BIOCORROSION IN THE MINING INDUSTRY ... BIG TANKS AND BIG PIPES

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1. ABSTRACT

In Australia, particularly the mining states of Queensland and Western Australia, the production of mineral resources is a significant contributor to the state's Gross Domestic Product. The production of aluminium, coal, copper, gold, iron ore, nickel, alumina and other metallic ores are all subject to corrosion processes. Some processes, such as the production of titanium dioxide, are really corrosion processes in a controlled environment. Nevertheless, the harsh and aggressive operational conditions can also enhance corrosion and the use of hyper saline bore water in the Eastern goldfields in Western Australia is a prime example of a naturally inoculated microbially mixed environment. A selection of case studies are presented for carbon steel, galvanised steel, a high chromium iron alloy (3CR12) and rubber, where microbial activity was the prime deterioration mechanism. Some case studies are included to show that bacteria are implicated in many corrosion failures of critical mine site assets including tankage (the perforation of Carbon in Leach tanks in the gold industry), the deterioration of large rubber lined process equipment, the deterioration of process cooling towers and the premature failure of stainless steel Reverse Osmosis water lines. This paper comments on some of the mechanisms of MIC, the predominant causative organisms, the diversity of susceptible materials observed and the likely consequences to production.

2. INTRODUCTION

With the recent strong financial impact and export driven success of Australian mining companies and concomitant higher resource prices, the mining industry should be using this time as an opportunity to maintain and replace assets that may have deteriorated over the recent past. Hence maintenance budgets have been increased and maintenance activities are currently on a high.

It is important to remember that materials deterioration is independent of the price of coal, gold, nickel, iron ore etc. It has been observed that many mine sites experience microbially influenced corrosion (MIC) after less than 12 months operation, but are aware only of the effect, remaining unaware of the cause and the active bacteria that provide the driving force for corrosion.

From the mid-nineties in Australia, the incidence of microbially influenced corrosion (MIC) has become more associated with the mining industry and this has been reflected in the increased reporting in technical literature and the interest in symposia such as this. A growing number of failures have been identified as the primary result of microorganism activity and this, although commonly known as MIC, is not usually a single process, but rather an association and interaction of various microbial types leading to corrosion. In summary, MIC can involve a plethora of organisms and mechanisms; and the microbial component is seldom straightforward or easily attributed to a single organism or a unique mechanism.

3. BACKGROUND

Deterioration of materials by living organisms have been commonly referred to as biodeterioration, and this phenomenon can encompass both metallic and non-metallic materials (including composites such as reinforced concrete). One of the problems in making engineers take notice of the extent, severity and consequence of biodeterioration is a lack of knowledge, information and disbelief that single celled fauna can physically deteriorate carbon and even stainless steel.

There has been and probably always will be a natural reluctance by engineers to appreciate that metal loss of up to 10mm/yr, but regularly 4.0 – 5.0mm/yr can be caused by life forms that can be accommodated on the head of a pin! It is only when this type of severe corrosion occurs on some piping, pressure vessel, equipment or tankage leading to perforation and the proof of microbially influenced corrosion is presented, that the significance of MIC is appreciated.

4. MICROBIALLY INFLUENCED CORROSION

A basic definition of microbially influenced corrosion (MIC) is corrosion associated with the action of microorganisms within a system. However, MIC is not usually one simple process but rather a combination of different microbial types in association with each other and with suitable physical, chemical and electrochemical parameters at the metal surface. The mechanisms involved with MIC can be seen in other types of corrosion.

4.1 Concentration Cells

Concentration cells can be set up when a bacterial growth develops heterogeneously on a metal surface. Concentration cells are also associated with tubercle deposits formed by iron oxidising bacteria. The mechanism for this corrosion is differential aeration where oxygen is depleted under the bacterial growth causing the area under the deposit to become anodic.

The microbial corrosion of iron and steel in neutral solutions is most commonly associated with the sulphate reducing bacteria (SRB). Sulphate reducing bacteria has been indicated by localised pitting corrosion under tubercle deposition on the tank walls of the carbon in leach (CIL) tank circuits in an Eastern Goldfields treatment facility as was first described by. [1] The corrosion usually occurs in the tanks with the lowest dissolved oxygen levels and the effect is usually felt all the way through the circuit to the Tailings thickener. Certain bacteria can also trap heavy metals such as copper and cadmium within their extracellular polymeric substance, resulting in the formation of ionic concentration cells.

4.2 Production of corrosive byproducts

Bacteria produce byproducts that can be corrosive to metals. These byproducts include inorganic acids, organic acids, sulphides and ammonia. In gold mines in South Africa, MIC has been attributed to the *Thiobacillus* species obtaining energy from the oxidation of sulphur. Sulphuric acid is produced, giving rise to a corrosive environment. *Ferrobacillus ferrooxidans* can accelerate the oxidation of pyrite deposits at low pH values. This bacterium is also usually found in association with thiobacilli, as part of the sulphur cycle. Ultimately, the oxidation of pyrites can produce acidic mine waters which is a major problem in some Australian declines leading to accelerated deterioration of underground infrastructure.

4.3 Stimulation of electrochemical reactions

The evolution of cathodic hydrogen from hydrogen sulphide can be caused by the production of the hydrogen sulphide by microorganisms. MIC as a phenomenon is likely when suitable nutrient, flow and environmental conditions occur with the presence of corrosion causing microbial life. Microbiological corrosion can be quite rapid in its attack, the type of metal loss associated mainly with the presence of SRB is localised pitting corrosion, where pitting at a rate in excess of 5mm/yr. is realistic.

4.4 Interference with corrosion management options

Microorganisms attack protective metallic and organic coatings exposing the underlying material to corrosion. The metal could corrode due to differential aeration or galvanic corrosion if the protective coating was a metal. Microorganisms can also alter the composition of corrosion inhibitors.

5. TYPES OF MICROORGANISMS

MIC is the name used to classify the interaction of corrosion and living organisms such as bacteria, fungi (moulds or yeasts), algae or slimes on a variety of substrates including non-metallic and novel alloy materials.

Microorganisms can and are classified by a mixture of categories including:

Metabolism

- The chemistry of their energy source, e.g. sulphate reducing bacteria (SRB), sulphide or sulphur oxidising bacteria (e.g. Thiobacillus), acid producing (e.g. Clostridium) bacteria or fungi.
- Carbon source for growth, e.g. acetate production or oxidation
- Elements accumulated by their metabolism, e.g. manganese fixing or oxidising iron (e.g. gallionella) bacteria.

Cell Shape

- Coccus (round)
- Bacillus (rod like)
- Vibrio (curved like a comma)
- Myces (fungi shaped)

Oxygen tolerance

- Anaerobes (will not tolerate oxygen in active form)
- Aerobes (must have oxygen to live)
- Facultative anaerobes (oxygen does not matter)
- Microaerophiles (prefer low levels of oxygen)

Microbiologists tend to classify by genus and strain with location sometimes included. MIC on iron and carbon steel had been proposed as early as 1910 and the first theory for MIC mechanisms was suggested during the 1930's. [2] This indicates that MIC has been a demonstrated and identifiable problem for at least the last50 - 60 years. Stott observed succinctly and elegantly, what most corrosion engineers took as anecdotal, and that is MIC, "*is not fundamentally different from any other type of electrochemical corrosion; it is simply that the chemical or physical conditions giving rise to the aggressive environment are produced by organisms as a by-product of their metabolism*." [3]

For many years corrosionists considered SRB as the most important corrosion-enhancing bacteria involved in MIC-assisted failures. Recently, however, there is a growing amount of evidence to suggest that SRB are not singularly the main cause of MIC, but also due to thevery nature of natural systems, groups of bacteria can be found to be co-operating together within microbial communities known as biofilms, and exacerbating corrosion. It is therefore useful to appreciate that corrosion deterioration can result from a number of factors, and MIC in many cases contributes significantly rather than being solely responsible. MIC in the mining industry is not as well defined or comprehensively described in the technical literature, being focussed mainly on the bioleaching of ores. Winter (1995) is one of the few people to refer to bacteria as a causative corrosion agent in the mining industry.

6. CASE STUDY SUMMARIES

In this section, six case study summaries are presented to show the diversity of MIC and the materials that are affaected. All are from the mining industry, including the corrosion of stainless steel and carbon steel raw water piping after 6 months and 10 months service respectively, then the corrosion of a high chromium alloy (3CRI2) under heap leaching conditions and finally the deterioration of natural rubber lining on a carbon steel substrate.

6.1 Case Study 1- Dust Suppression Piping (4 years in service)

The problem in this instance was the premature failure at a mine site after 4 years service of the hot dip galvanised (HDG) steel piping that transported fresh water from a collection dam to an allocated storage tank, over a length of 3 kilometres. The delivered water was used for dust suppression on the roads and Primary crusher where the bauxite ore was crushed. After approximately 4 - 5 years of service, random pipe end failure started to occur and this had escalated to parent spool perforation, mainly at the welds, but also at the parent plate.

The internal surface of the 5mm thick,150mm nominal bore HDG pipe fabricated in 12m pipe spools and connected with Victaulic couplings was being used for dust suppression water distribution. As water availability from these lines is critical particularly during summer (eg. 50 litres a second with 99% availability) it was imperative that the pipeline integrity was not compromised by corrosion.

Service history had shown that of the line utilised for water supply to the storage tank had had considerable pipe spool replacement due to perforation and that this line appeared prone to corrosion. The type of failure noticed on the 150NB pipe had been pipe perforations at random locations along the pipe circumference and at longitudinal seam welds. It had been documented that during the peak water demand the mean time between failures (MTBF) was in the order of 4.5 days with instances recorded returning a MTBF of only 1.75 days.

The internal pipe surface of the line had accumulated corrosion product/debris on the internal surfaces extending some 20 - 30mm from the internal surface and consisted of reddish brown tubercule growths with an underlying black deposit. Removal of the material for inspection of the parent pipe spool revealed a smoothly pitted substrate of bright, shiny appearance. This led to the sampling of accumulated material for further analytical testing

The neat samples were cultured and tested for SRB, iron bacteria and total bacterial present using recommended culture media after 21 days incubation at 30 degrees C. The predominant causative species appeared to be the SRB which were attached to the particles of corrosion product and there was a motile or planktonic count 1000 cells/ml, as well as *Gallionella* (the Iron bacteria} count was 300,000 cells/ml and the total bacterial count was 400,000 cells/ml.

Ultimately, the intake position of the pump was raised to a higher more oxygenated level and a water treatment (biocide) facility was installed at the pump inlet

Fig.1 A/B – Condition of the HDG pipe on opening and after removal of tubercles

6.2 Case Study 2- Reverse Osmosis piping (6 months in service)

The problem in this instance was the premature failure at a mine site after 4 years service of the hot dip galvanised (HDG) steel piping that transported fresh water from a collection dam to an allocated storage tank,

A section of stainless steel piping and associated flanges from a reverse osmosis (RO) pipe work circuit that had suffered premature corrosion (perforation within 6 months) had been inspected. The reverse osmosis (RO) circuit pipe were austenitic stainless steel components with the pipe sections and elbow manufactured from grade 304L material.

The pitting corrosion at the pipe work bore was consistent with microbiologically induced corrosion (MIC) as indicated by the significant build up of deposit on the internal surfaces, characteristic of bio-mound type formation, heavily undercut pitting with only small surface openings and subsurface, longitudinally oriented attack.

SEM analysis of the corrosion product identified the presence of sulphur, which along with the positive response to the presence of sulphate reducing bacteria (SRB) and *Galionella* indicating MIC as a possibility. The corrosion product analysis also gave a small proportion of chloride, the presence of which was also considered likely to have contributed to the localised attack. The tubercles of Gallionella (iron reducing bacteria) are known to be a potential causative agents in the corrosion of stainless steel water piping systems, particularly in combination with the SRB.

In this situation, the 304L stainless steel was changed out, better attention to welding consumables occurred and the RO system performance has been good.

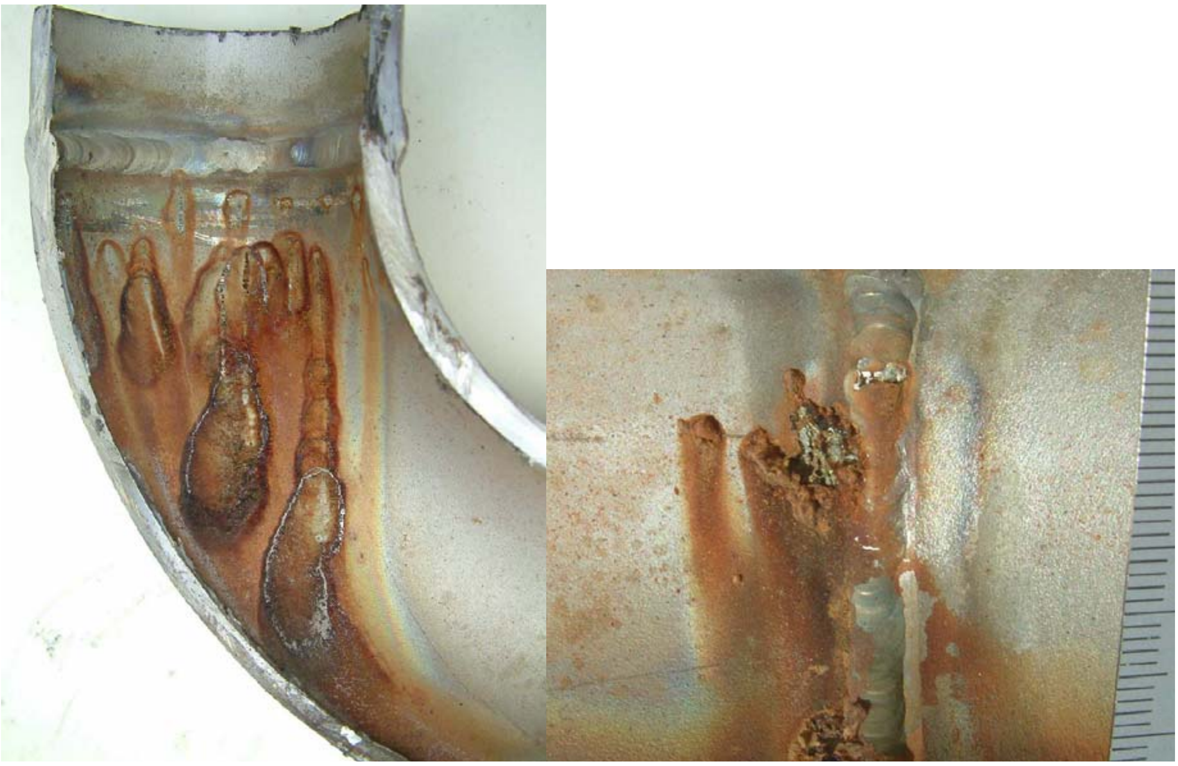

Fig 2A/B – General and close up view of 304 stainless steel piping in a Reverse Osmosis piping and general view of the reddish brown tubercle location on the pipe inside surface at the pipe to tee weld.

Fig. 2C – General view of the pit morphology under magnification (x100) at the pipe bore, with the narrow opening and smooth, rounded internal surface..

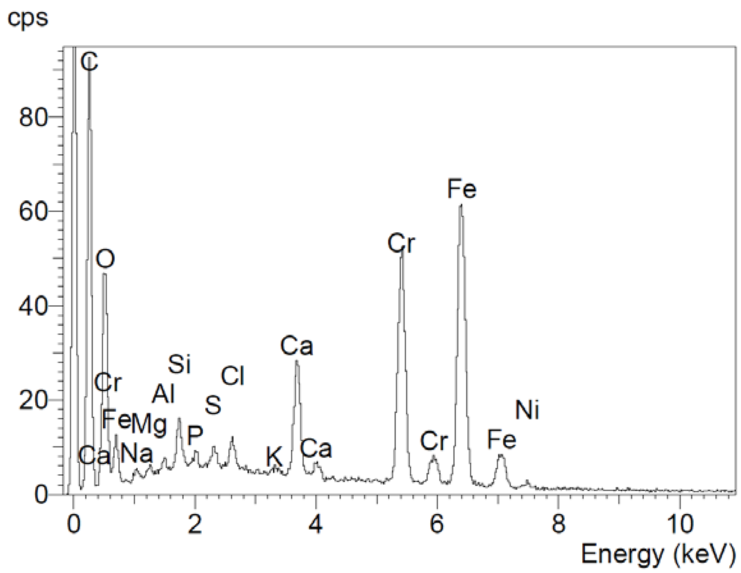

Fig. 2D - EDS analysis results of the corrosion product within one of the areas of pitting.

6.3 Case Study 3- Raw Water Piping (<12 months in service)

The problem in this instance was the premature failure at a minesite after 10 months service of the carbon steel piping associated with an untreated raw water service. The raw water was sourced from borefields and the water reported to a common raw water tank, from which the mine's non-potable water needs were satisfied. The piping most affected was the 40mm diameter piping that had a wall thickness of 3mm and contained a longitudinal weld seam. A site inspection of the internal surface to part of the 40mm diameter raw water pipe, which was part of the water distribution system on the plant, was conducted. There was the formation of internal tubercles (5 - 10mm in diameter and 4 - 6mm high) which although randomly distributed, showed some preponderance on the welds. An inspection after 10 months service showed that the pipe was perforating and some 9m of pipe had to be changed out, with three (3) perforations present in this section. There was some scaling and minor tuberculation present and removal of the scale inside the pipe exposed a layer of black deposit adhering to the pipe wall. Areas under the scale showed severe pitting, with jagged edged pits being observed.

A sample of the pipe was cut longitudinally and this revealed the presence of a thick reddish/brown coating on the internal surface. At the seam weld, corresponding to the pipe perforation location, a large voluminous tubercular deposit was apparent, which when removed, showing extensive corrosion at and of the weld. On the parent plate where the tuberculation had also occurred, only a small amount of general metal loss was evident, up to 300 micron deep.

Sections were cut to include areas of both un-corroded and corroded weld seam. The internal surface of the weld in undamaged areas shows the raised flash with minimal corrosion having occurred. Conversely, the microstructure found at the perforation in the seam indicates that the centre of the weld had corroded leaving the heat affected zones relatively unaffected as indicated by with preferential corrosion at the seam weld. In some areas the complete centre line of the weld, had corroded leading to perforation. It is of interest to note the structure of the corroded weld did show the presence of a suitable heat affected zone only produced by a correct weld procedure.

The main source of raw water at the site was from borefields. The water quality for the raw water is presented in table 1:

Table 1. Raw Water Quality

	Concentration (ppm)
Total Dissolved Solids	12,000-15000
Sulphates	1,000-10,000
Chlorides	5,000-10,000

This water was generally used for plant processes and washdown of equipment. The levels of TDS and chlorides suggested that the water could be corrosive to steel.

Quantitative bacterial testing was performed on both raw water and firewater samples to determine total aerobic bacteria, presence of iron bacteria and the levels of the anaerobic Sulphate Reducing Bacteria. The microbiological analysis was required to ascertain if the samples contained bacteria that had the potential to participate in microbiological influenced corrosion. The recommended procedure for viable bacterial enumeration was followed for all the bacterial counts.

In addition, microscopy, using both wet and stained preparations was performed to get an idea of the type and amount of bacteria present in the various samples. Several different morphological forms of bacteria were seen in the raw water pipe, raw water tank and the fire water samples.

Table 2. Bacterial enumeration results from Raw Water and Firewater samples

SAMPLE (Viable bacterial per ml)	AEROBIC	IRON BACTERIA	SRB
Raw Water Tank	65,000	50,000	160,000
Raw Water Pipe	820,000	60,000	160,000
Fire Water Line	120,000	48,000	13,000

Based upon the morphology of the cultured bacteria, all the samples contained a variety of bacterial species. The culturing of SRB from all the samples within 72 hours was indicative of high microbial activity and a strong likelihood ofMIC. The high counts of the iron depositing bacteria in three samples are also supportive of the MIC theory.

This problem was significantly reduced by introducing water quality management at the central raw water tank to which all the borefield sources reported.

6.4 Case Study 4 - Heap Leach Tanks (<2 Years service)

The problem in this instance was the premature failure at a minesite after 18 months service of the high chromium (3CRI2) steel tanks associated with a Heap Leach treatment program for processing of gold laden ores. Again the process water was sourced from borefields, but the Heap Leach process liquor was recycled to take maximum use of the dissolved chemicals. The tank parent plate and welds were both affected.

The adsorption tanks in the Dump Leach train were brought into service in 1994 and were about 18 months old. The use of 3CR12 was decided upon to reduce the time and cost associated with the fabrication of a coated carbon steel tank train. The Dump Leach facility at this gold mine was producing about 46% of gold output and treating about 10 million TPA. The tank heights varied form 9.5m - 4.5m, and were fabricated from a high chromium (3CRI2) steel, typically 5mm thick plate at the wall and floor plate. There was localised pitting observed and from measurements taken, the calculated corrosion rates were 3.3 -5.0mm/year being experienced on the Dump Leach tank train.

The water samples gave the following results:

Table 3. Water Quality

	Concentration (ppm)
pH	7.5-8.7
Total Dissolved Solids	7,000-8,900
Sulphate ion	1,500-2,500
Chlorides	1,600-2,300

Because of the remoteness of the site, testing for SRB was done on site by inoculation of media vials from likely corrosion areas in the Dump Leach tanks. Samples from both the floor and wall tubercles were selected and placed. After incubation, test results suggested very low levels of SRB at less than 100 cells/ml, which was well below the threshold number of about 1000 cells/ml thought to initiate MIC.

Nevertheless other plant parameters could well have contributed to localised attack and with the particular service of the tanks, there are a number of factors in place which make corrosion of the unprotected tank surfaces seem almost inevitable. These included:

- A high degree of oxygenation of the process water
- High ambient temperatures at site
- With the Dump Leach system, a water with likely high microbial activity (not necessarily SRB)
- Moderate flow velocities
- The presence of carbon granules with large surface area/volume ratio
- The presence of chlorides and sulphate levels in excess of 1000 ppm

With these parameters in place, the type and rate of corrosion is not unexpected. Galvanic attack of the alloy steel in the presence of a conductive electrolyte (water) and a well demonstrated cathodic material (granular carbon) was observed on the false floor and bottom of the tank where carbon granules had accumulated and in some cases adhered to the metal substrate.

The formation of tubercles on all horizontal weld and predominantly on edges, welds and corners of the lower tank section (below the false floor) and the creation of an occluded cell on the alloy steel had also lead to severe localised corrosion. Although SRB numbers were low, these are not the only microorganisms which promote tubercular growth (other iron bacteria such as Gallionella and Sphaerotilus do so more effectively). The solution to this corrosion problem was the application of a suitable high build organic coating system which acted as a barrier to the substrate material.

6.5 Case Study 5 - Rubber lined vessels/pipes (6 years old)

There had been a significant case of rubber deterioration noted at this mine, which had been getting more severe and extensive. When the deterioration was first noted the mechanism could not be determined, but equipment removed from service some 2 - 3 years previous were inspected in the salvage yard and were also showing similar signs of rubber deterioration. The problem in this instance was the continual breakdown of natural rubber on all lined vessels where the rubber lining was observed to start deteriorating after 6 months and continued until large sugar grain sized particles of rubber were being removed.

The rubber was 5 mm thick with an uneven surface on the side that had been exposed to the water. This surface contained craters or hollows. The deterioration appeared to be a localised loss of material varying in size from 5 - 25mm in diameter and extended to a depth of l0mm at worst. The general appearance of the rubber was dimpled, and it was not clear if the deterioration was limited to low velocity areas only. Ultimately, the rubber was being removed from the underlying steel substrate and colonisation by the SRB proceeded, with localised corrosion and perforation of the steel substrate resulting. The deterioration was extensive, and affected most rubber lined vessels throughout the process stream. Vessels at the front end of the process stream appeared to be worst affected. Interestingly, there had been no problems with high density polyethylene (HDPE), neoprene and synthetic rubbers in use on site.

Specific microbial testing was performed on both rubber and water samples removed from site. Based upon the initial microbial test results, it was determined that the deterioration in the rubber was due to microorganisms.

Fig 3A – General view of rubber lined Cyclone cover, badly affected by deterioration of the natural rubber lining used for internal protection.

Generally, several different bacterial species were cultured from all the tested rubber and water samples within 24 hours incubation. There was no fundamental difference between the collected samples apart from the comparative relative numbers of each species cultured from each sample. Identification of the different colonies based upon the morphology of the colonies, biochemical tests and microscopic investigations indicated that the majority were colonies formed from bacteria belonging to one of the following genera; *Bacillus, Pseudomonas, Flavobacteria, Achromobacter, Enterobacter, Citrobacter* and *Chromobacter* and the SRB provided a count exceeded 10^7 cells/ ml. From the rubber scrapes four morphologically different colonies of fungi, *Penicillium, Aspergillus, Cladosporium* and *Actinomyces*, were isolated.

Fig 3B – Close up of the rubber lined Cyclone cover, showing the "pitting" as the rubber deteriorated, prior to the exposure of the underlying steel and the MIC associated with the substrate steel.

Historically, it has been considered that rubber was a fairly stable compound immune from biodegradation and therefore the risk of micro-organisms affecting rubber was small. Investigations of rubber deterioration therefore rarely included tests for micro-organisms. It is now known that rubber is not immune from biodeterioration but the rate of deterioration may be influenced by the type of rubber product as well as the species of micro-organism involved.

6.6 Case Study 6 – Oxygen Plant Cooling Tower surface (6 years old)

The Oxygen Plant at any golf mine site is the main source of air for the production process, usually autoclave operation as well as a source for instrument air dryers. Air compressors and cooling towers at such a plant operate in moist humid environments across North Queensland and in PNG. These atmospheric conditions encourage coating breakdown by MIC, namely algal growth. This case study refers to the overall condition of an Oxygen Plant Cooling Tower, where the protective coating was showing extensive oxidation and weather damage allowing considerable coating staining and algal growth, factors that will accelerate coating damage. In addition, the algal growth on the surrounding concrete floor was a slip hazard.

It is known that microorganisms such as bacteria, fungi, and terrestrial algae have all been associated with coatings both cured and uncured. The chemical nature of the binder, the choice of pigment, and the pigment volume concentration are all known to affect the susceptibility of a coating film to attack by microorganisms. Fungi are present on the surface of paint films in two forms, either as the thread-like mycelia (actively growing and reproducing)or as clusters of spherical, dark coloured spores(when conditions for growth are less favourable). Numerous fungi are found on and within coating films, such as the *Aureobasidium pullula* first reported in 1948. [4]

The chlorophyll filled Algae, produce their own organic carbon from atmospheric carbon dioxide and light by photosynthesis. The algae may be filamentous or unicellular organisms and vary in color from green to brown to black with a presence and growth of terrestrial algae on coated surfaces being described. [5, 6] The Cyanobacteria (blue-green algae) *Oscillotoria* sp. and *Scytonema* sp. predominate in tropical conditions such as Northern Queensland and PNG. The bacteria genera commonly associated with spoiled paints include the *Pseudomonas, Aerobacter, Enterobacter, Flavobacterium,* and *Bacillus* also found anaerobic bacteria in contaminated water-borne coatings and raw materials. [7, 8] It was observed that these anaerobic bacteria were capable of utilising organic coating components as nutrients.

The predominant causative agent in this case was was an algae which could not be specifically identified when examined. The situation was rectified by the use of high pressure water blasted with grit injection on the more extensively corroded areas accessed and the application of a algaecide loaded high build epoxy coating system for use on the entire cooling tower section.

Fig 4 A/B – Algal growth over the high build epoxy on an Oxygen plant cooling tower, including the piping.

7. CONCLUSIONS

The consequences of corrosion to the mining industry are high. One of the last survey of the costs and significance of corrosion to the mining industry suggested that in excess of 75% of minesites considered corrosion a moderate to severe problem at the specific sites. [10] Of interest was the "cost associated with corrosion". Response to cost related questions got the most imprecise answers with many minesites not able to provide a cost of corrosion value.

With the processing of ore in the mining industry requiring the use of considerable amounts of water (much of which is nutrient laden because of the source), diverse ore sources, high organic contents and locations within the process where both aerobic and anaerobic conditions can exist, it is highly likely that MIC can occur and even predominate. Although only sparsely reported in the mining related technical literature, it is apparent that MIC is present to a varying extent on diverse material substrates in the mining processing and needs to be considered by both design and maintenance personnel.

As a consequence of this, there should be a heightened MIC awareness present in the mining industry. With the increasing incidents of MIC in the mining industry, increasing the MIC awareness of technical and engineering personnel can only be beneficial.

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9. AUTHOR DETAILS

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