MICROBIOLOGICAL INDUCED CORROSION
A CITED CASE IN OHAAKI GEOTHERMAL POWER STATION

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ABSTRACT

Most of the corrosion on the materials comprising the circulating water (CW) system in Ohaaki are microbiologically induced. Sulfur, nitrogen and slime producing bacteria are recognised in the deterioration of the materials since they produced strong acids (i.e. H_2SO_4) during metabolism. The main defence wherein corrosion is controlled is by dosing a biocide in the circulating water, and coating the inner wall of the cooling tower which is **"out of** *the reach" of biocide. A spray gun was installed in order to reach the vapour zone's wall with biocide treated circulating water. Therefore, the case of microbiologically induced corrosion cited in Ohaaki reduces the efficiency and quality of the materials making the CW system, thus increases maintenance costs.*

1.0 INTRODUCTION

The cooling water system in the rejection of heat in Ohaaki geothermal power station is a circulating **water** (CW) system. Around the water circuit. circulating waters are basically ***steam*** condensates and these are being cooled in the concrete **cooling** tower by the **incoming** *air* by natural draught. It was predicted beforehand by Glover and Mroczek **(1990)** that the waters in **the** cooling tower basin would be **near** neutral (pH–6.6). Therefore, the water is suitable for use for the cooling requirement of the CW system.

The conditions in the tower provide essential elements for the bacterial growth such as heat, moisture and gases. Other organic matter and nutrients that serve as food for the bacteria come from the surroundings of Ohaaki since **this** is located in **an** agricultural and forestry environment. The bacteria that thrive in the tower initiate chemical redox reactions for their energy requirement. The products of these reactions are usually acids (i.e. H_2SO_4 and HNO_3) which cause corrosion of the materials comprising the CW system (i.e. concrete corrosion).

The main defence adopted to combat the proliferation of the microorganisms is by dosing a biocide in the cooling water instead of pH adjustment (i.e. NaOH dosing). The walls that are "out of the reach of biocide are coated with a curing membrane and epoxy. In the vapour zone, a spray gun is used to treat the walls with circulating biocide. This is done since the curing membrane in some portions of the vapour zone has deteriorated.

2.0 MICROBIOCHEMISTRY OF COOLING WATER CIRCUIT

In the environment in **Ohaaki,** the presence of dust, pollen, insects, inorganic phosphorous and organic matter that are entrained in the cooling tower provide food and **support** for the microorganisms. Around the cooling water circuit, they exist as slime producing bacteria, groups of *sulfur* and nitrogen bacteria.

2.1 Slime Producing Bacteria

The term slime refers to biofouling or biological films. These are the undesirable inaterials that are being formed on the cooling tower concrete and other parts of the cooling water circuit. These formations do not only contain colonies of the microorganisms but also the combinations of cellular by-products and debris. An example common in industry are the Pseudomonas which are oxygen scavengers which harbour anaerobic bacteria. In the slime, algae and fungi can also be present.

A habitat exists within the layers of the biofilms. In the film where oxygen is absent, anaerobic bacteria can thrive and on the outside, aerobic bacteria are present. The chemistry therefore of the inner part of the biofilm is distinctly different fiom that of the chemistry of the outer layer. In the inside of the film, hydrogen sulfide and organic gases are usually the products from the anaerobic reaction in this environment.

The rate of the formation of the biofilms can be limited by two processes. These are hydrodynamic erosion and sloughing. Hydrodynamic erosion is the natural process of abrading the film by the water flowing on its surface. The rate of hydrodynamic erosion increases with fluid velocity and with the thickness of the biofilm. Sloughing is a random process whereby portions of the biofilm are simply lost fiom the surface. The depletion of the nutrients deep within the film may be involved. Sloughing seems to be more pronounced in thicker and low density biofilms (Eagar et. al., **1996**).

The slime producing bacteria reduce the efficiency of cooling water packs where they cause significant energy losses in the wate: distribution system as a result of increased frictional resistance and by affecting the mass and heat transfer coefficient of the designed packs.

2.2 Sulfur Groups of Bacteria

There are two main groups of sulfur bacteria. These are the aerobic and anaerobic bacteria. The aerobic bacteria use available oxygen in the environment and anaerobic bacteria utilize the oxygen attached fiom other elements like the radicals $SO_4^=$ and NO_3^-.

2.2.1 Sulfur Oxidising Bacteria

The most common and recognised to be responsible in the corrosion mechanisms in Ohaaki are the aerobic bacteria Thiobacillus. These are aerobic autotrophic bacteria that obtain their energy via a number of reactions involving the oxidation of reduced sulfur species.

$$2H_2S + 2O_2 \rightarrow H_2S_2O_3 + H_2O \qquad (1)$$

$$5S_2O_3^= + 4O_2 + H_2O \rightarrow 5SO_4^= + H_2SO_4 + 4S \qquad (2)$$

$$4S + 6O_2 + 4H_2O \rightarrow 4H_2SO_4 \qquad (3)$$

Both these oxidation reactions are controlled by the physical and microbiological mechanisms. Enumeration of these bacteria found four main Thiobacillus species that exist at different pH conditions (Milde et. al., 1982). The initial colonisation is by the T-intermidus and T. novellus which grow at neutral to alkaline pH conditions. As corrosion proceeds and the pH drops below 6, the number of the Neopolitanus increases. Below pH 5, T- thioxidans dominate the population and able to survive and grow down to pH 0.5. Therefore, the best correlation on concrete corrosion rates can be established proportionally with the number of T-thioxidans. The acidity of the waters in the CW system will be increased by further evaporation process.

2.2.2 Sulfate Reducing Bacteria

This type of bacteria is typified by Desulfovibrio Desulfuricans whch use oxygen from $SO_4^=$ to $S^=$ by hydrogen, catalysed by enzyme Hvdroaenase , has little disagreement. The sulfate reducing bacteria are anaerobes and are generally found to co-exist with the aerobic oxygen scavengers **(Pseudomonas)** and have been found under slime deposits whch serve as a shield enabling these bacteria to thrive. Von Wolzogen Kuhr expressed the following reaction mechanisms:

$8H_2O \rightarrow 8OH^- + 8H^+$	Electrolytic dissociation of water	(4)
$4Fe \rightarrow 4Fe^{++} + 8e^-$	Anode Reaction	(5)
$8H^+ + 8e^- \rightarrow 8H$	Cathode reaction	(6)
$SO_4^= + 8H \rightarrow S^= + 4H_2O$	Cathodic depolarisation	(7)
$Fe* + S^= \rightarrow FeS$	Corrosion product at the anode	(8)
$3Fe^{++} + 6(OH)^- \rightarrow 3Fe(OH)_2$	Corrosion product at the anode	(9)
$4Fe + SO_4^= + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2(OH)^-$	Overall reaction	(10)

2.3 Nitrogen Bacteria

The circulating cooling water in Ohaaki contains high concentrations of ammonia stripped from the geothermal *steam.* Coupled with the surroundings of the cooling water system, this provide an ideal environment for the nitrogen cycling bacteria to exist and propagate.

2.3.1 Nitrifying Bacteria

The nitrifying bacteria are the most likely group of nitrogen metabolising bacteria that are active in the cooling water circuit (Downes, 1990). At the elevated temperatures (~35°C), high ammonia concentrations and aeration provide favorable environment for the microorganisms. Oxidation of ammonia to nitrite are represented by the two-step reactions given:

$$NH_4^+ \rightarrow NH_2OH \rightarrow NOH \rightarrow NO_2^- \qquad (15)$$

This is accomplished by bacteria physiologically represented by Nitrosomonas species.

$$NO; \rightarrow NO_3^- \qquad (16)$$

Reaction (16) is performed by Nitrobacter and unlike the reaction in equation (15), no intermediate reaction is involved.

Nitrite oxidation is reported to be more inhibited than ammonia oxidation at high pH values resulting in nitrite accumulation under alkaline condition in excess of pH *8.5* (Hall et. al., 1992). Nitrifying bacteria also grow on particle surfaces probably due to the buffering capacity of the particles. This is an important characteristic as two hydrogen ions are liberated from ammonia to nitrite. In poorly buffered environment acid conditions can inhibit nitrification (Downes, 1990). Nitrifying bacteria prefer neutral to alkaline conditions (pH 6-9). Their importance stems from their ability to reduce what are initially high pH's on fresh concrete surfaces (pH 9-12) to level which will also allow the *sulfur* oxidising bacteria to become established (Bacon et. al., 1995).

2.3.2 Denitrification

Denitrification is a process defined as dessimilatory reduction by aerobic bacteria converting $NO_3^-$and NO; to gaseous oxides like nitric oxides (NO) and nitrous oxide (N_2O), which may be further reduced to nitrogen (N_2). In the absence of oxygen or at low oxygen concentration, they *can* use oxygen from nitrogen oxides. Most are heterotrophic and utilise nitrogen oxides as acceptors of electrons produced by the oxidation of organic carbon:

$$\text{Glucose} + 4.8\,NO_3^- + 4.8H^+ \rightarrow 6CO_2 + 8.4\,H_2O + N_2 \qquad (17)$$

Thiobacillus Denitrificans couple denitrification to the oxidation of reduced sulfur compounds.

$$6S + 4NO_3^- + 2e \rightarrow 6SO_2^- + 2H_2 \qquad (18)$$

3.0 MONITORING PARAMETERS

Water samples are collected regularly at the cooling water basin on a weekly basis. The chemical analysed are pH, Cl^-, NO_2^-, NO_3^-, $S_2O_3^=$, $SO_4^=$ and HCO_3^-. Condensate water samples are also collected weekly from the condensate drips from the cooling tower wall in the vapour zone and pH, $SO_4^=$ and NO_3^- are analysed The pH of the biofilm's base on the concrete walls (i.e. vapour zone) is monitored but is not done on a regular basis.

A slime board is installed beside the 1520 mm FRP (fibre reinforced plastic) pipe. A portion of the water from the FRP tube going to the cooling tower is by-passed through this board and then discharged to the cooling tower basin.

The number of bacteria is counted and the pH of the water in the cooling tower basin is analysed These monitoring and analysis are done weekly by Buckman Laboratory. The population of the bacteria per milliliter is proportional to the weight of slime collected per week and the pH of the water is inversely proportional, that is, pH drops with increasing number of bacteria and vice-versa. The general trends give ideas to the chemist if dosing has been efficient.

The Cl^- content of the water is being analysed in order to find out if carry-over of separated waters from the flash vessel is being carried with the separated *steam* going to the turbines. The results obtained here may seem to be ambiguous and not necessary for a variety of reasons. First. if there is intermittent water entrainment, the results will be delayed and may not be representative since there will be dilution of the Cl^- ions due to the large amount of cooling water circulating in the circuit. It can only be detected if separated water has continuously been flooded from the separator for a considerable period of time. Second, if monitoring is done weekly, upsets that have occurred during intermittent periods within the week will not be given immediate solutions to check the reliability of instrumentations in the steam gathering system. It will only tell whether water entrainment in the steam has occurred during the week and it will be very hard to trace when the upset has occurred. But Cl^- values will give information on the potential of the cooling water if corrosion is assisted by chloride ions (i.e. crevice corrosion).

The NO; and NO_3^- are analysed to monitor the activity of nitrifying bacteria. The $S_2O_4^=$ and $SO_4^=$ are also analysed to monitor the activity of the sulfur oxidising bacteria.

4.0 MECHANISMS OF CONCRETE CORROSION

The cooling tower in the power station is made up of concrete composed of sulfate resistant portland cement and pumiceous pozzolan. The pumice required for the construction of the tower was mined on site. A report on the application of concrete technology to enhance the durability of the Ohaaki cooling tower cited that inclusion of pozzolan would significantly reduce the expansion and swelling of the concrete caused by acid attack (Bruce et. al., 1987). "Strong sulfuric acid will dissolve all constituents of a hardened cement to produce salts of calcium, iron, aluminum and silica gel" (Clereland, 1982). In some circumtances, the acid will also cause swelling and expansion of the cement wall that will result in entangling of the cement bond causing failure on the material. The reactions between sulfuric acid and calcium compounds in the cement are given in equations (19) and (20):

$$Ca(OH)_2 + H_2SO_4 \rightarrow Ca^{++} + SO_4^{=} + 2H_2O \qquad (19)$$

$$3CaO \cdot SiO_2\, 3H_2O + 3H_2SO_4 \rightarrow 3\,Ca^{++} + 3SO_4^{=} + 6H_2O + SiO_2 \qquad (20)$$

Another strong acid that would significantly corrode the concrete is nitric acid The reaction mechanism of HNO_3 with cement if given in equation (21):

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca^{++} + 2NO_3^{-} + 2H_2O \qquad (21)$$

The water produced in the condenser is deionised from alkaline metals and therefore, its condition due to concentration gradient will leach the concrete wall. The dissociation reaction is given in equation (22):

$$Ca(OH)_2 \rightarrow Ca^{++} + 2OH^{-} \qquad (22)$$

5.0 CONCRETE CORROSION

The conditions of the cooling tower concrete *can* be best described from its physical features by Visual observations and thorough measurements around the cooling tower. Severe corrosion for example *can* be observed and measured easily in the tidal zone in the cooling tower basin, in the vapour zone and other areas such as the culvert and structure supports and beams. Corrosion at a rate of 20mm over a period of six months at some locations (i.e. tidal zone) were observed where at the base of the biofilms had a pH~2.0 (Bacon et. al., 1995).

5.1 Tidal Zone in the Cooling Tower Basin

The tidal zone in the cooling tower basin is one location where severe corrosion is evident (*see* Fig. 1.0). The height of the corroded part of the wall indicates the fluctuations of water levels in the basin. This is the location where the bacteria thrive. Particulate of *sulfur* and slimy organic matter have deposited on most of the surfaces of the concrete wall in contact with the liquid phase. Their build-up has resulted in the production of sulfuric acid causing an aggressive corrosion on the concrete wall.

Fig. 1.0 Illustration of the tidal zone in the cooling tower basin which had already been epoxy coated for protection from further corrosion damage. The damaged part indicates the fluctuations of water levels and occupation of the bacteria.

5.2 Vapour Zone in the Cooling Tower

The vapour zone in the cooling tower is coated with AC 6501 curing membrane. On the surface where the coating has peeled off, the curing membrane is not anymore protecting the walls from the acidic condensates. However, the coating has served its purpose during the first two to three years of operation of the power plant (Rowe.1994). In areas where the membrane is still intact. the concrete appears to have a sound surface. It can be seen that the surface of the walls is covered with slimy materials and their nature is not yet known (Rowe, 1994). Figures 2.0 and 3.0 show the cooling tower vapour zone conditions. Figure 2.0 shows the damaged portion and Fig. 3.0 illustrates the portion where the curing membrane is *still* intact. Figure 4.a and 4.b are illustrations of the roof of the culvert and concrete pack support, respectively, wherein. an epoxy coating was applied.

Fig. 2.0 Portion in the vapour zone in the cooling tower, wherein, the curing membrane is no longer protecting the surface.

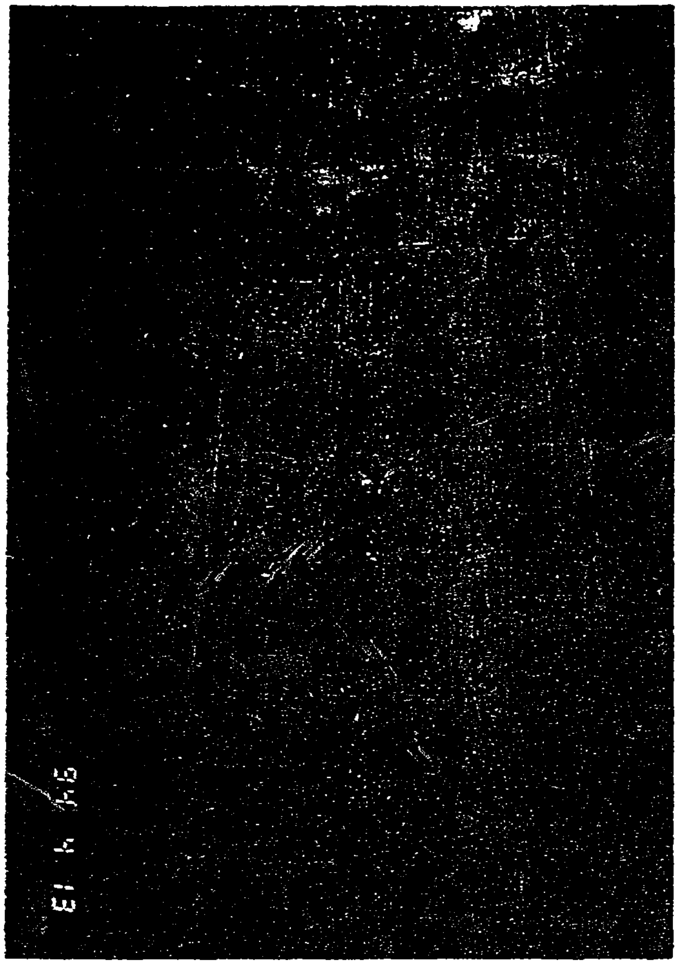

Fig. 3.0 Portions in the vapour zone in the cooling tower that are still protected by the curing membrane. The surfaces are wet, coloured greenish and brownish, and are slimy to touch.

Fig. 4.a Damaged portion on the roof of the culvert whch **had** been epoxy coated already.

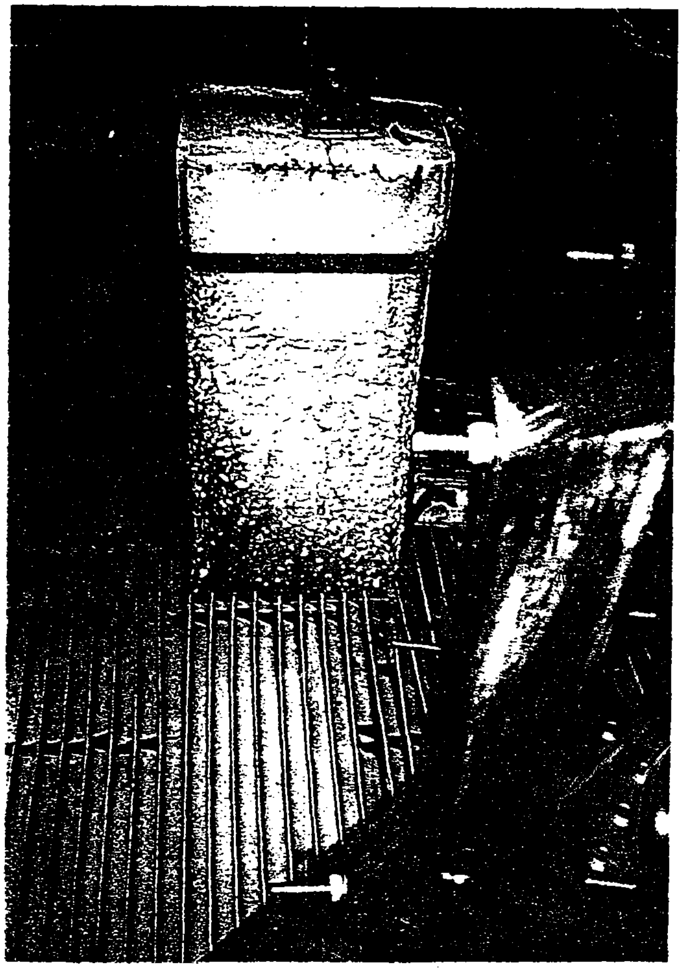

Fig. 4 b Corrosion on the concrete pack support which had been epoxy coated already

6.0 METAL CORROSION

A pilot scale cooling tower experiment had already been done in Ohaaki power station on September 1987 up to January 1988. The aim was to simulate the chemistry of the condensate and to find its corrosivity. The well that supplied the system was BR22. The metals used mere stainless steel grades 304 and 316. Full exposure of these materials was **76** days. The full detailed schemes **of** the pilot cooling tower system can be referred to the IPD interim report RI 2306 dated 19 April 1988 (Webster et. al.). This report claimed that the results had fully simulated the CW chemistry.

The final report entitled "Bacterial Induced Corrosion" - RI 2628 was prepared which was primarily devoted to assessing the biocide dosing during the latter part of the experiment conducted on July to October 1988. The chemistry of the CW system during the latter part had not fully simulated since the separation of steam was not efficient. The contamination of chloride and silica were evidenced by the silica precipitation on the samples (Johnson et. al., 1989).

6.1 Type 304 Stainless Steel

It **was** found out in the experiment that type stainless steel grade 304 would likely be affected by pitting corrosion. It **is** thought that sulfate reducing bacteria is responsible in the pitting corrosion mechanism since severe damage **was** observed in the location in anaerobic condition. Pitting corrosion rates were as high as 2.5mm/year (Webster. et. al., 1988). Thus type of corrosion on the latter **part** of the experiment was also figured out by **Johnson** et. *al.* (1989). Figure 5.0 illustrates the **pitting type** corrosion.

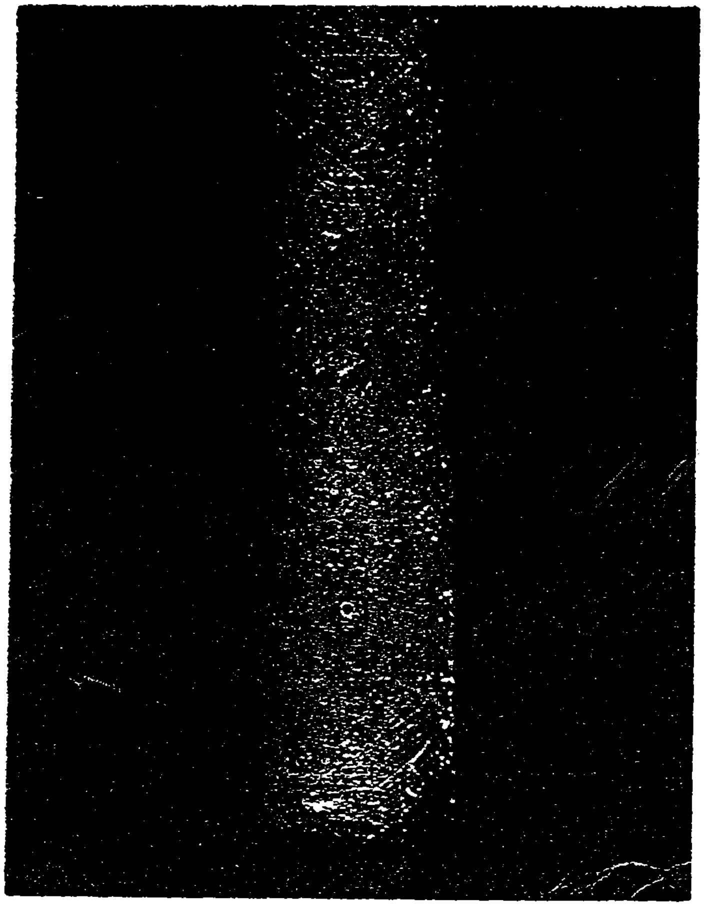

Fig. 5.0 Pitting corrosion in 304 stainless steel with some tubercle covers. Magnification 3.9 x.

6.2 Type 316 **Stainless** Steel

Corrosion of grade 316 stainless steel was not detected from the specimens **during** the first part of the experiment (Webster et. al., 1988) but according to Johnson et. al. (1989), it may likely experience crevice corrosion when in contact with PVC compared when it is in contact with the same metal. **This** may be attributed to the adherent property of the slime bacteria on the exposures of the **metal** with different materials. The corrosion on stainless steel 316 was caused by the **sulfur** oxidising bacteria as the damage occurred at the aerated region in the presence *of* elemental *sulfur.* Whether the crevice corrosion **was** assisted **by** chloride ions contamination is uncertain (Johnson et. al., 1989). What is shown in Figure 6.0 **is** a case of a marking on the metal.

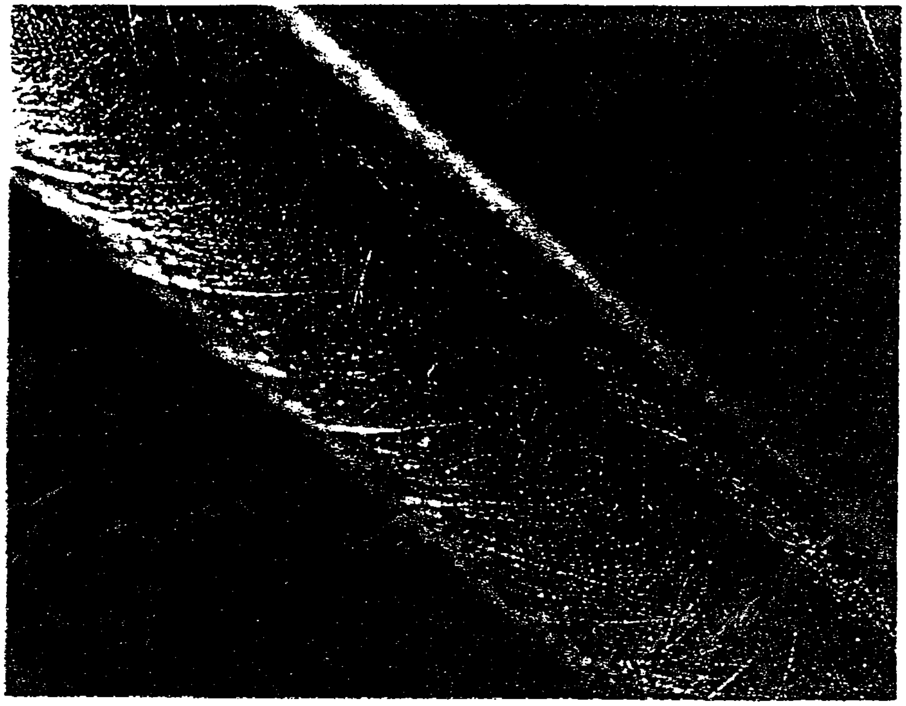

Fig. 6.0 Marking found on 3 16 stainless neel. Magnification 7.5x.

7.0 MITIGATING MEASURES

The chemistry of the circulating cooling water is controlled by the dosing of biocide and dispersant continuously to the cooling tower pond. Organic nonoxidising biocide is used in order to prevent oxidation of sulfur and sulphides from producing more sulfuric acid in the system. Biodispersant is also used in order to break down initially the mucopolysacharide membranes of the bacteria so as the biocide can penetrate the cells.

Sodium hydroxide (NaOH) was not used since calculations earlier by Glover and Mroczeck (1990) predicted that the waters in the cooling tower basin will be near neutral and pH adjustment would not be necessary. It was predicted then that the chemistry of the circulating water making it acidic would be induced microbiologically. NaOH will also absorb more sulphides from H_2S and this may readily be available for H_2SO_4 conversion by sulfur oxidising bacteria. Other reasons are that it is uneconomical. difficult to handle and hazardous.

The **vapour** zone. tidal zones and other parts of the cooling tower that are "out of the reach' of bioccide are protected **by AC** 6501 **curing** membrane and epoxy. **A** spray gun **was** also constructed in order to reach and treat the **vapour** zone with circulated biocide solution from the cooling tower basin.

8.0 CONCLUSIONS AND RECOMMENDATIONS

In Ohaaki geothermal power station, it is recognised that corrosion is induced by microbiological actions. This is the reason that biocide is used to keep the cooling water in the CW system neutral. Nonoxidising biocide is used in order to avoid oxidation of the reduced sulfur in producing more sulfuric acid.

Basically, the bacteria that are involved in the microbiologically induced corrosion (MIC) can be classified into three main groups **of** bacteria that are active in the CW system. These **are** the slime producing bacteria, *sulfur* and nitrogen bacteria.

In the cooling tower concrete, **sulfur** oxidising bacteria and nitrifying bacteria are responsible for the corrosion. These are being proven in three ways: **a) by** the chemistry of the condensates **from** the wall in the vapour zone whch give high concentrations of nitrates and sulfates; b) very acidic waters on the biofilms on the concrete wall which give a pH–2.0; and c) presence of elemental **sulfur.** Dissolution **by** steam condensates is also involved in the corrosion process of the concrete wall.

It was proven during the pilot scale experiment that the cooling water in the CW system is corrosive. This is based on the results of SS type **304** samples which were corroded with pitting and localised types of corrosion. SS **type** 316 is more superior material compared with SS type 304. but it is likely to experience crevice corrosion, and it is recommended that crevice design should be avoided. Basically, it was pointed out that **sulfur** bacteria were responsible in the deterioration of the materials. In identifying the **types** whether it is aerobic or anaerobic depends on the location where corrosion **occurred.**

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