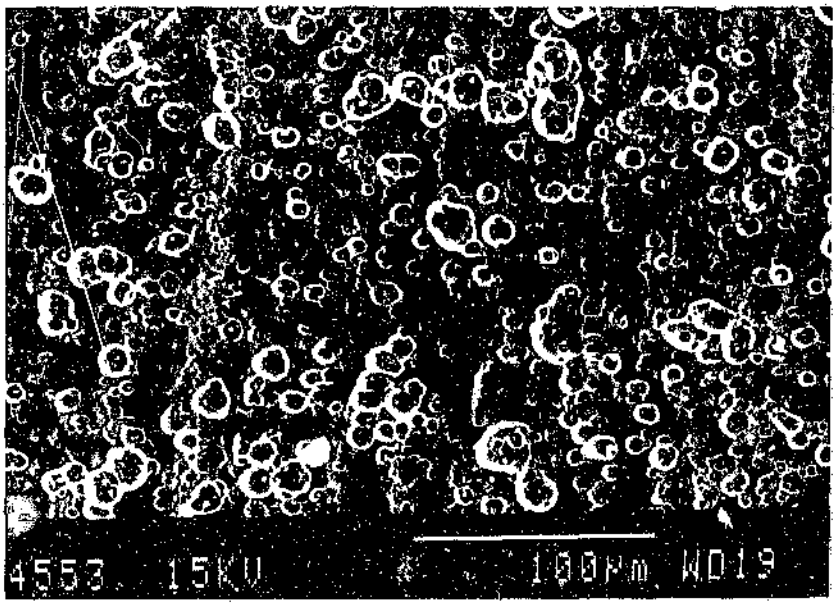

Figure 114. Pitting under scale deposit in 6261 in flow loop with bacteria.

4.3.1 Weight loss test results

Weight loss test results for the alloys under flow conditions in both sterile and bacterially infected water are shown in Fig. 115. The actual values may be found in the table in Appendix D.

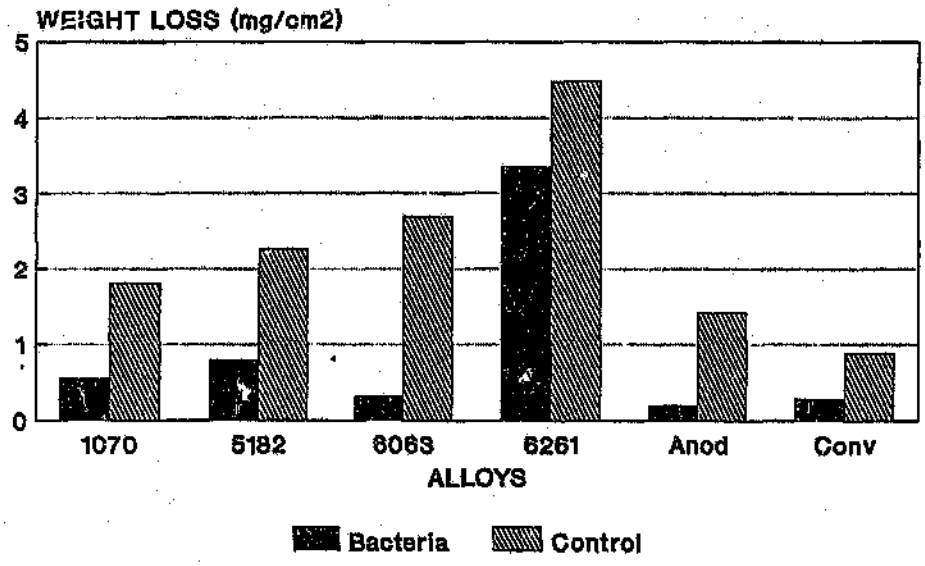

Figure 115

4.4 ELECTROCHEMICAL TESTS - STATIC

4.4.1 Potentiodynamic scans

This technique is of value when comparing alloys in a given environment and offers a rapid means of obtaining relative general corrosion rates of a number of alloys. The general corrosion rate results are summarised in the table below.

Table 4. Corrosion rates from static immersion tests in mine water and medium.

		MINE WATER	MEDIUM
	Alloys	Corrosion rate (mpy)	Corrosion rate (mpy)
D.desulfuricans	1070	0.23	0.18
	5182	0.35	0.14
	6063	0.48	0.05
	6261	0.34	0.13
Mixed SRB	1070	0.92	0.02
	5182	0.40	0.03
	6063	0.27	0.02
	6261	1.23	0.35
Control SRB	1070	0.71	0.14
	5182	0.14	0.52
	6063	0.42	0.08
	6261	0.59	0.20
Pseudomonas	1070	0.29	0.08
	5182	0.67	0.61
	6063	0.30	0.04
	6261	0.42	0.52
Pseudomonas (C)	1070	0.07	0.17
	5182	0.03	1.70
	6063	0.46	0.06
	6261	0.21	0.14

4.4.2 Cyclic polarization scans.

Pitting scans were conducted for all alloys in both medium and mine water containing either ammonium sulphate (AS) or ferrous ammonium sulphate (FAS) as a redox poising chemical.

Fig. 116 represents a typical pitting curve defining the various symbols used for the main characteristic pitting potentials. The amount of hysteresis is directly proportional to the crevice resistance of the alloy.

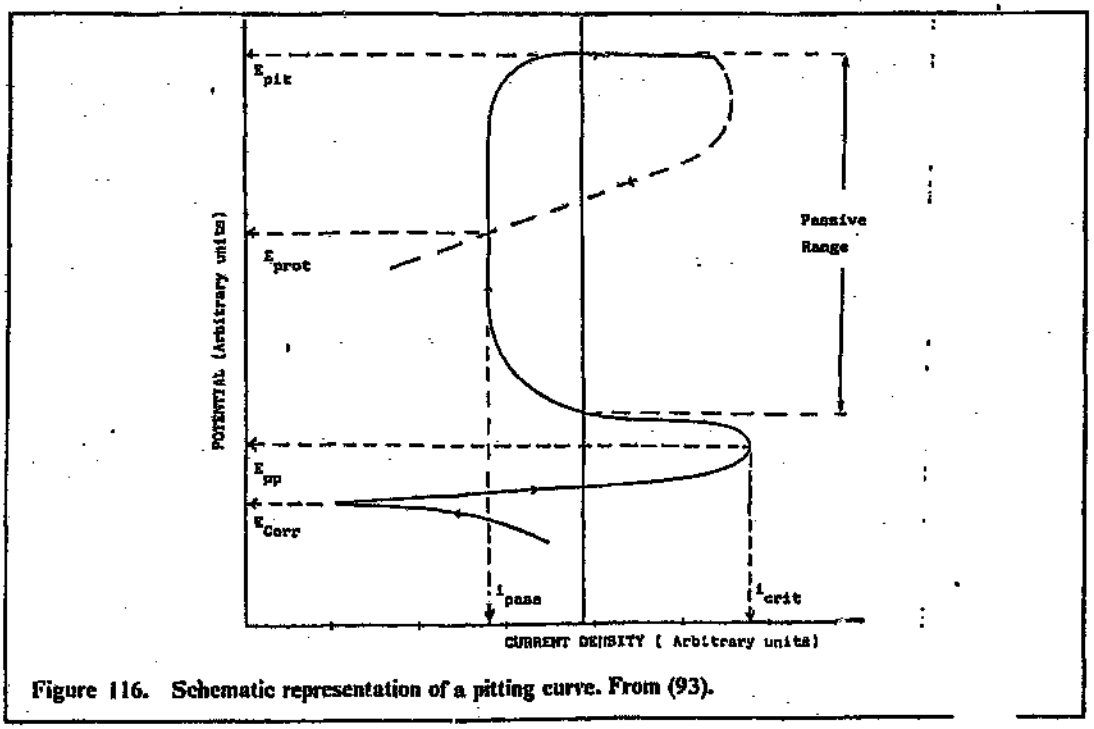

Figure 116. Schematic representation of a pitting curve. From (93).

Fig. 117 shows the pitting curves of alloy 5182 in sterile mine water and a culture of *D.desulfuricans* both containing AS. The passive current density for sterile medium was higher than that for bacteria indicating that the passive film on the surface of the control specimen did not confer adequate corrosion resistance. The return scan for the sterile control showed that once formed, the pits were able to repassivate to a certain extent. This was not so for the samples exposed to bacteria where the large hysteresis loop formed by the return scan indicated an inability of the pits to repassivate once formed. Although both test and control samples passivated spontaneously in the mine water, the bacterial cultures brought about a marked decrease in the perfect passivation range (Epp - Ecorr).

The pitting curves of all the aluminium alloys in the mine water containing AS generally showed that the bacterial cultures brought about a drop in the perfect passivation range and adversely affected the ability of pits to repassivate.

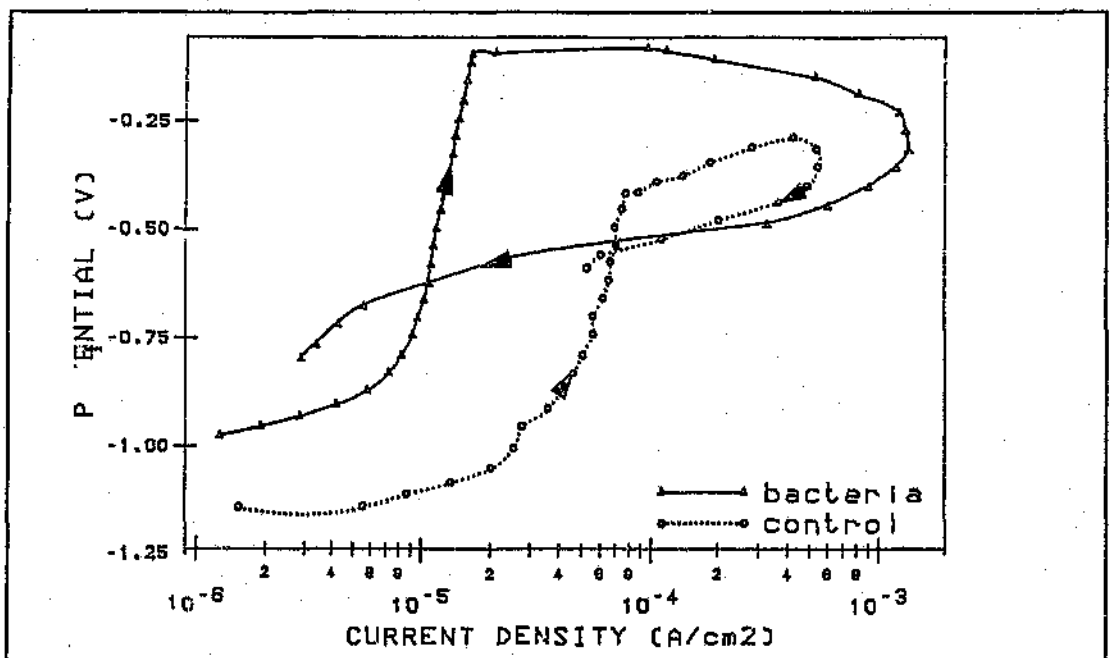

Figure 117. Pitting curve of 5182.

The effect of the SRB cultures on the aluminium alloys in mine water containing FAS was more aggressive. Fig. 118 shows the pitting curve of alloy 6063 in sterile mine water and in a culture of *D.desulfuricans* both containing FAS. The curve in sterile mine water showed spontaneous passivation in the solution and a large passive range. The return scan returned to the left of the foreward scan indicating instant repassivation of the pits. In bacterial cultures, the passive range was reduced and the pits were unable to repassivate as indicated by the large hysteresis loop formed by the return scan. The passive current density, however, remained higher for the sterile controls. This tends to show that the passive film which formed in the presence of FAS and bacteria con-

ferred adequate corrosion resistance to the alloys. However, once the film ruptured and pits were formed, repassivation could not take place.

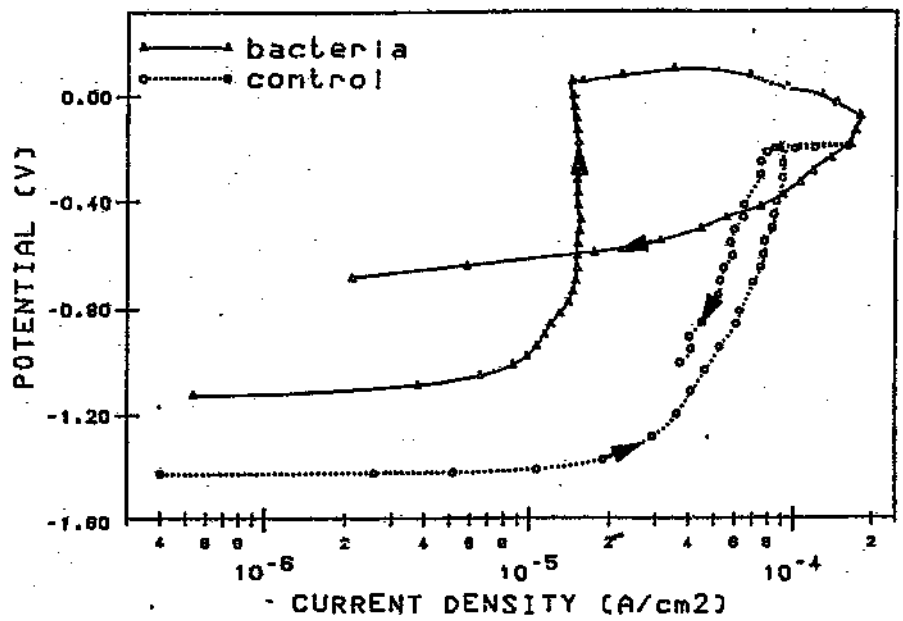

Figure 118. Pitting curve of alloy 6063

The pitting curves of 3CR12 in sterile mine water and cultures of *D.desulfuricans* both containing AS are presented in Fig. 119. The shapes of these curves are very different from those for aluminium. The pitting curve in sterile medium showed that the alloy passivated in the water. The passive current density was low and the return scan returned to the left of the forward scan indicating instant pit repassivation. The curve for the scan in the bacterial culture was markedly different, exhibiting a greatly increased passive current density and an active peak. The return scan indicated that the pits were unable to repassivate once formed. The shapes of the pitting curves in mine water containing FAS were similar indicating that the FeS layer did not confer adequate corrosion protection on the 3CR12.

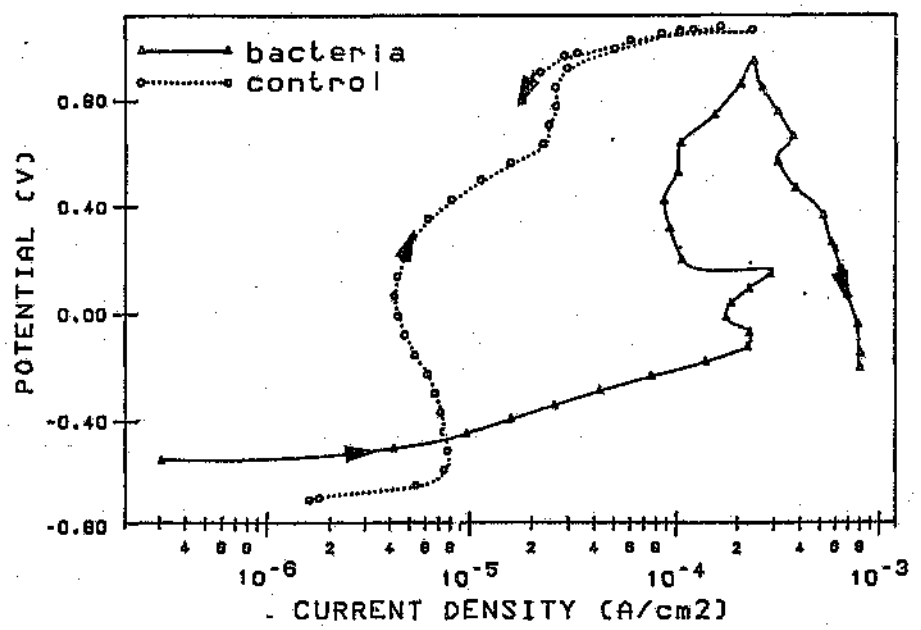

Figure 119. Pitting curve for 3CR12.

In medium, the curves from scans for aluminium alloys in bacterial cultures followed the general trend of those in mine water. Fig. 120 shows the pitting curves of alloy 6261 in a culture of *D. desulfuricans* in medium and the sterile control. The bacteria brought about a decrease in the passive range and in this case showed a slight increase in passive current density compared to the control. The pits were unable to repassivate once formed. The higher passive current density in medium compared with mine water suggests that the passive film formed in medium is less protective than that formed in mine water. This could be due to the presence of a high sulphate concentration in the mine water which acts as a corrosion inhibitor.

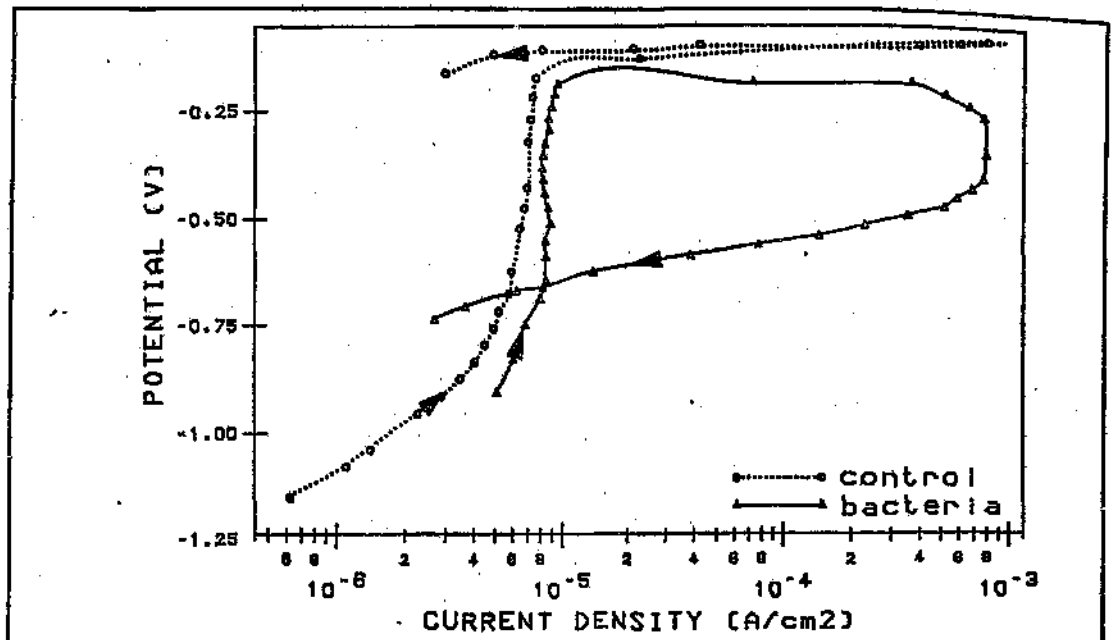

Figure 120. Pitting curve of 6261.

The pitting curves of aluminium alloys in *Pseudomonas* cultures showed more activity than those in SRB cultures. Fig. 121 shows an active peak for the bacterial curve, an inability for pit repassivation and a decrease in passive range.

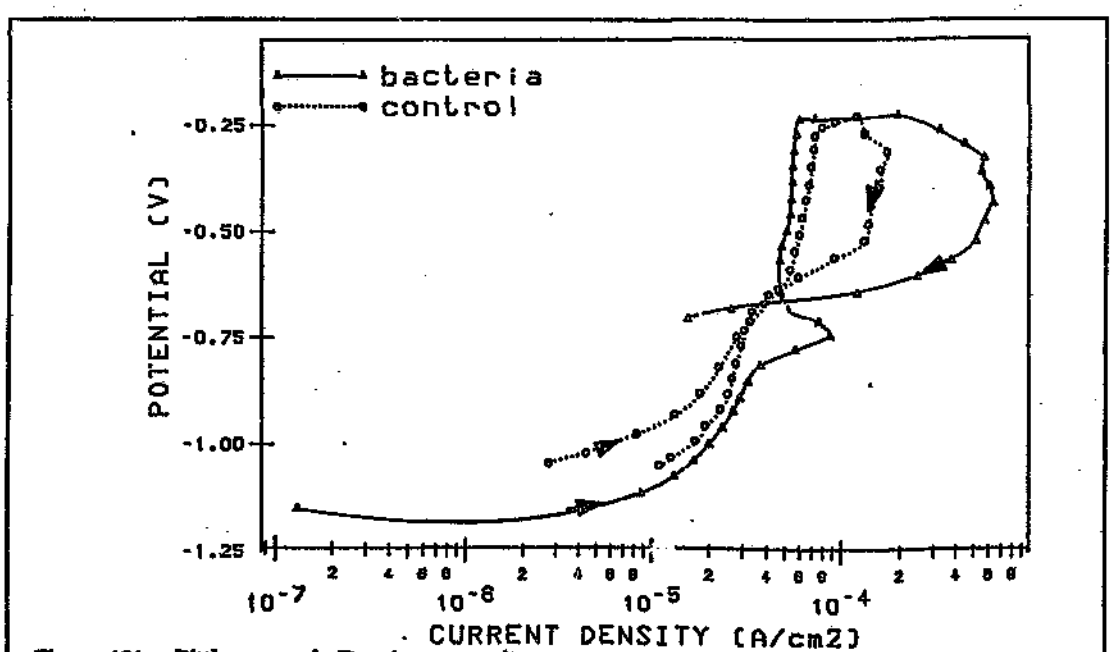

Figure 121. Pitting curve in Pseudomonas culture.

The free corrosion potentials (Ecorr) of the aluminium alloys and 3CR12 in mine water are shown in Figs. 122 and 123. In the absence of FAS, there was a drop in the Ecorr values for 3CR12 in SRB cultures. This is in agreement with work by Cragnolino and Tuovinen (22) which showed that H_2S decreases Ecorr values of stainless steels. In the case of the aluminium alloys, however, the SRB shifted the Ecorr values to more noble potentials compared to the sterile controls suggesting that the bacteria enhanced the conditions for passivity.

In mine water containing FAS there was a decrease in Ecorr values for all aluminium alloys exposed to SRB cultures. This effect was not as pronounced for the 3CR12 specimen which suggests that the FeS layer had formed a passive film on the latter alloy surface, but was contributing to the corrosive effects of bacteria in the case of the aluminium alloys, possibly by interfering with the formation of a stable protective oxide layer on the alloy surface. Generally in mine water there was not much difference between the effect of *D.desulfuricans* and the mixed SRB culture on the Ecorr values.

The medium was less aggressive than the mine water as seen by an overall enoblement of the Ecorr values (Figs. 124 and 125). The same trend as for mine water was followed however, ie. more active Ecorr values in bacterial cultures containing FAS compared to sterile controls. *D.desulfuricans* cultures were generally more active than the mixed SRB cultures in medium with FAS suggesting a higher growth rate and production of H_2S. The 3CR12 samples showed a drop in Ecorr values in bacterial cultures with FAS. In this case the FeS film probably contained flaws and thus did not offer protection.

The *Pseudomonas* cultures (Fig. 126) in all cases had the effect of lowering the Ecorr values below those of the sterile controls.

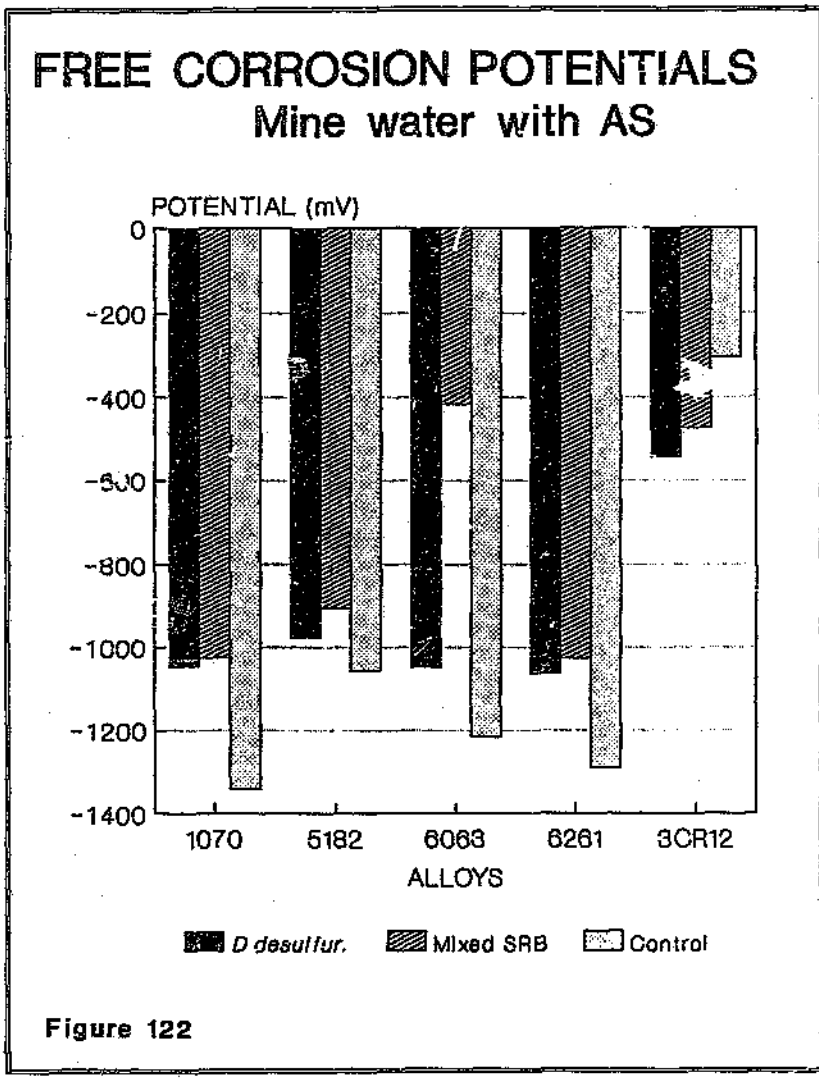

Figure 122

RESULTS

FREE CORROSION POTENTIALS
Mine water with FAS

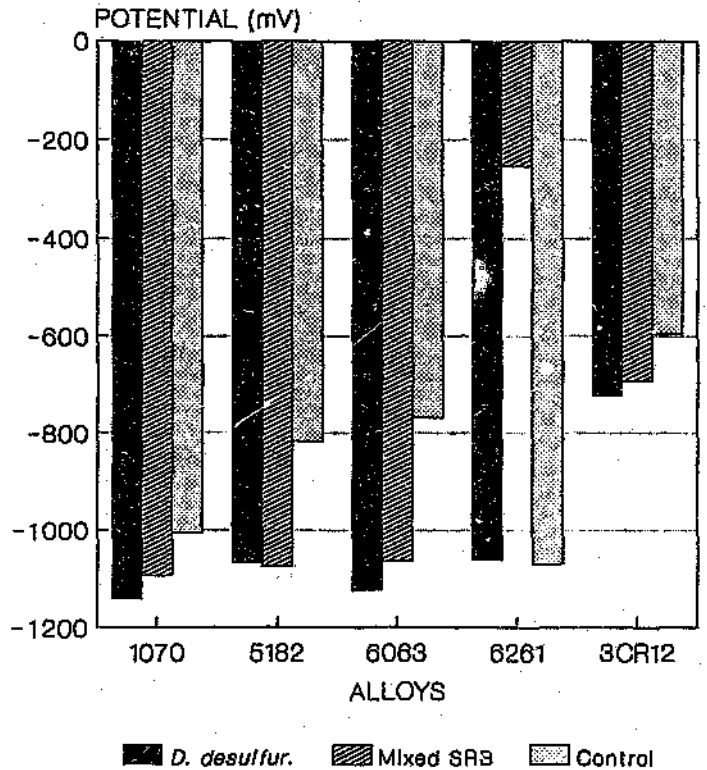

Figure 123

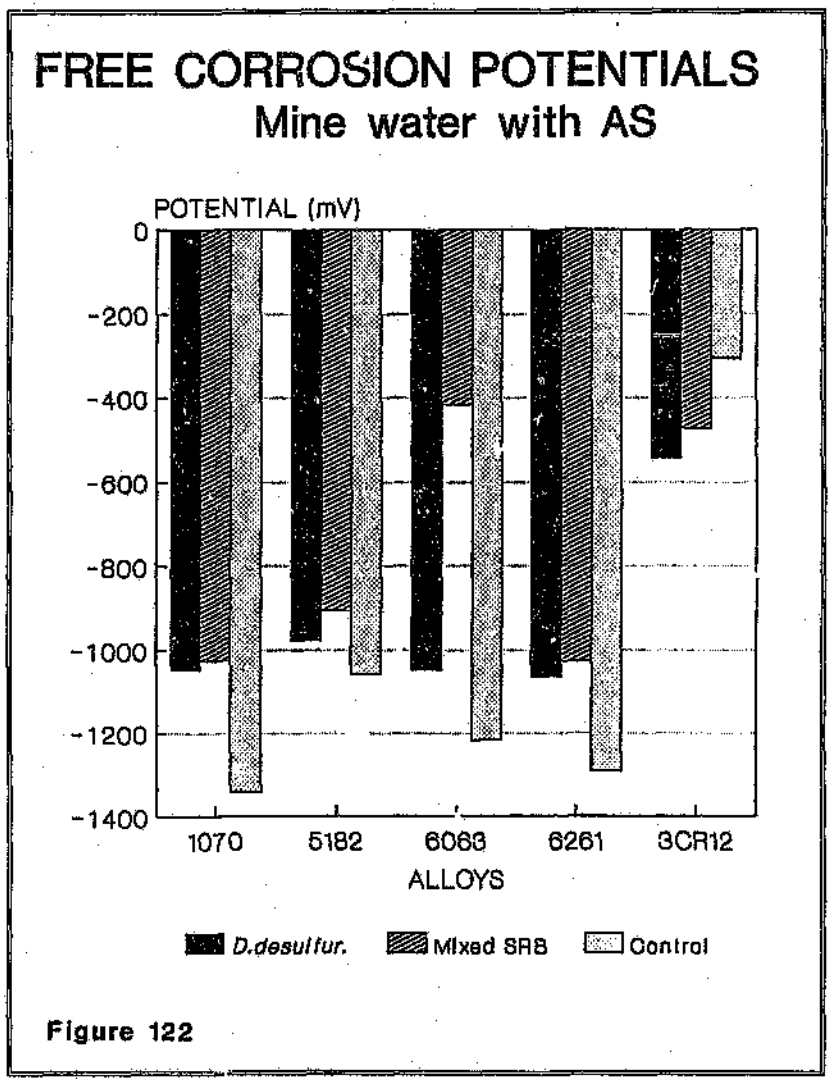

Figure 122

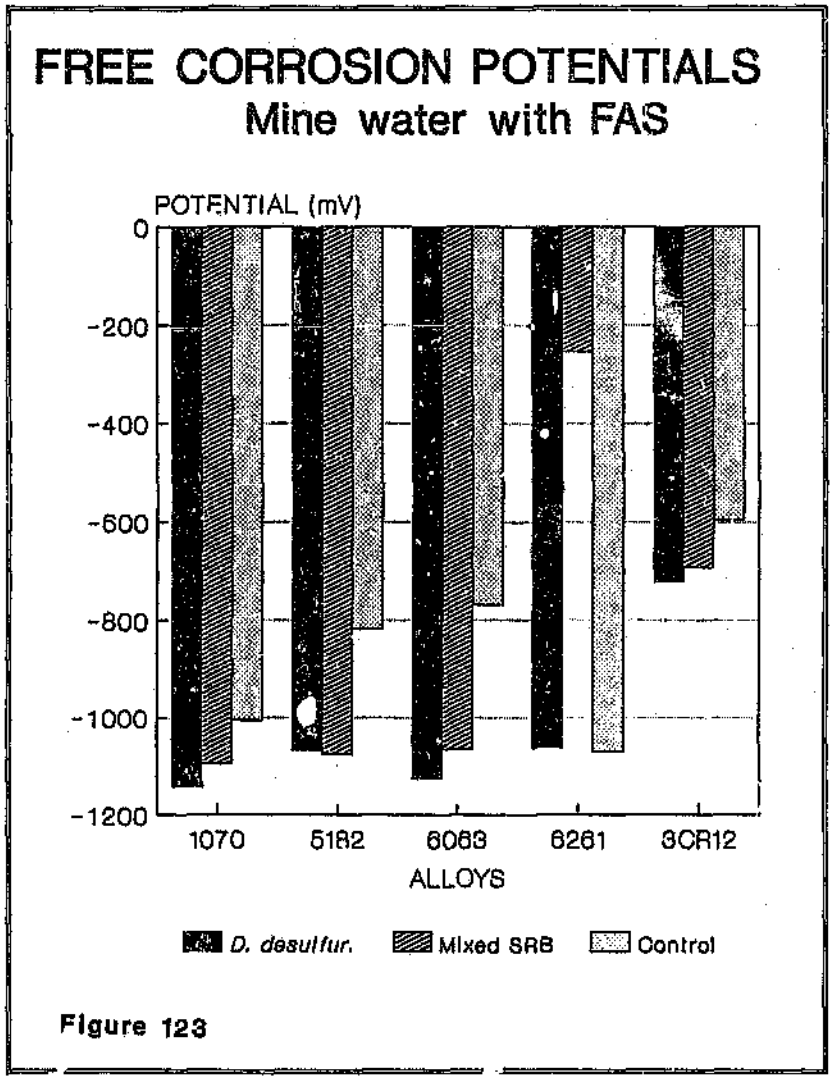

Figure 123

FREE CORROSION POTENTIALS
Medium with AS

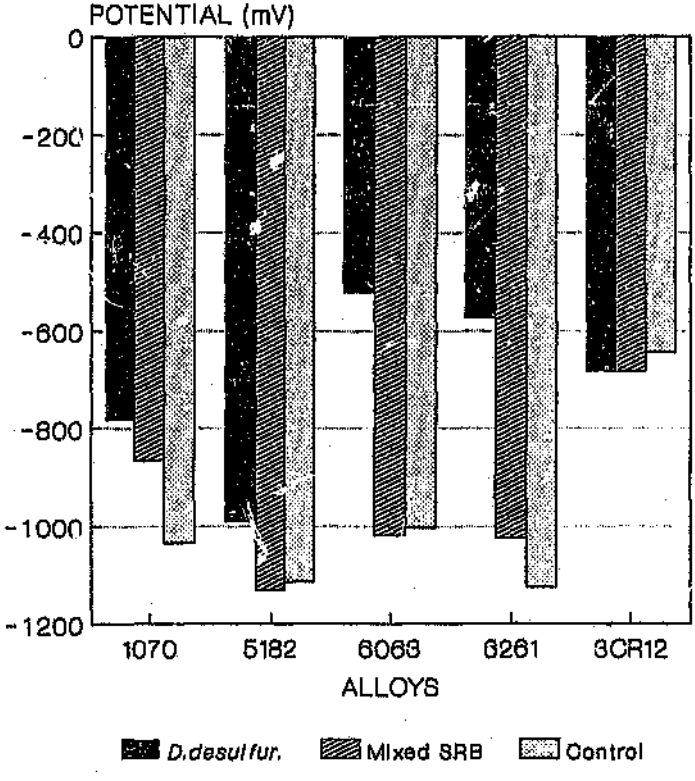

Figure 124

FREE CORROSION POTENTIALS
Medium with FAS

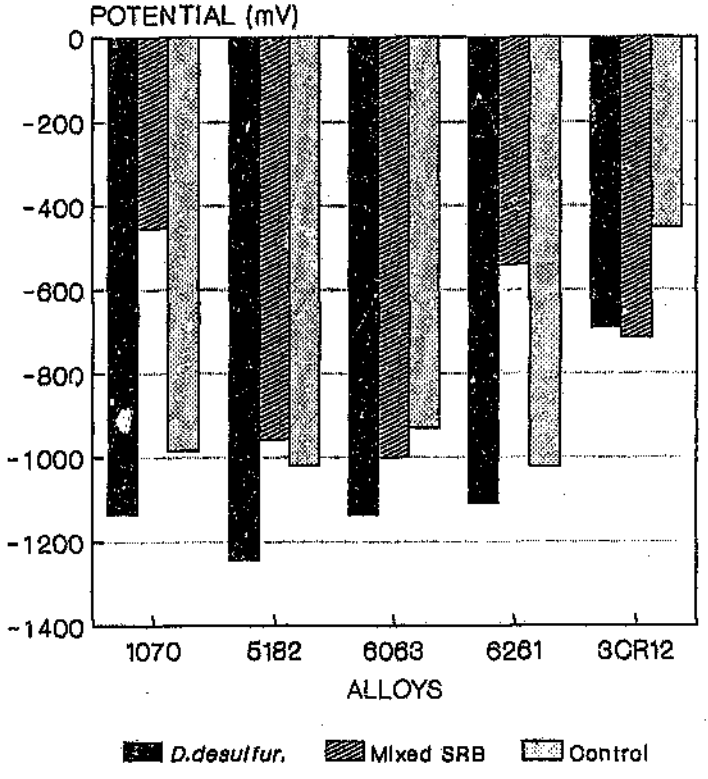

Figure 125

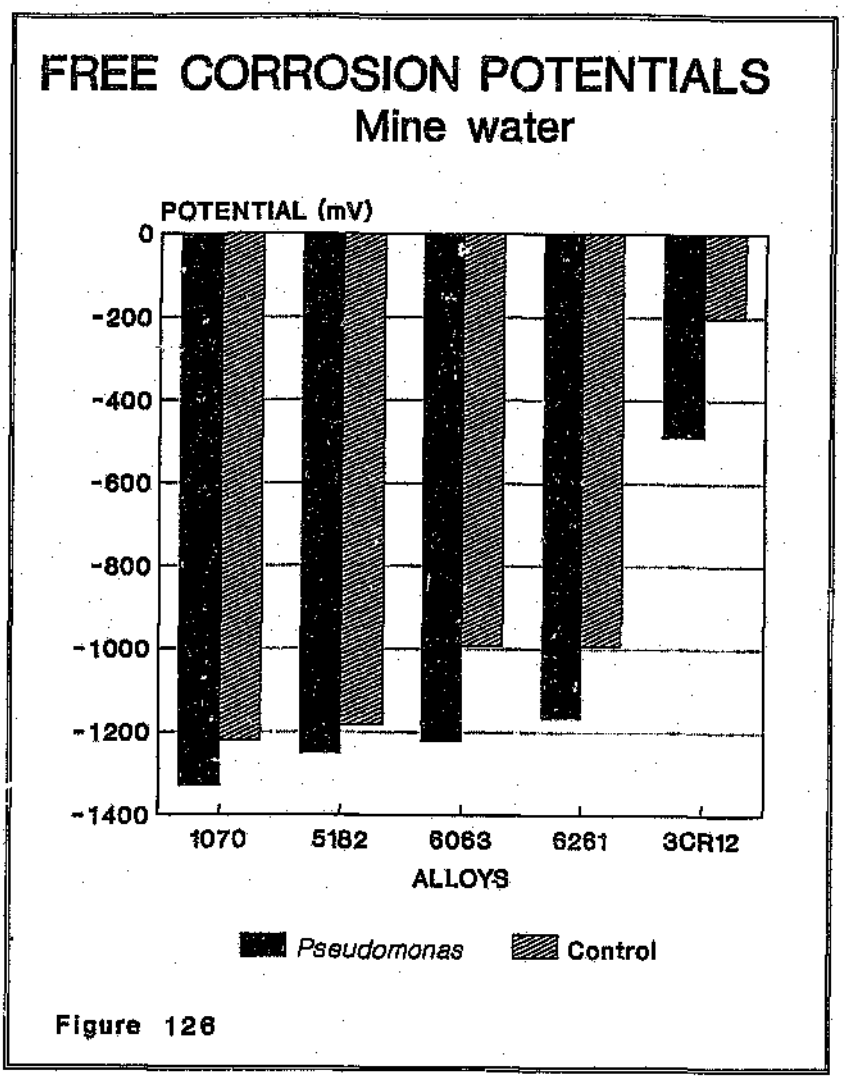

Figure 126

Passive ranges of the alloys in mine water are presented in Figs. 127 and 128. In mine waters containing AS, the passive range decreased in bacterial cultures for all alloys except the 5182 in the *D.desulfuricans* culture. This latter case can be explained by the shape of the pitting curve (Fig. 117) where it can be seen that the imperfect passive range (Ep - Ecorr) was greater for the bacterial culture than for the sterile control. However, the perfect passive range (Epp - Ecorr) was decreased in bacterial cultures. In the case of 3CR12, the active peak formed in the bacterial cultures (Fig. 119) caused a decrease in the passive range. Generally in mine water with FAS, the aluminium alloys exposed to bacterial cultures exhibited a larger passive range than the sterile controls. This could be due to the passivating effect of the FeS layer. An exception was found for the 1070 alloy where the bacteria decreased the passive range. This is the least alloyed of the aluminium samples and was possibly unable to form a stable protective passive film. The passive range of the 3CR12 was decreased by the SRB cultures.

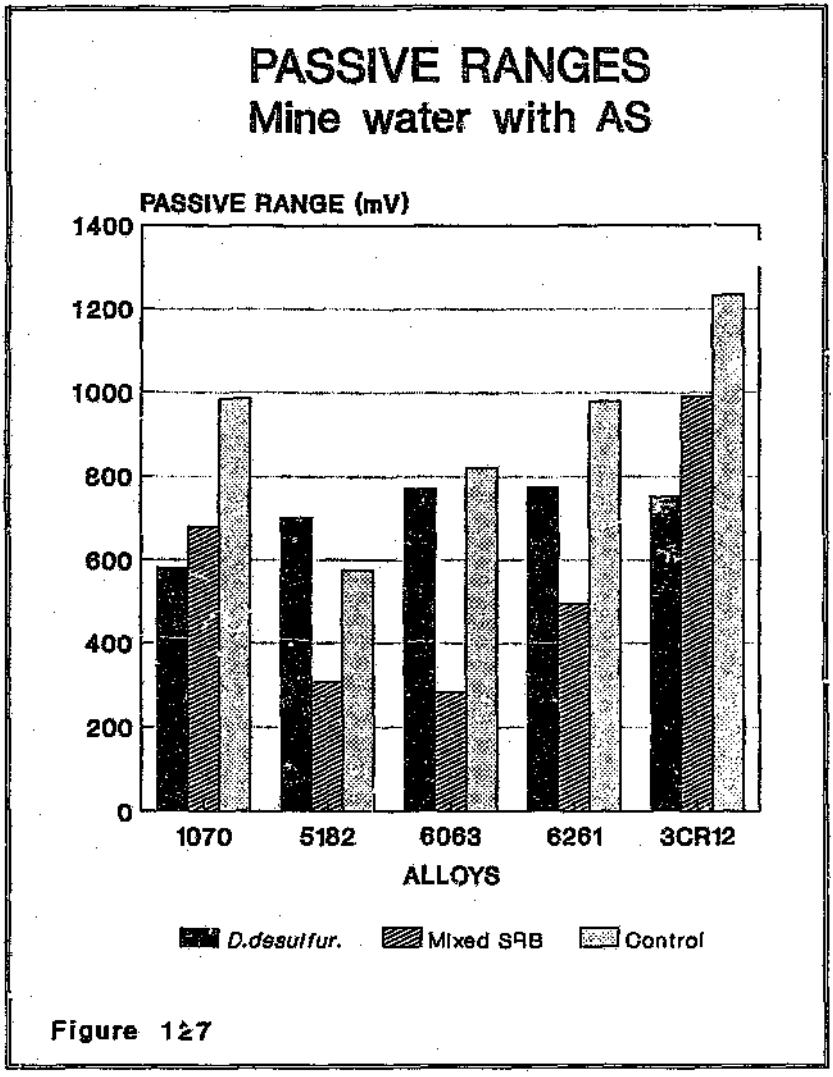

Figure 1&7

RESULTS

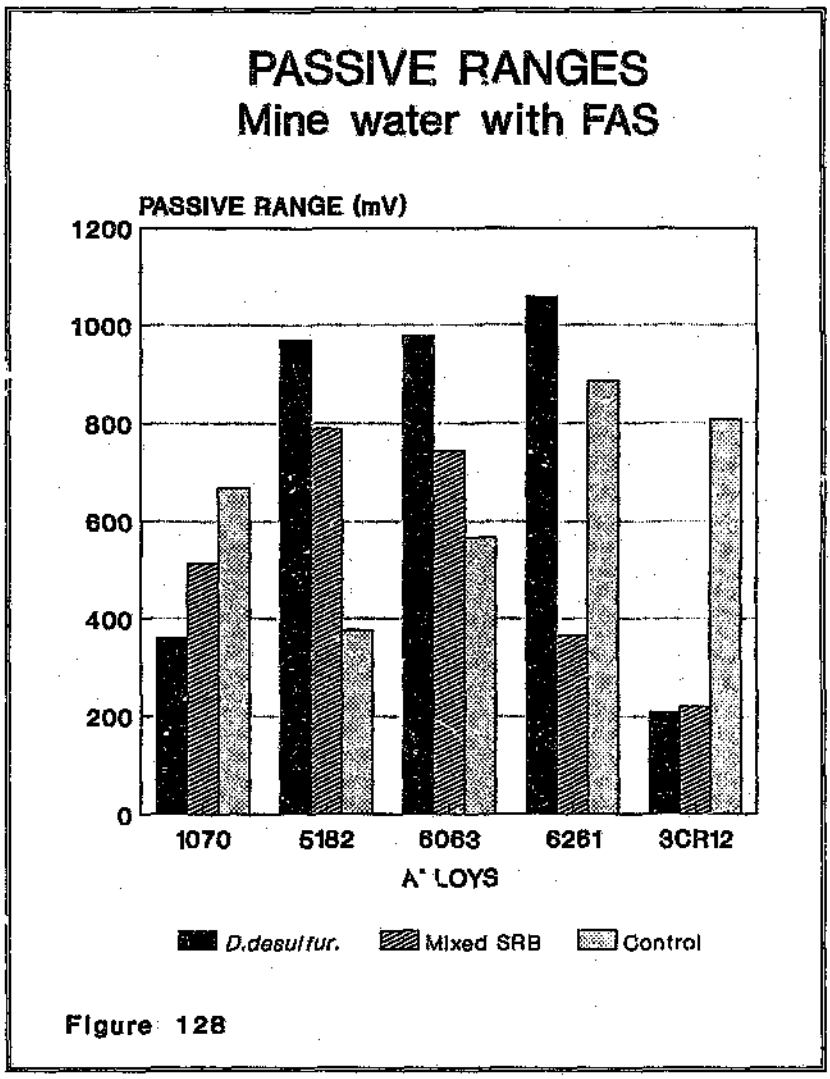
PASSIVE RANGES
Mine water with FAS
PASSIVE RANGE (mV)
1200
1000
800
600
400
200
0
1070
5182
6063
6261
3CR12
ALLOYS
D.desulfur.
Mixed SRB
Control

Figure 128

PASSIVE RANGES
Medium with AS

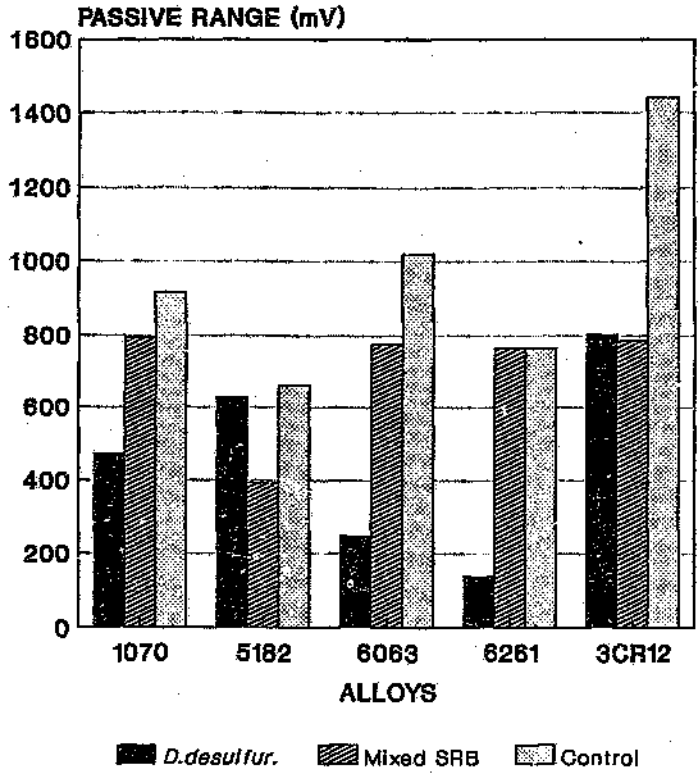

Figure 129

PASSIVE RANGES
Medium with FAS

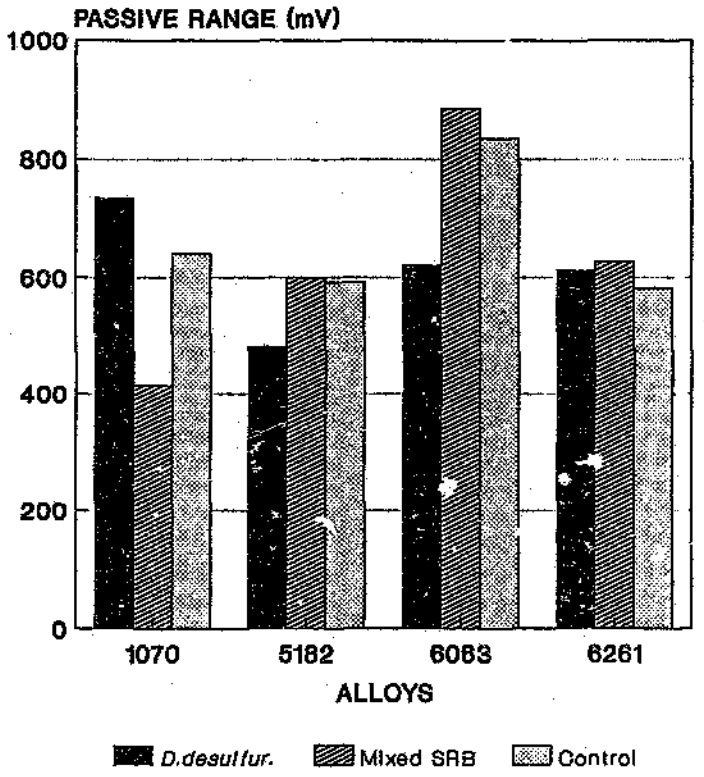

Figure 130

PASSIVE RANGES
Mine water with AS

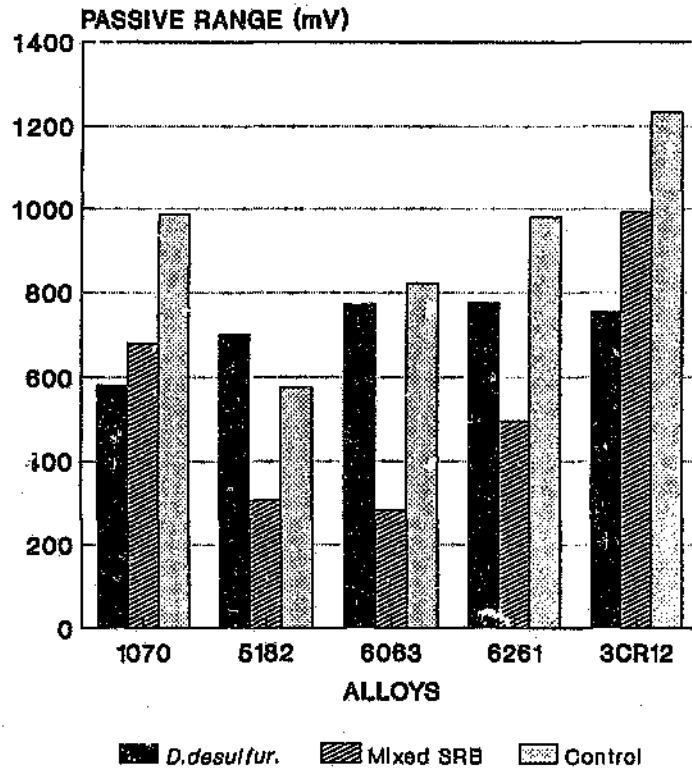

Figure 127

PASSIVE RANGES
Mine water with FAS

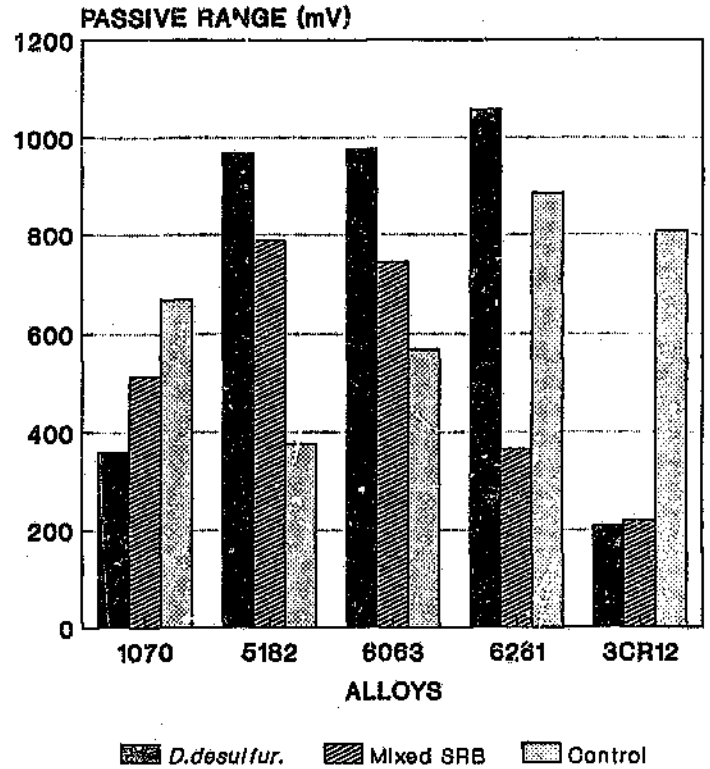

Figure 128

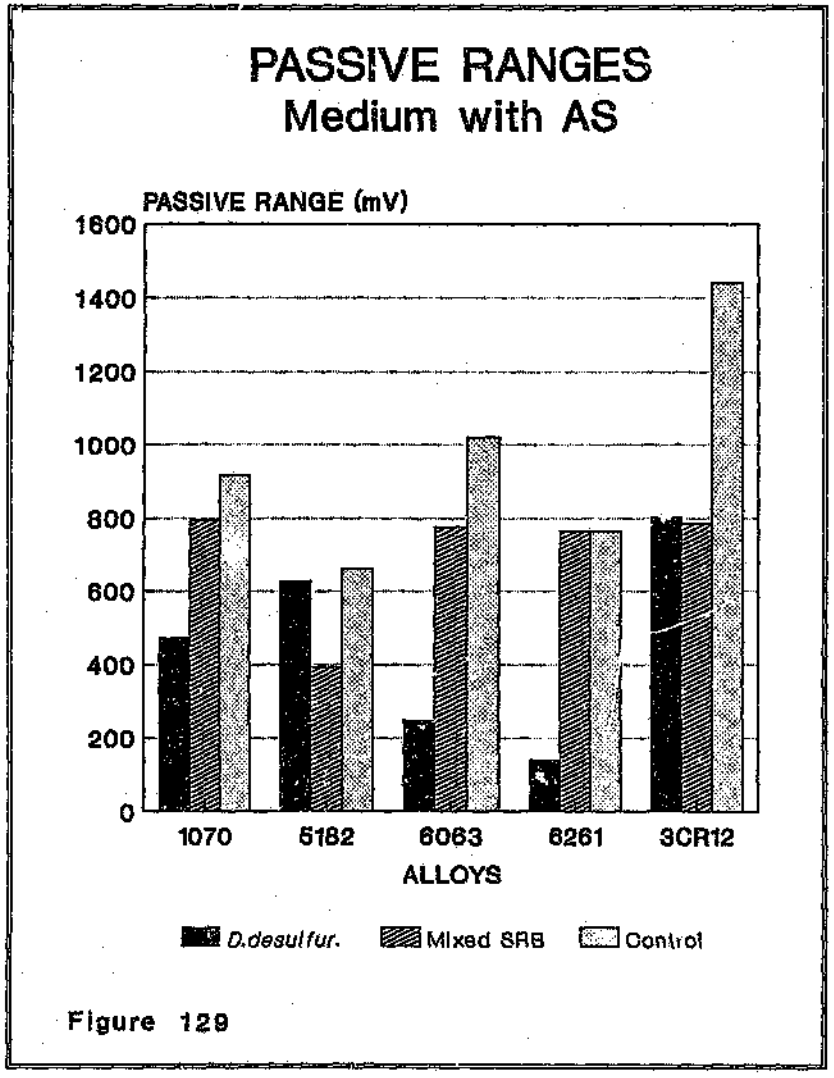

Figure 129

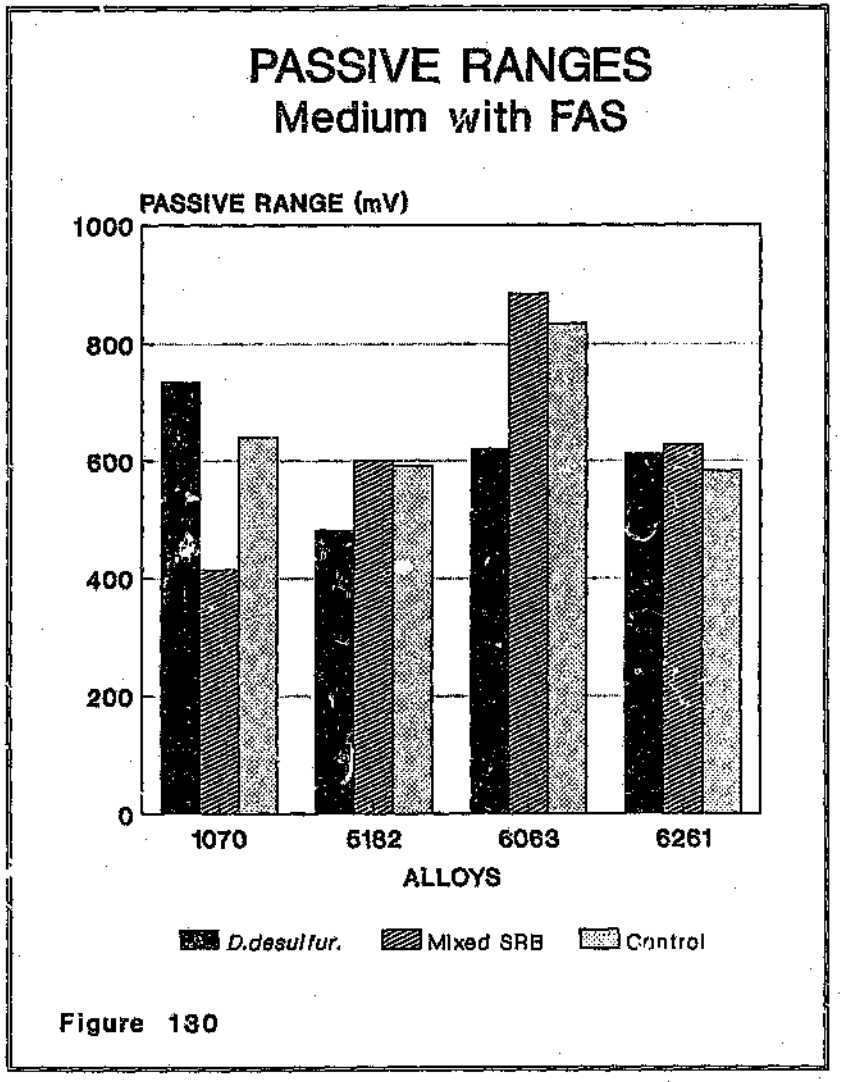

Figure 130

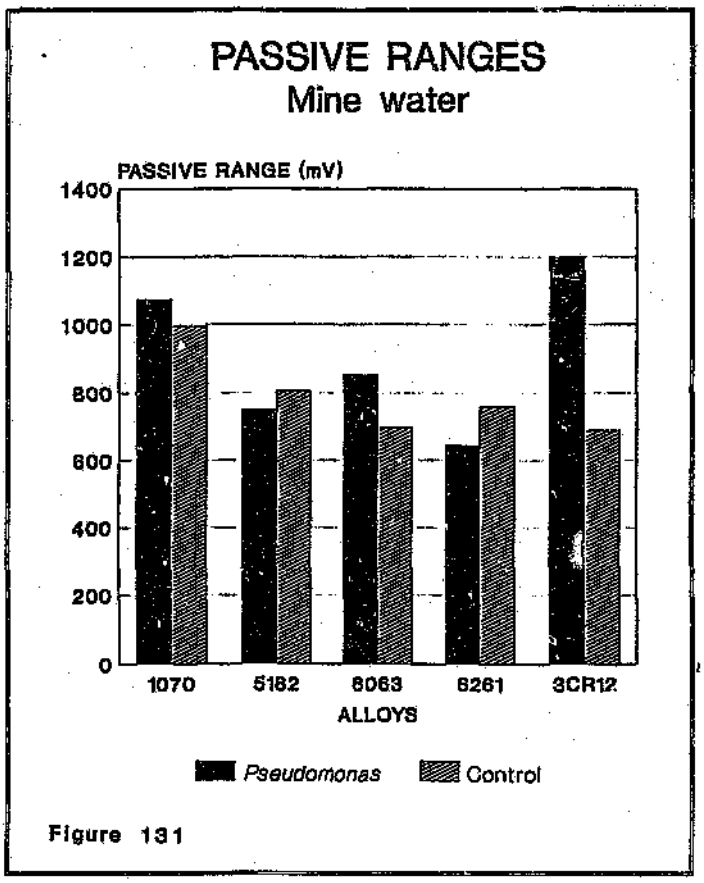

Figure 131

In medium with AS (Fig. 129) the bacterial cultures brought about a decrease in passive range for all test samples. In the medium containing FAS (Fig. 130) there was no general trend. In cases where the passive range in bacterial cultures was greater than that in sterile medium, it can be assumed that the FeS film was imperfect or unstable and did not afford protection.

Overall the results seem to indicate that when SRB are present in an environment, in the absence of a protective FeS layer or in the presence of a defective layer, the passive range of both aluminium alloys and 3CR12 is decreased. This decrease can bring about pitting and/or crevice corrosion. It was also observed in all cases in the sterile controls that alloy 5182 exhibited the smallest passive range. Since this is the most highly alloyed of the specimens, pits initiating at intermetallic inclusions would decrease the passive range.

In the case of *Pseudomonas* cultures (Fig. 131) the passive range was generally greater than that for sterile controls, except for the 5182 and 6261 alloys which contain the highest percentage of alloying elements and thus more sites for pit nucleation.

In Figs. 132 and 133 the passive anodic current densities for the samples in mine water are presented. There was a substantial increase in the passive current density in the presence of SRB for the 3CR12 samples. Sulphide incorporated into the passive film on the surface could render it less protective. It has been postulated (22) that sulphur species accelerate corrosion by adsorbing onto the metal surface once chloride induced breakdown of the passive film has taken place.

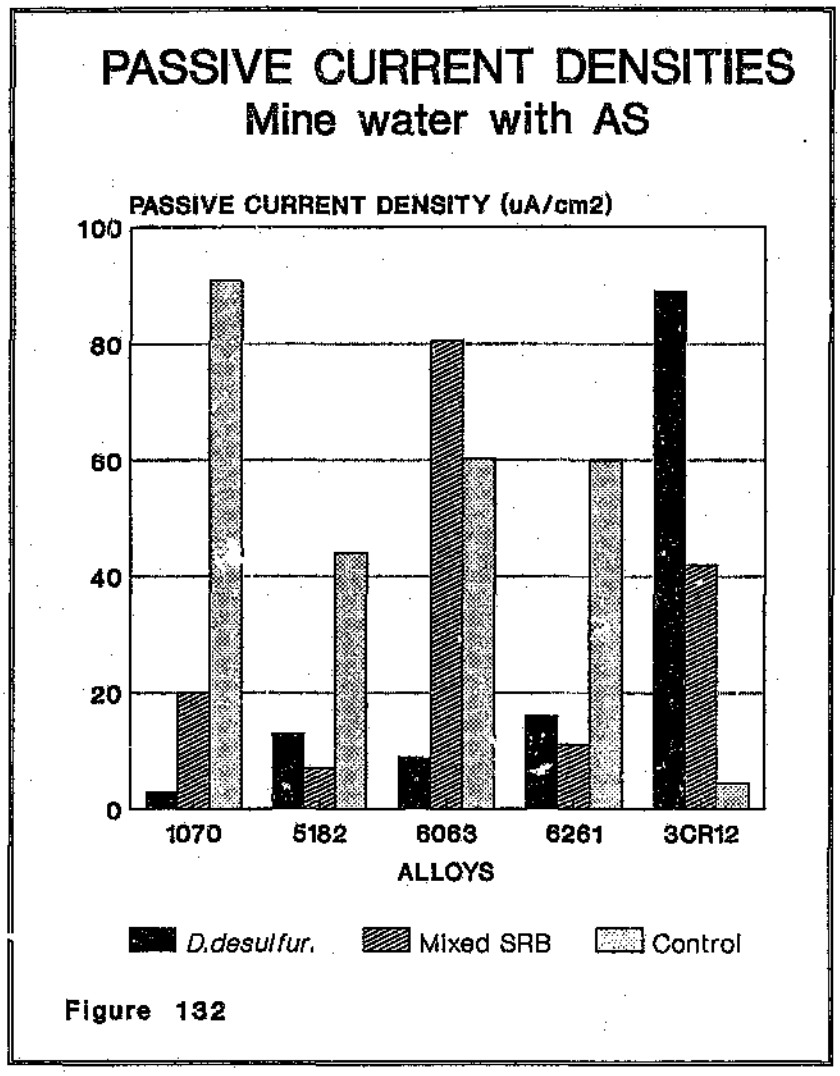

Figure 132

In the case of aluminium alloys the higher passive current densities for controls as compared to test samples suggests that the aluminium oxide protective layer was more stable in the bacterial cultures and thus afforded protection. Generally in mine water with FAS there was a slightly higher passive current density for samples exposed to SRB, once again suggesting the interference of FeS in the passive film formation.

In medium (Figs. 134 and 135) the passive current density was greatly increased in the presence of SRB for the 3CR12 specimens. The same general trend as that in mine water was followed by the aluminium alloys.

The aluminium alloys in *Pseudomonas* cultures (Fig. 136) exhibited larger passive current densities than the sterile controls suggesting that a stable passive film was formed in the presence of the bacteria.

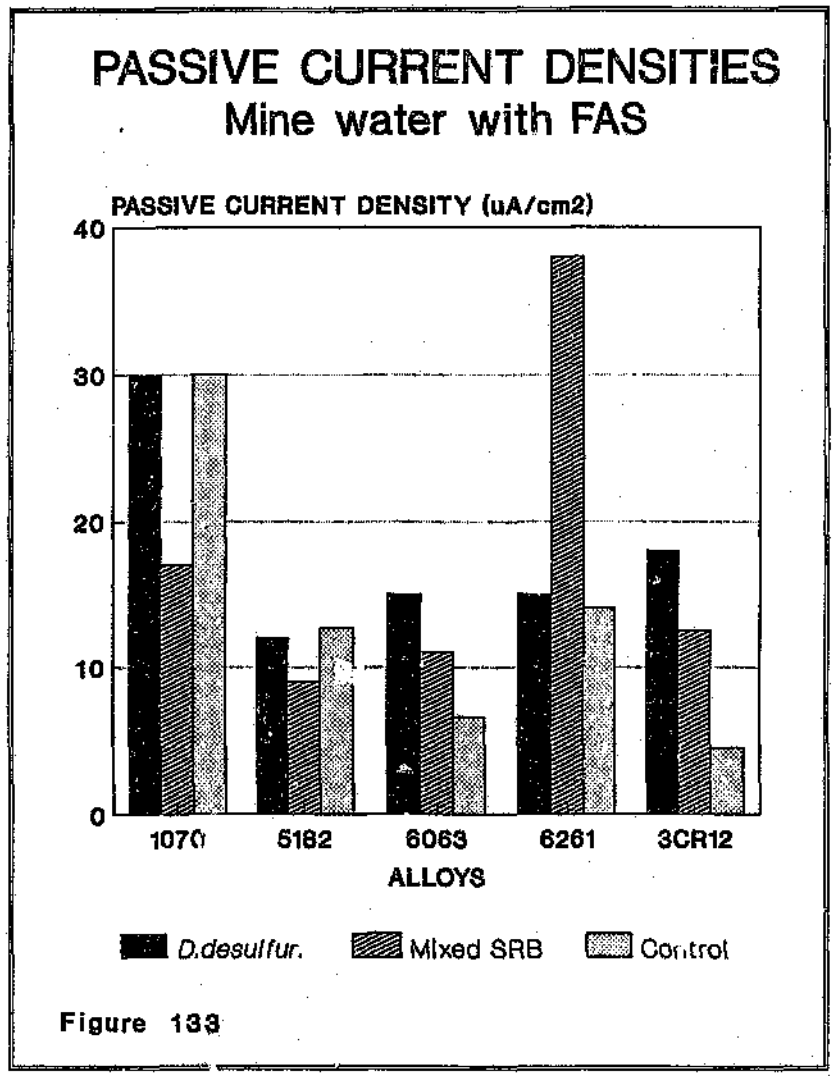

Figure 133

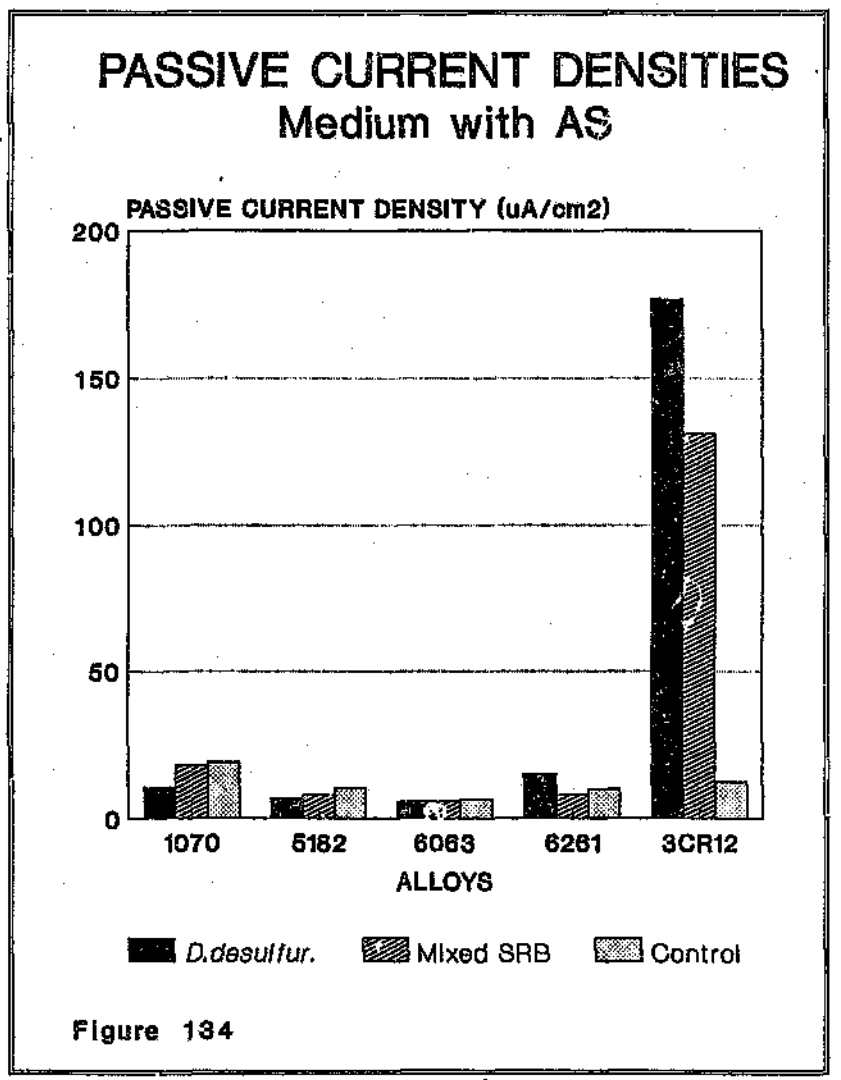

Figure 134

PASSIVE CURRENT DENSITIES
Medium with FAS

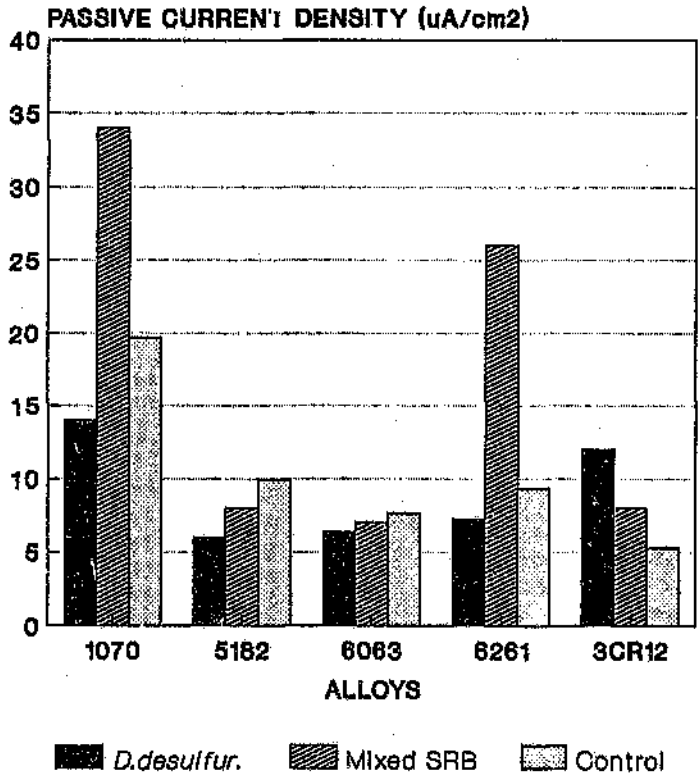

Figure 135

PASSIVE CURRENT DENSITIES
Mine water

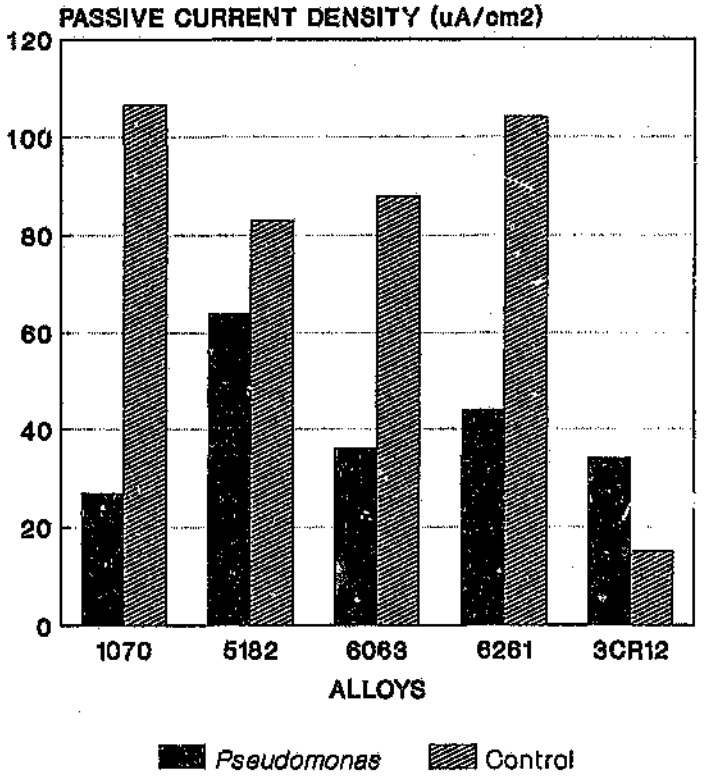

Figure 136

4.4.3 Tafel extrapolation

Tafel plots for all alloys in bacterial cultures and sterile solution in both medium and mine water were carried out. There was no significant change in the Tafel slopes of all specimens exposed to bacterial cultures in mine water compared to those in the sterile test waters.

In the medium, however, the 3CR12 specimens in *D. desulfuricans* cultures showed a significant increase in the cathodic slope (196 mv/decade) compared to the control (40 mv/decade). In the mixed SRB culture, the increase was negligible. In the case of mild steel, there was a significant increase in cathodic slope both in *D. desulfuricans* and mixed SRB cultures (46- and 56 mv/decade respectively) compared to the control (19 mv/decade). These results indicate that the corrosion system was possibly under cathodic control.

In the case of the aluminium alloys, there was no significant change in either cathodic or anodic Tafel slopes compared to the control.

4.5 ELECTROCHEMICAL TESTS - FLOW CONDITIONS

4.5.1 Cyclic polarization

Pitting scans were conducted for aluminium alloys in sterile mine water and then in mine water containing bacteria. Two different conditions were tested viz. a scan after 1-3 hours stabilization, and a scan after 3 days stabilization. All scans were reversed at a current density of $100\mu A/cm^2$.

Figs. 137 and 138 show typical curves for alloys under both sterile and test conditions. Overall, the passive range was greater for the control samples as compared with the test samples. In both cases, however, the pits failed to repassivate as indicated by the failure of the return scan to cross the forward scan.

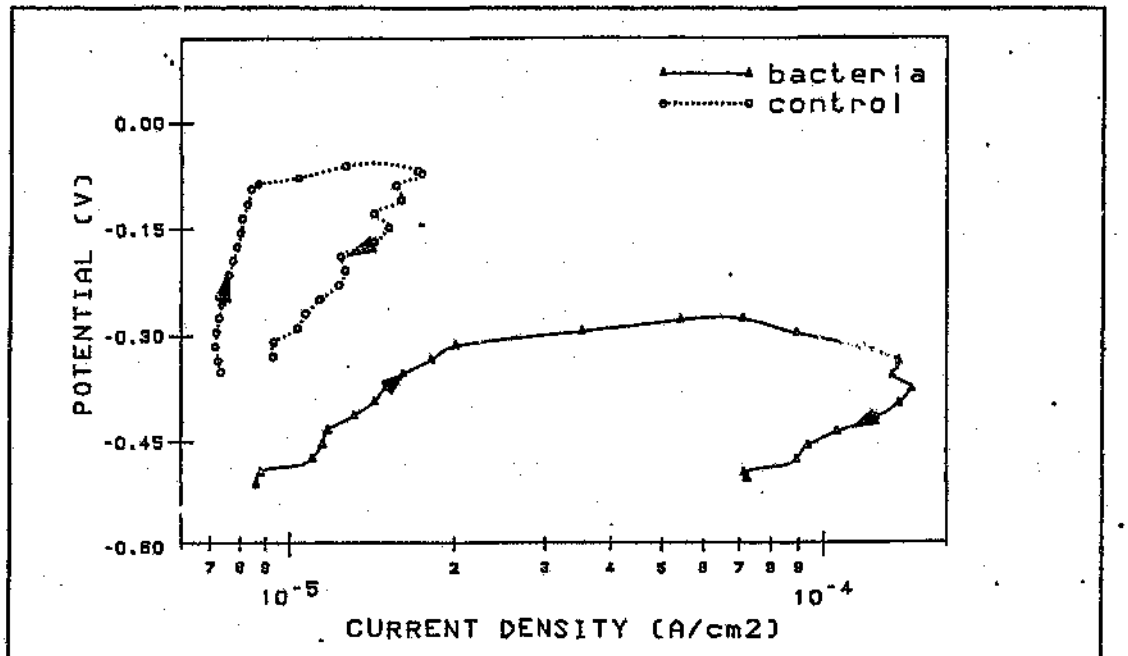

Figure 137. Pitting curve of alloy 5182 (3 hrs)

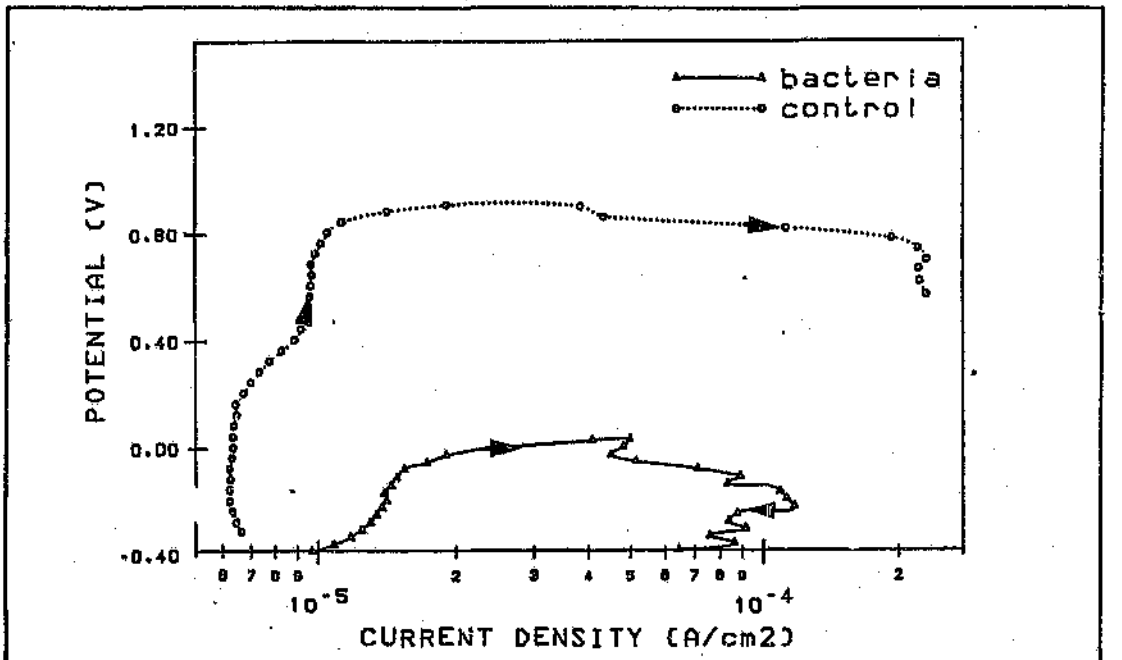

Figure 138. Pitting curve of alloy 1070 (3 days)

Under flow conditions the effect of the bacteria on the metal takes longer to manifest itself than would be the case for a sample exposed to a vigorously growing laboratory culture. This was confirmed by examination of the immersion samples as mentioned previously. Thus in comparing the Ecorr values, passive ranges and passive current densities of control and test samples, the results may not be a true reflection of the situation ie. it is difficult to ascertain whether the bacteria are exerting an influence or whether the difference is due to the slight difference in water composition. Figs. 139 - 144 show the free corrosion potential, passive ranges and passive current densities for the alloys in mine water after different periods of stabilisation. In all cases it can be seen that with time there was an enoblement of Ecorr values, an increase in passive range and a decrease in passive current density for all alloys both in sterile mine water and in mine water containing bacteria. These results suggest the buildup of a protective passive layer with time. However, as seen by the shapes of the polarization curves, once pits have formed they are unable to repassivate. This could be brought about when eventually the developing biofilm would cause the protective film to rupture, thereby promoting corrosion.

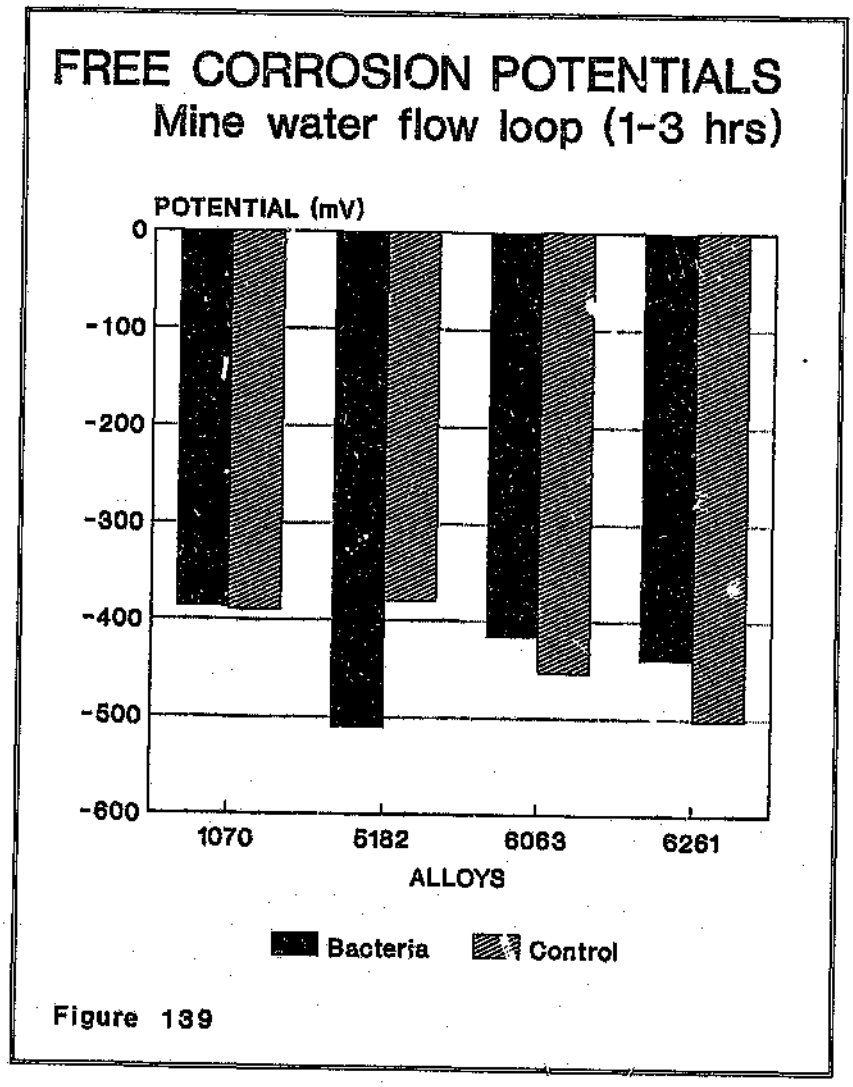

Figure 139

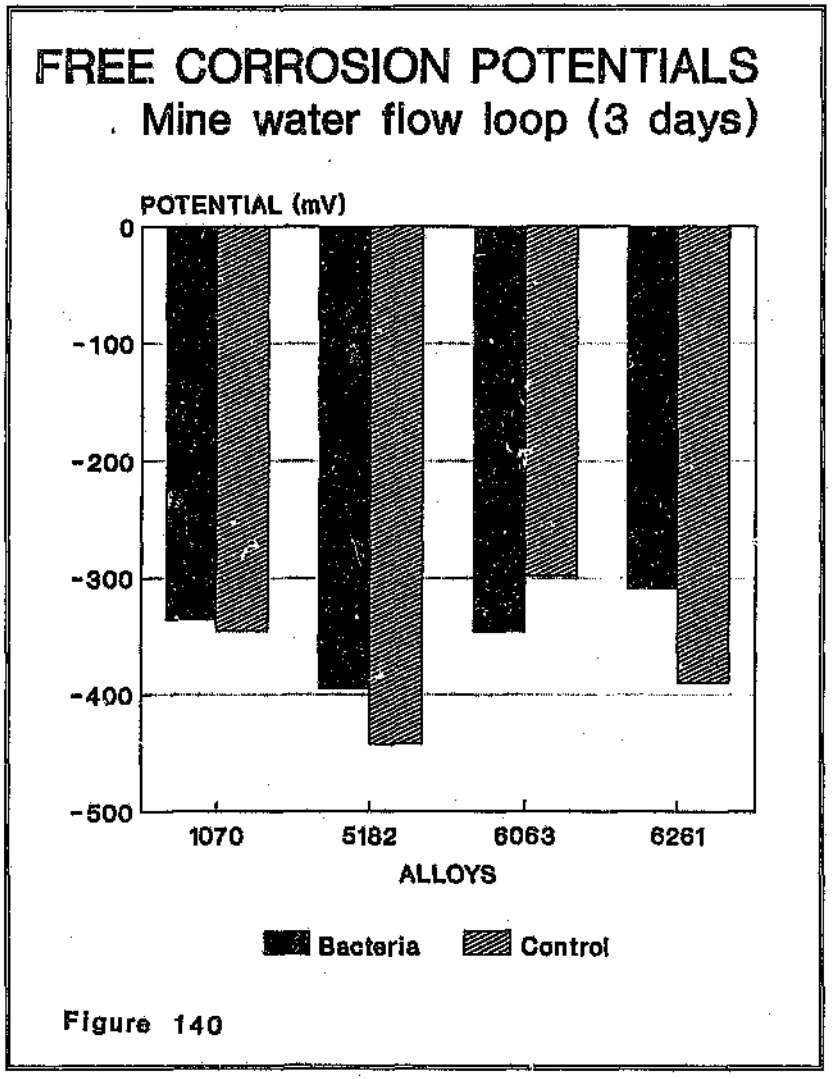

Figure 140

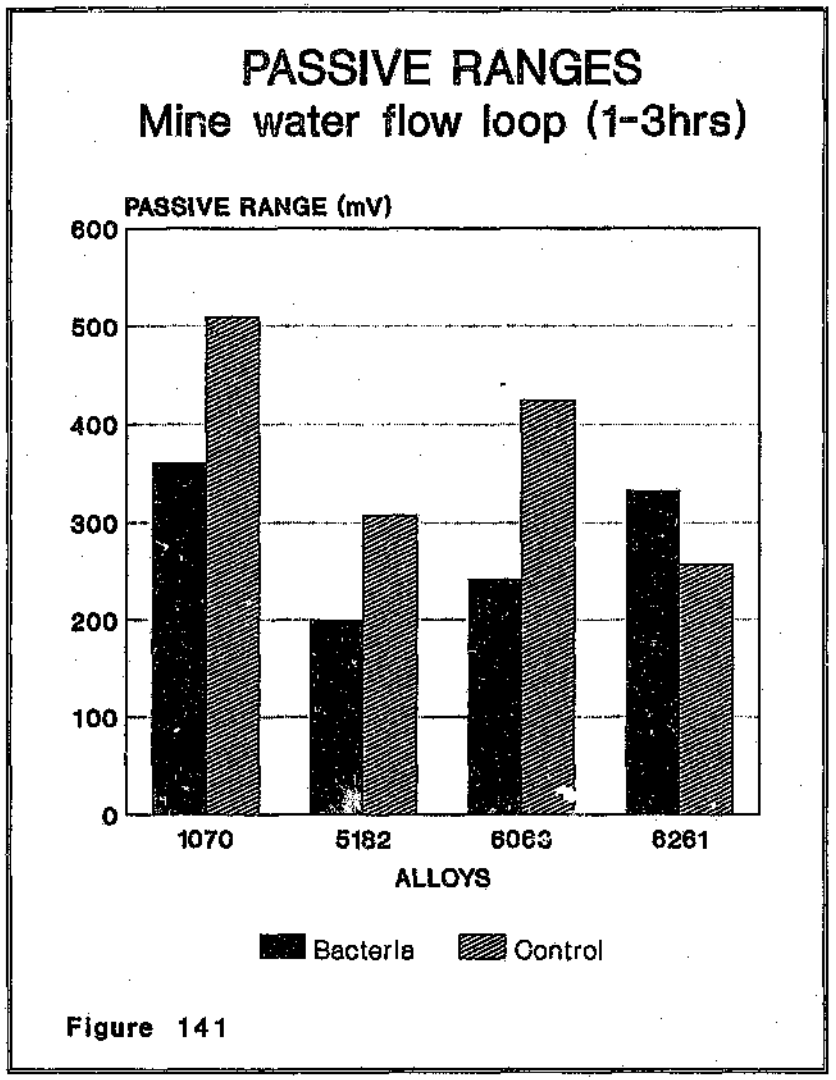

Figure 141

PASSIVE RANGES
Mine water flow loop (3 days)

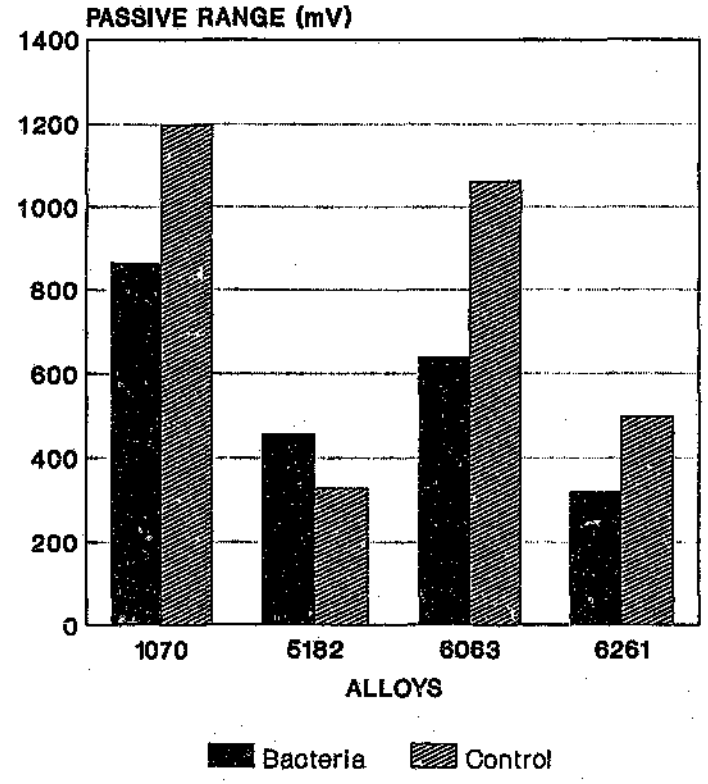

Figure 142

PASSIVE CURRENT DENSITIES
Mine water flow loop (1-3 hrs)

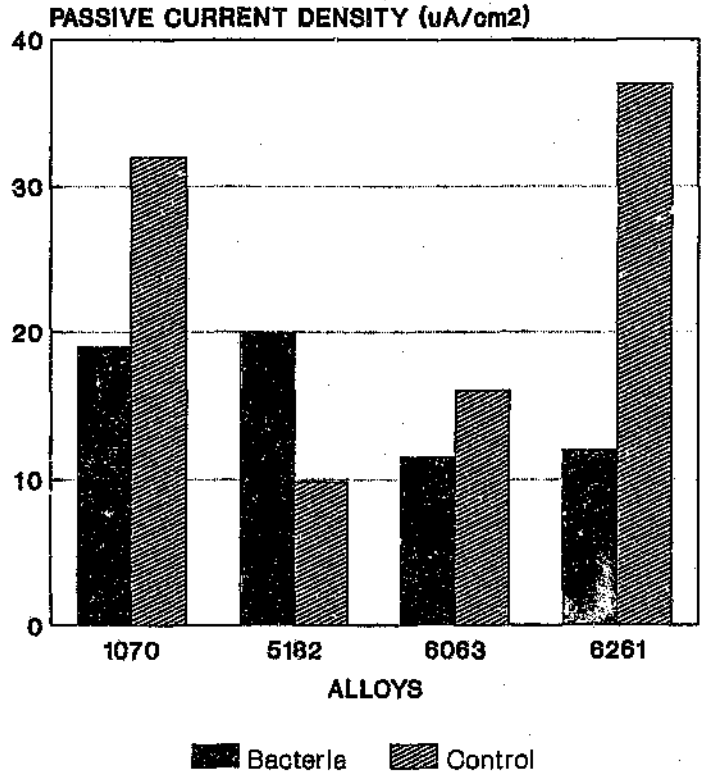

Figure 143

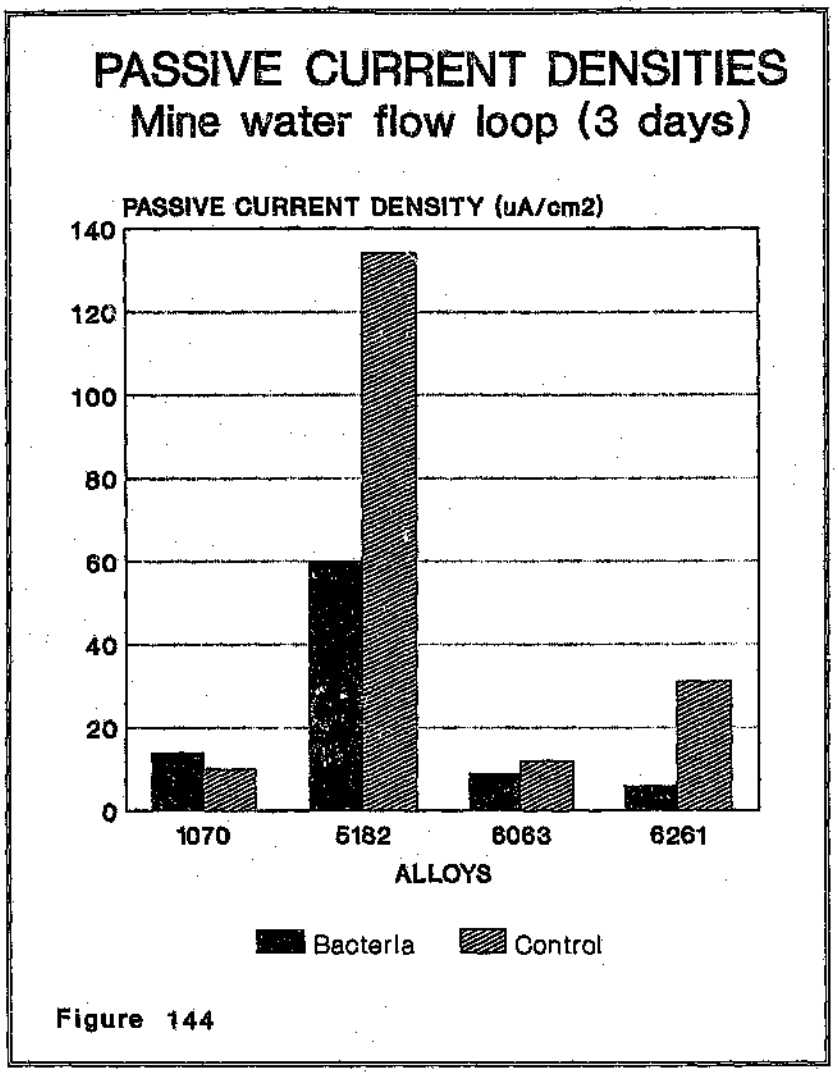
PASSIVE CURRENT DENSITIES
Mine water flow loop (3 days)
PASSIVE CURRENT DENSITY (uA/cm2)
140
120
100
80
60
40
20
0
1070
5182
6063
6261
ALLOYS
Bacteria
Control

Figure 144

5.0 DISCUSSION

5.1 Mine Survey

The adverse corrosion effects of micro-organisms in many industrial applications, as borne out by corrosion and biofilming leading to loss of essential heat transfer, decreased flow rates, product losses or deterioration, increased maintenance requirements etc, are well documented. In addition, the detrimental roles that SRB play in these activities has been widely studied. These organisms are ubiquitous and are found in habitats ranging from fresh and sea water, to oil wells and cutting emulsions. It was therefore not surprising that these organisms were found in abundance on in situ exposed corrosion test coupons in mine waters. The presence of fungal masses and moulds on alloy surfaces most certainly provided ideal anaerobic conditions for the growth of SRB. The *Pseudomonas spp.* also play an important role in biofilm formation. These organisms colonize the fungal mats, producing a slime which aids in creating anaerobic niches within the biofilms.

In a bacterial population structure study of water cooling systems on various South African mines, Cloete et al (95) found that *Pseudomonas flourescens* was the predominant bacterium encountered in the majority of systems studied. This was followed by *P. picketti, P. putida, P. stuzeri* and *Chromobacter violaceum* The dominant bacteria showed a wide temperature tolerance indicating that they are able to grow and form biofilms in various sections of the plant. Unfortunately, the study concentrated on aerobic organisms and thus the presence of SRB was not investigated. The dominant presence of *Pseudomonas spp.*, however, indicates that these organisms play an important role in biofouling.

The results show clearly that microbial species are present on aluminium alloys in mine water where they form adherent biofilms. In agreement with Hedrick et al (70), the type of attack found on the Al alloys viz. intergranular corrosion, exfoliation and pitting is indicative of microbial involvement in the corrosion process since a predominance of pitting was found to occur in the chemical corrosion system.

5.2 IMMERSION TESTS - STATIC

5.2.1 Weight loss results

Results from total immersion tests under static conditions showed that the Al alloys, both in sterile medium and in SRB cultures, underwent very little corrosion as measured by weight loss. The values ranged from between 0,07-0,19 mg/cm^2 for *D.desulfuricans* cultures, between 0,006-0,06 mg/cm^2 for mixed SRB cultures and between 0,006-0,13 mg/cm^2 for sterile controls.

Weight losses on 3CR12 samples, carried out for comparative purposes, were also low, both in bacterial cultures (0,66mg/cm^2 for mixed SRB cultures and 1,17 mg/cm ^{2} for *D.desulfuricans* cultures) and in sterile medium (0,5 mg/cm^2). As expected, mild steel specimens underwent more corrosion with the largest weight loss being 2,7mg/cm^2 in *D.desuulfuricans* cultures. This figure did not differ significantly from that for the control (2,2 mg/cm^2). This latter result agrees with results from Mara & Williams (96) and Ringas (93) who found that difference in weight loss between mild steel coupons in sterile medium and bacterial cultures did not vary much. They attributed this to the formation of a tightly adherent FeS film which was somewhat protective and provided resistance polarization. This explanation could also account for low weight losses of the 3CR12 coupons.

Weight loss results from immersion tests in mine water showed that this was a far more aggressive environment. This was especially noticeable for the aluminium alloys in sterile deaerated mine water. The 5182 alloy showed a massive weight loss of 82,3 mg/cm^2 . On removal from the flasks, the coupons were covered by a thick white voluminous mass which was soapy to the touch. The pH of the medium was found to be 9,2. This would explain the large weight loss since at this pH the oxide film is no longer stable or protective and would thus allow for generalized corrosion. The weight losses for the alloys in SRB cultures were reasonably low. Although colonization of the alloys did take place, this was not as prolific as growth in the nutritive medium. MPN counts in fact revealed lower bacterial numbers. This would be expected, since the mine water would not contain many essential nutrients in high enough concentrations.

The mild steel specimens showed greater weight loss in bacterial cultures than in sterile mine water. The surface of this alloy was perhaps able to absorb essential nutrients more easily and hence attract more bacteria. The reason for low weight losses in the 3CR12 specimens could be attributed to an adherent FeS layer which afforded protection. On the mild steel specimen, on the other hand, this layer may have cracked due to bacterial growth and thus promoted corrosion.

The *Pseudomonas* cultures both in medium and in mine water definitely had some effect on the Al alloys as seen by the greater weight losses experienced by test samples compared to the controls. This was more noticeable in the mine water in which weight losses of between .6,26 and 7,90 mg/cm^2 were recorded.

Pseudomonas species have been found to bring about corrosion of aluminium alloys. In immersion tests with various microorganisms, including *P.aerugirosa*, Hedrick et al (69) found weight losses of between 0,015 to 0,574% on alloy 7178 after 90 days. *Pseudomonas* cultures were also found by Blanchard and Goucher (85) to accelerate corrosion of alloys 7075 and 2024. This was thought to be due to large molecular weight molecules synthesised by the organisms. As mentioned previously, Hedrick and coworkers (27, 69, 71, 86) also formulated the hypothesis that the corrosion of Al alloys by aerobic microorganisms results from the removal of certain metallic atoms from the crystal lattice of the alloy by extracellular enzyme activity. They found that Al alloys high in Mg and Zn were more susceptible to corrosion by a mixed culture of *C.resinae* and *Pseudomonas spp.* than alloys with low Mg and Zn content. In the present tests the 5182 alloy, which has the highest Mg,

Mn and Zn content, showed the largest weight loss and was covered by large amounts of corrosion product. This, and the fact that there was greater weight loss in the mine water (which has far fewer nutrients) than in the medium, could support the theory that the microorganisms are obtaining their metal requirements from the alloy. Plate counts revealed that the mine water supported a relatively large *Pseudomonas* population, and the findings of Cloet et al (95) as mentioned previously would tend to support this.

The low weight losses recorded for the 3CR12 specimens in both the mine water and medium indicated that the *Pseudomonas* cultures had little effect on this alloy. The mild steel specimens underwent higher weight losses in the *Pseudomonas* cultures compared with weight loss results after exposure to SRB. However, this could be attributed to the lack of a protective FeS layer as well as to the aeration of the medium which promotes corrosion.

Since pitting attack was the more prevalent form of corrosion on the aluminium alloys and can result in catastrophic corrosion with only a small amount of weight loss, the alloys cannot be rated by weight loss criteria alone. The nature of the attack must be studied. For this reason, SEM examinations were performed, the results of which could explain the low weight loss results obtained.

5.3 IMMERSION TESTS - FLOW CONDITIONS

5.3.1 Weight loss results

Generally, weight losses under flow conditions were greater than those in the static immersion tests. This result was also obtained by Buchan (58) in a study of aluminium alloys in two different mine waters. The difference in mass loss results between the sterile water and that containing bacteria can be explained by the fact that the waters, though fairly similar, did vary with respect to pH and total dissolved solids.

Colonization of the alloys was sparse even though bacteria were present in the water, as borne out by regular plate counts and the presence of the beginning of slime formation on the inside of the plastic tubes housing the specimens. It has been found (97) that transport of cells and nutrients to a surface takes place by Brownian diffusion along a concentration gradient in the absence of flow. An increase in flow velocity decreases the thickness of the boundary layer across which diffusion takes place, and with the onset of turbulence, turbulent diffusion very substantially increases the mass transport to the substrate wall. Thus the transport of cells, abiotic particles and potential nutrients to the surface is increased. Under these conditions, rapid adhesion and biofilm development should be favoured. However, a high velocity also increases shear forces over the surface which may reduce the overall efficiency of microbial attachment processes, and the increased shear stress at the surface will tend to remove attached biomass.

The failure of bacterial attachment to the alloy surfaces could be explained by the above. The coupons were positioned in the centre of the pipe, an area of turbulent flow. This would also explain the initiation of slime formation on the pipe walls where, due to the boundary layer, shear stresses were minimal, thus allowing for bacterial adhesion.

Thus any weight losses were probably due to the corrosive action of the mine water alone. In the case of the 6261 alloy, however, the presence of the scale layer and bacterial cells, would tend to suggest some microbial involvement. The extrusion marks would have presented a fairly rough surface which, under flow conditions, would increase the amount of turbulence and thus the mass transport of cells and nutrients to the surface.

5.4 SEM OBSERVATIONS

As expected colonization of the alloy surfaces in medium was well developed, as this represented an ideal situation in which nutrients were in plentiful supply. The type of colonization ie. formation of tubercles covered by bacteria, is similar to that found on ferrous metals by other workers. Under these conditions, both the *D.desulfuricans* and the mixed SRB cultures formed healthy biofilms and were able to bring about corrosion in the form of random pitting and intergranular attack. In the case of the 5182 alloy, pitting seemed to initiate preferentially at inclusions. This type of corrosion would explain the low weight loss results obtained.

In mine waters, colonization took place to a much lesser extent. This was especially so under flow conditions as has been explained above. The situation in the static mine water tests could have been due to the low concentrations of essential nutrients in the water. The volume of water to surface area of specimens was not particularly great and changes with sterile stocks of mine water were only made twice a week. This would also explain why colonization was more prolific in the mixed SRB culture. Since this culture contained a variety of organisms, including facultative anaerobes, the SRB within this consortium could obtain essential nutrients and environmental protection from the microbial community. In contrast, the *D.desulfuricans* culture could only utilize the nutrients present in the mine water.

The extent of the corrosive attack seen on aluminium alloys in mine waters as compared to those in the medium were distinctly different. In the former, pits were initiated in most cases at inclusions. Particles of intermetallic phases are reported to be the common sites for pit nucleation in aluminium and its alloys with other elements (98). Pits were found to nucleate in a 5-series alloy on particles of intermetallic compounds of the following approximate composition:- (Cr, Fe, Mn)Al_6 . The second phases and precipitates are often anodic to the primary phase or solid solution and thus are points of preferential attack. The alloying elements may also introduce inhomogeneities to the oxide film and so decrease its efficacy as a barrier to further oxidation (98).

The 1070 alloy, which is a commercial purity aluminium containing less than 1% alloying elements, showed less pitting damage than the other alloys. The corrosion manifested itself mainly as selective phase dissolution.

In cultures of mixed SRB, and more so in *Pseudomonas* cultures, the 5182 alloy seemed to suffer selective attack in the form of pitting at grain boundaries. Different impurities may segregate to the grain boundaries in metals and this is thought to be the main reason for the higher reactivity of grain boundaries relative to the grains. Susceptibility of grain boundaries to pitting is due to the presence of segregated impurities and/or precipitated particles (98). The 5182 alloy is an Al-Mg alloy in which the Mg_2 Al precipitates are anodic to the solid solution and will thus undergo preferential corrosion. The addition of Si increases the solution potential to nearer that of pure aluminium and with proper control random precipitation should reduce selective attack at grain boundaries. In these tests however, pits were initiated at Mg_2 Al precipitates as well as at intermetallic compounds containing Fe and Mn. Buchan (58) also reported selective attack of precipitates at grain boundries in a 5251 aluminium alloy in mine water.

The 6-series Al-Mg-Si alloys may show preferential attack at particles containing Mg and Si which are not in the ratio of 2:1 respectively. Fe and Mn precipitates also seemed to adversely affect the pitting in both SRB and *Pseudomonas* cultures.

The ferrous alloys did not seem to be affected by microstructure, a result borne out by Mara and Williams (96) in the corrosion of mild steel by SRB.

Another factor to be taken into consideration in mine waters is the presence of Cu ions. The presence of a small number of Cu ions in fresh water has been found to stimulate initiation of pitting by depositing a layer of copper particles on $FeAl_3$ making them much more efficient as cathodes for corrosion processes (98). The water analysis indicated that copper was present in the mine waters used and the presence of a copper layer on the 6261 alloy was comfirmed by EDAX analysis.

Thus it seems that mine waters contaminated with bacteria present an aggressive environment for aluminium alloys leading to pitting at alloying inclusions (which was especially marked in the 5182 alloy), dissolution of secondary phases and intergranular attack. The aggressiveness of mine waters towards Al alloys was also reported by Buchan (58) and McEwan (67).

5.5 ELECTROCHEMICAL TESTS

Tests were carried out in both mine water and nutritive medium and though the former solution was more aggressive, the behaviour of the alloys in both solutions followed a similar trend. The different redox poising chemicals used viz. AS and FAS affected the properties of the solutions by introducing Fe ions in the latter case which could then complex with the sulphide formed through the action of SRB.

Results from tests on 3CR12 correlated well with results of Ringas (93). The alloy passivated both in sterile medium and mine water containing AS as it did in these solutions containing FAS. In the latter case, however, the passive ranges were lower. Scans performed in SRB cultures showed a marked difference exhibiting a more active free corrosion potential, a reduced passive range, an active peak, hysteresis in the return scan and a greatly increased passive current density. These results indicate that these bacteria adversely affected the corrosion resistance of this alloy by decreasing the crevice corrosion resistance (as indicated by the amount of hysteresis and the formation of an active peak), and by decreasing the potentials of safe operation through incorporation of sulphide in the passive film which makes it less protective. In the presence of FAS, the formation of FeS on the alloy surface had the effect of either aiding passivation when it was a tightly adherent film, or promoting corrosion when it occured as a loose bulky mass. The Ecorr values became more active due to the action of H_2S formed by the SRB.

The performance of the aluminium alloys was not as clearcut. Pitting scans in both the sterile mine water and medium containing AS, showed that the aluminium alloys passivated and the reverse scans returned to the left of the forward scans indicating that spontaneous repassivation took place.

In SRB cultures in solutions containing AS the effect was to decrease the passive range and adversely affect the crevice corrosion resistance of the alloys. Although the passive current density was low for both control and test samples, alloys exposed to bacterial cultures showed decreased values. In addition, the bacteria shifted the Ecorr values to more noble potentials, compared to the sterile controls. It would thus appear that the bacteria enhanced the conditions for passivity in the aluminium alloys. It is considered likely that the above effects were related to corrosion product build - up (through bacterial action), which functioned as a temporary diffusion barrier and slowed down the corrosion process. From the EDAX analysis, the formation of an aluminium sulphide layer, which could function as a diffusion barrier, was apparent. Such layers are, however, only effective if they are in the uncracked condition. Should flaws occur, localised penetration would be expected to take place. Under industrial conditions, cracking of the surface layers would be more likely than in the stagnant, non-turbulent, non-abrasive laboratory experiments.

It has been shown that incorporation of sulphide in the passive film renders it less protective, delays repassivation and can increase the likelihood of crevice attack (99). In this case the sulphide may have influenced the crevice corrosion resistance of the alloys, though the high sulphate content of the solution (especially that in mine water) helped form a more stable passive film.

The addition of FAS to the mine water and medium did not affect the behaviour of the sterile controls. In SRB cultures, however, there was a marked effect. The free corrosion potentials became more active, the passive current densities increased in most cases and the perfect passive ranges were decreased. In addition the crevice corrosion resistance was adversely affected. These findings suggest that the presence of the FeS is the major factor affecting the corrosion resistance of the alloys. The increase in passive current density and the decrease of the perfect passive range in the presence of FeS suggests that this interfered with the passive film formation.

The involvement of H_2S may also be considered here. It has been postulated that H_2S may play a role in corrosion. As HS^- ion concentration increases in a crevice, H^+ ions migrate to the crevice in order to achieve charge neutrality, thereby increasing the acidity locally (93). In electrochemical tests, the test cell was adapted to allow for deaeration of the headspace alone thus resulting in minimal loss of H_2S from the medium. Although Ecorr values became more active in the presence of FAS, thus suggesting H_2S involvement, in solutions containing AS there was no such effect. This suggests that FeS is exerting the main influence. This could be due to the complex acting as local cathodes on the aluminium surface thereby increasing its susceptibility to pitting.

These findings indicate that in mine water containing SRB, both aluminium alloys and 3CR12 would suffer accelerated corrosion due to the presence of sulphide (reduced from sulphate in the mine water by SRB) and Fe (due to oxidation of pyrite).

In *Pseudomonas* cultures, bacteria had the effect of decreasing the perfect passive range and adversely affecting the crevice corrosion resistance of the aluminium alloys as indicated by the formation of an active peak and an inability for repassivation.

Results from Tafel extrapolations for all Al alloys in both bacterial cultures and sterile controls indicated no significant change in the Tafel slopes of scans performed on the specimens exposed to bacteria compared to those in sterile medium. However, in the case of 3CR12 and mild steel specimens which were exposed to flourishing SRB cultures in nutrative medium, an increase in the cathodic Tafel slope in the bacterial cultures suggested that cathodic depolarization was in fact taking place. This was not the case in SRB cultures in mine water where the bacterial numbers were possibly too low to exert any effect.

In the case of the Al alloys, the electrochemical corrosion test results tend to suggest that the presence of bacterial species adversely affect their corrosion resistance by interfering indirectly with passive film formation, as well as by decreasing their crevice corrosion resistance and ability for pit repassivation. The importance of FeS in the corrosion process was also ascertained. The theory of microbial utilisation of alloying elements could well apply in the case of *Pseudomonas* cultures. The mode of corrosion by SRB is not as clear, but cathodic depolarisation by H_2S and FeS may occur.

5.6 RANKING OF AL ALLOYS

The relative performance of the alloys under various conditions in the test waters was determined by ranking them according to three different test result criteria, viz. weight loss (WL), general corrosion rate (CR) and passive range (PR). The alloy showing the least weight loss, the lowest corrosion rate and the highest passive range was given a value of 1, while the worst performer received a rating of 4. The ratings for the tests were added together and the alloy with the lowest total was judged the best performer. It must be stressed, however, that this is a fairly subjective approach and is intended to serve only as a very rough guide. The results are given below.

Table 5. Ranking of alloys

	Alloys	WL(mg/cm^2)	CR(mpy)	PR	TOTAL
D.desulfuricans	1070	2	1	4	7
	5182	4	3	3	10
	6063	3	4	2	9
	6261	1	2	1	4
SRB(M)	1070	2	3	3	8
	5182	1	1	1	3
	6063	3	2	2	7
	6261	4	4	4	12
SRB(C)	1070	3	4	2	9
	5182	4	1	4	9
	6063	2	2	3	7
	6261	1	3	1	5
Pseudomonas	1070	2	1	1	4
	5182	4	4	3	11
	6063	1	2	2	5
	6261	3	3	4	10
Pseudomonas(C)	1070	4	2	1	7
	5182	3	1	3	7
	6063	1	4	2	7
	6261	3	3	4	10

Overall, the 5182 alloy was the worst performer. This could be attributed to the preferential attack of intermetallic inclusions, especially since the 5182 alloy has the highest percentage of alloying elements of all the Al alloys tested. In the case of the *Pseudomonas* culture, the ranking followed exactly the trend of amounts of alloying additions with 1070 (a commercial purity alloy) suffering the least corrosion and the 5182 alloy the most.

6.0 CONCLUSIONS

- From the mine survey, it is evident that microbes are present in mine waters, are able to colonize the aluminium alloy surfaces and seem to bring about pitting and intergranular corrosion. Furthermore the presence of sulphur species at the base of the pits and the absence of chlorides suggest microbial influence.

- Immersion test results indicate that in situations where nutrients are in plentiful supply, microbes proliferate on aluminium surfaces and bring about pitting and intergranular corrosion.

- Under conditions where essential nutrients are in short supply, biofilm development will be slow. However, once a complex microbial consortium has developed, the biofilm will assist in trapping and concentrating nutrients as well as giving environmental protection to detrimental organisms which would then almost certainly bring about aluminium corrosion.

- Anodizing and conversion coating Al alloys may temporarily protect the surfaces from becoming colonized by microorganisms. Any defect or damage to the coating will immediately promote colonization.

- In the presence of SRB the integrity and protective nature of the passive films on aluminium alloy surfaces tested were adversely affected. The crevice corrosion resistance and pit repassivation abilities of the alloys were decreased. This led to the formation of pits and intergranular attack. The involvement of FeS in the corrosion process was established and it is postulated that this may act as a cathodic depolariser.

- The mode of corrosion of Al alloys by *Pseudomonas spp.* seems to be due to utilization of alloying elements by the bacteria.

- The aluminium alloys with the most alloying additions underwent more corrosion due to preferential pitting attack at intermetallic inclusions.

7.0 RECOMMENDATIONS

- The study of biofilms in environments that resemble in situ situations as closely as possible can produce valuable information. The use of a Robbins Device (100) in cooling water systems on mines to study natural populations and type of corrosive attack should be carried out.
- Further work should be carried out on methods of altering the Al alloy surfaces in order to prevent microbial attachment.
- Further investigations to determine the mechanism of microbial corrosion are needed.
- Due to severe pitting, the alloys tested would not be recommended for use in mine waters.

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9.0 APPENDICES

APPENDIX A

Sulphate Reducing Medium

Sodium lactate	7,0g
Beef extract	1,0g
Peptone	2,0g
$MgSO_4 .7H_2O$	2,0g
$Na_2 SO_4$	1,5g
$K_2 HPO_4$	0,5g
$CaCl_2$	0,1g
Distilled water	1L

Prepare solution and adjust pH to 7,5.

APPENDIX B

Cleaning Solution

Dissolve 30g CrO_3 in 500 ml distilled water.
Add 36 ml H_3PO_4 (specific gravity 1.689)
Add distilled water to 1 L.

APPENDIX C

Weight Loss Test Results

Static Tests - Mine water

Alloys	*D.desulfuricans*	Mixed SRB	Control SRB	*Pseudo*	*Pseudo* (C)
1070	2.1	0.3	40.9	6	0.46
5182	3.24	0.19	82.31	7.9	0.36
6063	2.19	0.34	26.3	6.26	0.14
6261	1.78	0.52	16.6	7.0	0.18
3CR12	0.22	0.07	0.39	0.16	0.1
MS	4.74	10.16	0.46	5.69	4.66

Static Tests - Medium

Alloys	*D.desulfuricans*	Mixed SRB	Control SRB	*Pseudo*	*Pseudo* (C)
1070	0.19	0.04	0.04	1.36	0.05
5182	0.14	0.06	0.13	2.04	0.06
6063	0.07	0.006	0.006	1.00	0.005
6216	0.07	0.05	0.006	1 9	0.006
3CR12	1.17	0.66	0.5	0.12	0.08
MS	2.70	2.21	2.23	5.81	4.73

Weight losses are in mg/cm^2.

APPENDIX D

Weight Loss Test Results - Flow Loop

Alloy	Bacteria	Control
1070	0.556	1.81
5182	0.794	2.265
6063	0.316	2.69
6261	3.353	4.47
Anodized	0.195	1.42
Conv. coated	0.286	0.880

Weight losses are in mg/cm^2 .

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Name of thesis: Microbial corrosion of aluminium alloys in mine water.

PUBLISHER:
University of the Witwatersrand, Johannesburg
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