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THE INCIDENCE OF MICROBIALY INFLUENCED CORROSION IN THE MINING INDUSTRY AND THE CONSEQUENCE ON PRODUCTION.

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ABSTRACT

In Western Australia (WA), the production of mineral resources is a significant contributor to the state's Gross Domestic Product. The production of gold, iron ore, nickel, alumina and lithium are all subject to corrosion processes.

The harsh and aggressive conditions in Western Australia enhance corrosion activity and the use of saline borewater loaded with bacterial life for process water at many minesites create a naturally inoculated microbially mixed environment. Many sites are experiencing microbially influenced corrosion (MIC) after less than 12 months operation and there is a need to inform design teams of this deterioration possibility and it's consequences.

Over the last decade in Australia, the incidence of microbially influenced corrosion (MIC) has become more prevalent in the mining industry in Australia and this is reflected in the increased reporting in the technical literature. A growing number of failures have been identified as the result of microorganism activity. This is commonly known as MIC, which is generally not usually a single process, but rather an association and interaction of various microbial types leading to corrosion. In brief, 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.

A selection of case studies are presented for carbon steel, a high chromium iron alloy (3CR12) and rubber, where microbial activity was the prime deterioration mechanism. These case studies include deterioration to large rubber lined ore treatment equipment used in the extraction of minerals, the deterioration of process tanks and the premature failure of carbon steel cooling 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.

Keywords: Corrosion, Microbial Corrosion, MIC, Mining Industry

1. GENERAL INFORMATION

With the recent downturn in the mining industry due to lower resource prices, the industry in general has been cautious about spending and the budget areas first reduced have been the Maintenance Budgets. From a corrosion viewpoint, this has limited consequence in the short term, but as time goes on, usually 12 – 18 months, the number of corrosion related failures begin to increase. It is important to remember that materials deterioration is independent of the price of gold, nickel, iron ore etc.

2. INTRODUCTION

Deterioration of materials by living organisms have been commonly referred to as biodeterioration, and this phenomenon can encompass both metallic and non-metallic metallic materials (including 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 a disbelief that single celled fauna can physically deteriorate steel.

3. BACKGROUND

There has been and probably always will be a natural reluctance by maintenance engineers to accept that metal loss of up to 10mm/yr can be attributed to animals held in herds on the head of a pin! It is only when this type of severe corrosion occurs on some equipment or tankage and the proof of microbially influenced corrosion is presented, that the significance of this type of corrosion is appreciated.

4. MICROBIALLY INFLUENCED CORROSION

A basic definition of microbially influenced corrosion (MIC) is corrosion associated with the action of microorganisms in the 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 been 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 usually caused by sulphate reducing bacteria (SRB). Sulphate reducing bacteria has been indicated by localised pitting corrosion under tubercle deposition on the tank walls of the carbon contactor circuit in an Eastern Goldfields treatment facility (Kendrick 1996). The corrosion occurred in the tanks with the lowest dissolved oxygen levels. Other thickener tanks in the circuit were also affected by the presence of sulphate reducing bacteria.

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 usually found in association with *thiobacilli*. Ultimately, the oxidation of pyrites can produce acidic mine waters.

Bacteria can produce hydrogen or hydrogen sulphide which can also lead to hydrogen embrittlement.

4.3 Stimulation of electrochemical reactions

The evolution of cathodic hydrogen from hydrogen sulfide is caused by the production of the hydrogen sulfide 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, eg sulphate reducing bacteria (eg SRB), sulphide or sulphur oxidising bacteria (eg Thiobacillus), acid producing (eg Clostridium) bacteria or fungi
  - carbon source for growth, eg acetate production or oxidation
  - elements accumulated by their metabolism, eg manganese fixing or oxidising iron (eg gallionella) bacteria.

- Cell Shape
  - Coccus (round)
  - Bacillus (rod like)
  - Vibrio (curved like a comma)

- Myces (fungi shapes)

- 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 (von Wolzogen Kurh & van der Vlugt 1934). This indicates that MIC has been a demonstrated and identifiable problem for at least the last 50 - 60 years.

Stott (1993) 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."

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 some industries (eg mining) is not as well defined or described in the technical literature, being focussed mainly on 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, three case study summaries are presented to show the diversity of MIC. All are from the mining industry, one the corrosion of carbon steel Raw water piping after 10 months service, then the corrosion of a high chromium alloy (3CR12) under heap leaching conditions and finally the deterioration of natural rubber lining on a carbon steel substrate.

Case Study 1 – Raw Water Piping (10 months old)

The problem in this instance was the premature failure a 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 uncorroded 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 center 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 obtained ranges from:

Total Dissolved Solids 12,000 - 15,000 ppm
Sulphates 1,000 - 2,500 ppm
Chlorides 5,000 - 10,000 ppm

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 were 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 1: Bacterial enumeration results from Raw Water and Firewater samples

SAMPLE (Viable bacteria 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 of MIC. The high counts of the iron depositing bacteria in three samples is 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 bore field sources reported.

Case Study 2 – Heap Leach Tanks (18 months old)
The problem in this instance was the premature failure at a minesite after 18 months service of the high chromium (3CR12) 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 3 CR12 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 was fabricated from a high chromium (3CR12) 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:
pH 7.5 - 8.7
Total Dissolved Solids 7,000 - 8,900 ppm
Sulphate ion 1,500 - 2,500 ppm
Chlorides 1,600 - 2,300 ppm.

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 numbers 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 parameter 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.

Case Study 3 – 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 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 particles of rubber were being removed.

The deterioration appeared to be a localised loss of material varying in size from 5 - 25mm in diameter and extended to a depth of 10mm 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 have been no problems with high density polyethylene (HDPE), neoprene and synthetic rubbers currently 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, there was a strong possibility the deterioration in the rubber was due to microorganisms

Historically, it has been considered that rubber was a fairly stable compound immune from biodegradation and therefor 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.

Dependent upon the source of the information, the number of different types of micro-organisms that are claimed to be involved in the biodeterioration of rubber and the rubber products are high. It varies from single species to several different species depending upon the depth of the study and the source of the rubber product being investigated. In spite of the limited technical literature on this topic, it is clear that deterioration of rubber can be due to a variety of different microbial species including the following:-

- Strains of Actinomyces including *Streptomyces*.
- Fungi from several genera including *Aspergillus* species.
- *Thiobacilli* or sulphur oxidising bacteria.
- Pseudomonads including *Flavobacteria*.
- Achromobacter.
- Members of the *Bacillus* group of bacteria.

Unfortunately, all of the above were cultured to varying degrees from the rubber and water samples provided for these tests.

7. CONCLUSIONS

The consequences of corrosion to the mining industry are high. A recent survey of the costs and significance of corrosion to the mining industry suggested that in excess of 75% of minesite considered corrosion a moderate to severe problem at the specific sites (Thompson 1999). Of interest was the "costs 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, diverse ore sources, high organic contents and locations within the process where anaerobic conditions can exist, it is highly likely that MIC can occur.

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 done by education, both continuing and formal.

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