Microbiology and Corrosion in Geothermal Natural Draft Cooling Towers

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Key Words: Cooling Tower, microbiology, concrete, corrosion

ABSTRACT

Closed circuit cooling water systems provide ideal environments for the proliferation of micro organisms reducing operating efficiency and increasing plant maintenance costs. Geothermal systems are particularly prone to fouling and Microbiologically Induced Corrosion (MIC) due to the presence of several groups of autotrophic bacteria which obtain their energy from the oxidation of gases present in geothermal steam. Although chemical speciation in geothemial cooling water will be similar in most circulating cooling systems the concentrations of the constituents will vary depending upon such factors as steam chemistry, borewater carryover, condenser performance and microbiological activity. The latter may have a profound affect upon the pH and the concentrations of sulphate and nitrate in particular. Within the Ohaaki natural draft cooling tower concrete corrosion has occurred in several areas "out of the reach" of bactericides dosed into the cooling water. Within the vapour zone of the tower and on the shell wall in particular, corrosion will be controlled by the direct application of bactericides via a spray gun.

1. INTRODUCTION

The need for corrosion resistant construction materials for geothermal cooling water systems is well recognised within the geothermal industry particularly when concrete is an essential component as is the case with natural draught cooling towers (Kennerley 1980). Not so well understood are the corrosion mechanisms responsible for the corrosion of concrete in these structures.

The role of specific groups of bacteria in geothermal cooling water systems stems from the ideal physical and chemical environment provided and in particular the hydrogen sulphide and ammonia present in geothermal steam. The presence of algae in the system also has an influence on system chemistry.

Inorganic phosphorus is an essential requirement for biological growth. Although geothermally sourced makeup water in generally deficient in inorganic phosphorus, where additional make up water is required and that water is sourced from a stream or river then the effect of introducing phosphate to the system can have a marked effect upon biological growth and hence Microbiologically Induced Corrosion.

Concrete corrosion in the Ohaaki cooling tower has been sufficient to be of immediate concern only in areas within the vapour zone of the tower. In particular significant corrosion has occurred at the "tidal zone" of the pond wall (Figure 1), to the pack support structure (Figure 2) and the roof of the distribution canal (Figure 3) hence these areas have now been provided with an epoxy coating. A similar corrosion mechanism has been shown to be operating on the internal surface of the tower shell, and while it does not show the same degree of attack, the potential for serious corrosion remains. The installation of a spray gun to allow for the application of bactericides to all vapour zone surfaces has been selected as the means of control.

2. MICROBIOLOGY OF GEOTHERMAL COOLING WATER SYSTEMS

Geothermal cooling water systems are renowned for their ability to become acidic as a result of the proliferation of sulphur oxidising bacteria. Bacteria, like all living organisms, require essential nutrients for survival including inorganic phosphorus, an element normally absent from geothermal steam.

Figure 1. Cooling Tower Pond Wall Corrosion

Figure 2. Cooling Tower Pack Support Structure

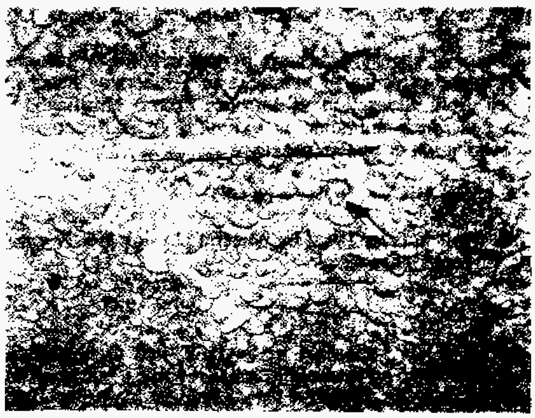

Figure 3. Cooling Tower Distribution Canal

At Ohaaki this deficiency is made up for by the stations location within an agricultural and forestry environment where dust, pollen and insects appear to provide sufficient phusphorus for the needs of micro-organisms. Elsewhere the dosing of phosphate based corrosion inhibitors has been known to enhance the proliferation of sulphur oxidising bacteria. (Mercado. 1980)

The large flow through the Ohaaki CW system, with a constant blowdown of ahout 300 tonnes per hour. is likewise no protection from MIC. The vast majority of organisms in such systems are sessile bacteria rather than planktonic and hence not affected by flow. Further it is these sessile bacteria which are invariably responsible for what ever corrosion or fouling that exists.

2.1 BACTERIA

Major groups of bacteria commonly found in geothemial systems we:

Slime Producers

Under extreme conditions slime producing bacteria. such as Pseudomonas and Aerohacter, together with filamentous algae, can occlude cooling tower packs and heat exchangers reducing their efficiency. Within these slime layers (biofilms) a habitat exists which is to a large extent protected from its surroundings and as a consequence organisms, which may not be able to survive as planktonic bacteria are able to proliferate and construct their own protected environment with a chemistry distinctly different from that outside the slime layer. In geothermal systems these slime accumulations may trap sulphur particles and hence sulphur oxidising hacteria. As a result such biofilms are able to become much more acidic than the adjacent circulating cooling water.

Sulphur Oxidising Bacteria (SOB's)

The existence of sulphur oxidisers results frum the presence of hydrogen sulphide in geothennal steam. The Thiobacilli are aerobic autotrophs which obtain their energy vie a number of reactions involving the oxidation of a number of reduced sulphur species.

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

$$5S_2O_3^{2-} + 4O_2 + H_2O \rightarrow 5SO_4^{2-} + H_2SO_4 + 4S \quad (2)$$

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

These oxidation steps are via both chemical and biological pathways with intermediate oxidation products, particularly sulphur. predominating via the chemical route and sulphate predominating from bacterial oxidation. Concentrations of sulphate can hence. bc used as rough estimates of SOB activity. Sulphur oxidising bacteria are particularly important in geothermal systems where they may be responsible for highly acidic and highly corrosive conditiuns developing not only in the cooling water itself, but also at sites within the vapour zone of the tower away from the action of bactericides.

Nitrogen Bacteria

Nitrogen fixing bacteria possess *the* ability to convert nitrogen gas directly to ammonia. Representatives include the unicellular blue-green algae (cyanobacteria) which are cnmmonly found in natural draught cooling lowers in the form of tough green sheets adhering to the inner surface of shell In natural draught cooling towers.

The activity of nitrifying bacteria in geothermal CW systems stems from both the presence of ammonia in geothermal steam and that produced from the action of nitrogen fixers. Nitrification is the process by which ammonia is oxidised, generally completely to nitrate. Oxidation occurs in two steps.

$$NH_4^+ \rightarrow NH_2OH \rightarrow NOH \rightarrow NO_2^- \quad (4)$$

The first (4) Is accomplished by bacteria physiologically represented by the Nitrosomonas species

$$NO_2^- \rightarrow NO_3^- \quad (5)$$

The second (5) is performed by bacteria such as Nitrobacter but unlike the first step no intermediates are involved. Nitrite oxidation is reported to he more inhibited than ammonia oxidation at high pH values resulting in nitrite accumulation under alkaline conditions in excess of pH 8.5 (Hall *et. al* 1942) Nitrifying bacteria grow well nn particle surfaces probably due to the buffering capacity of the particles. This is an important cunsideration as two hydrogen ions are liberated in the oxidation of ammonia to nitrate and in poorly buffered environments acid conditions can inhibit nitrification.

Nitrifying bacteria prefer neutral to alkaline conditions (pH6 - 9). Their importance stems from their ability to reduce what are initially high pH's on fresh concrete surfaces (pH 9 - 12) to a level which will allow sulphur oxidising bacteria lo become established.

2.2 Bacterial Control

Bactericides can bc generally categorised intn two groups - oxidising and nun oxidising. In conventional CW systems oxidising biocides such as chlorine and ozone are used to good effect. Non oxidising biocides *are* normally used in geothermal systems in order to avoid the oxidation of hydrogen sulphide to elemental sulphur. Sulphur in commonly present as a result of oxidation by atmospheric oxygen though this is limited in its extent. Potentially all incoming H_2S is available for oxidation and in the Ohaaki system total oxidation would result in the production of about *270* tomes of sulphur per year - a somewhat daunting disposal problem!

Particulate sulphur in the Ohaaki system has deposited on most surfaces in contact with the liquid phase. The build up of sulphur in the "tidal zone" on the cooling tower pond wall (Figure 1) has resulted in some particularly aggressive concrete corrosion. The ability of sulphur oxidising bacteria to oxidise free sulphur is evident here with surface (ie below the deposit) pH's as low as 2 resulting in a corrosion rille of about 20mm in some areas over a period of six months - a demonstration of aggressive corrosion in areas out of the reach of biocides dosed into the cooling water.

The use of nun oxidising hiocides requires that screening trials hc carried out prior to use; many are quite specific in terms of their efficacy against the numerous species of hacteria which exist in any given system. In addition some organic biocides such as 2,2-dibromo -3-nitrilopropionamide (DBNPA) hydrolyse under alkaline conditions while others eg. glutaraldehyde and methylisothiazolone are much more resistant. Yet others are degraded by ammonia or hydrogen sulphide.

Perhaps the most important issue when considering biocides is the fact that their use needs to be targeted at sessile organisms rather than planktonic (free floating) bacteria. Such organisms constitute the majority nf bacteria in any circulating cooling system and *are* of course those responsible fur the fouling and corrosion which we wish to control. Many organic biocides are incapable of penetrating the protective mucopolysacharide layer, a component of all such biofilms and the use of a biodispersant is necessary to facilitate the penetration of biocides intn the film.

3. THE OHAAKI CW SYSTEM

3.1 Concrete

The Ohaaki cooling tower is constructed from sulphate resistant Portland cement and pumiceous pozzolan, the pumice required being freely available at the site. All previous testing indicated that the inclusion of pozzolan significantly reduced sulphate induced expansion and swelling associated with acid attack Bruce *et al.*, (1987). Cleland (1982) pninted at thai - "strong sulphuric acid will dissolve all constituents of hardened Portland cement to prnduce salts of calcium. iron and aluminium and also silica gel". In some circumstances it will also cause expansion. Typical reactions between sulphuric acid and calcium compounds in the cement me show below (6 & 7):

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O \quad (6)$$

$$3CaO\,SiO_2 3H_2O + 3H_2SO_4 \rightarrow 3CaSO_4 + 6H_2O + SiO_2 \quad (7)$$

3.2 Water Chemistry

As suggested, coding water chemistry is dependent not only upon the partitioning of geothermal gases within direct contact condensers but also upon the activity of bacteria within the system. Typical Ohaaki CW system chemistry, shown in Tahle 1, is typical fur geothermal systems which are dosed with bactericides and hence with bacterial activity "under control".

3.3 Vapour Zone Chemistry

Vapour zones within CW systems arid cooling towers in particular, contain all the elements essential to bacterial growth such as moisture, heat, gases (H_2S & NH_3) and other essential nutrients. On the other hand few towers are provided with the means of applying biocides to those areas despite the fact that bacterial and algal growth may haw a detrimental effect on the efficiency of the tower and its ability to withstand corrosion.

Table 1. Ohaaki Cooling Water Chemistry

		CT Basin	Hot Well
pH		6.9	5.9
H_2S	mg/l	0.09	1.7
SO_3^{2-}	"	nil	nil
SO_4^{2-}	"	46	45
$S_2O_3^{2-}$	"	4.1	6.3
CO_3^{2-}	"	188	232
NH_3	"	60	59
Cl^-	"	1.3	1.3
NO_2^-	"	1.2	1.2
NO_3^-	"	3.7	3.8

Shell surface condensate chemistry at Ohaaki (Table 2) suggests the existence of large populations of both nitrifying and sulphur oxidising bacteria and their ability to produce an acidic surface condensate. Of more importance is the potential which exists for even lower pH's as has already occurred in other areas within the vapour zone of the tower. Both the low pH and the moderately high sulphate are important considerations for the long term integrity of the shell concrete.

TABLE 2. Typical Shell Condensate Chemistry

pH	4.1
SO_4^{2-}	893 mg/l
NO_3^-	1116 "

3.4 Bacterial Control

At Ohaaki bacterial control is currently maintained by continuous dosing with bactericides such as BL1174 [Poly{oxyethylene (dimethylimino)ethylene(dimethylimino)ethylene dichloride] and isothiazolones. Periodic shock dosing with a glutaraldehyde/methylene bis-thiocyanate mix (Nalco F1155) ensures the longer term efficacy of continuously dosed bactericides.

With corrosion on the inner surface of the shell at an early stage it was evident from the studies carried out that the potential for severe corrosion existed and a means of containing the damage was required. Since the corrosion mechanism was primarily microbiological it was decided that the best means of control was the direct application of a bactericide; the application of an epoxy coating having been rejected due to the cost of production losses.

A subsequent trial application of Nalco F1155 applied by spray at a concentration of 35 mg/l reduced the numbers of sulphur oxidising bacteria by three orders of magnitude from an initial level of $10^7/cm^{-2}$ (Hall *et al.*, 1992).

The installation of a spray gun above the gas stack at the centre of the tower (Figures 4 & 5) will, when commissioned, allow the application of biocides to both the shell wall and all other surfaces within the vapour zone.

Precommissioning monitoring of surface condensate (Figure 6 & Table 2) indicate declining numbers of sulphur oxidising bacteria in condensate "runoff" under winter conditions with stable pH and relatively high sulphates. This monitoring will continue to determine the effects of biocide applications.

Figure 4. Gas Stack and Spray Gun Mounting Platform

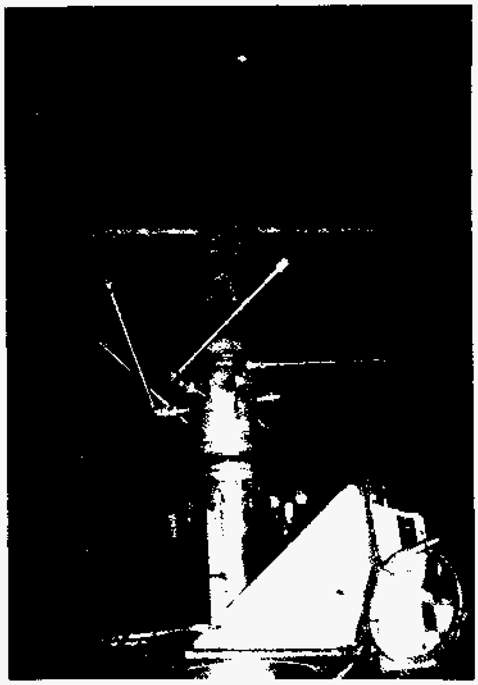

Figure 5. Spray Gun

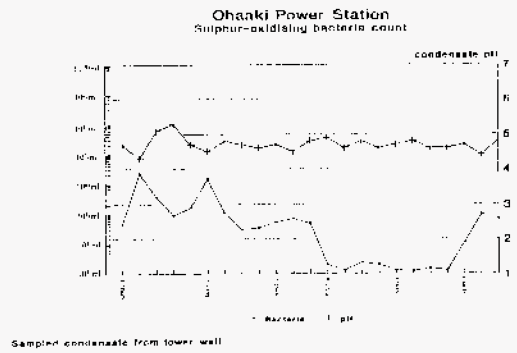

Figure 6. Shell Surface Condensate Monitoring

4. DISCUSSION

Investigations into the mechanisms for concrete corrosion in the Ohaaki cooling tower have demonstrated that rapid attack can occur within the vapour zone of geothermal towers despite the fact that good control has been maintained within the cooling water with the use of appropriate biocides.

The selection of construction materials for geothermal cooling systems should be considered against an understanding of the fundamentals of Microbiological Induced Corrosion. Their selection based on anticipated cooling water chemistry alone is not recommended. Where concrete is the preferred construction material the use of appropriate coatings, especially within the vapour zones of geothermal CW systems, is recommended.

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