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In situ corrosion control in industrial water systems

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Abstract

The main objective of this study was to evaluate the efficacy of a biocide and a corrosion inhibitor against the corrosion of a circulating pipe in a cooling tower. Isothiazolone was tested as the industrial biocide. The results showed that the biocide by itself or combined with a dispersant was not efficient to control corrosion in the industrial system. Corrosion rates of 0.324 mm/year were recorded in both the presence and absence of the biocide. Corrosion control was successfully accomplished by using a corrosion inhibitor. In the latter case the maximum corrosion rate of 0.024 mm/year were obtained.

Introduction

The accumulation of microorganisms and metabolic products on metal surfaces contributes to the corrosion process, which reduces the lifetime of industrial materials. Corrosion is rarely related to a single mechanism or to one species of microorganisms. A wide range of microorganisms, including both aerobic and anaerobic bacteria and fungi, have been found on the surface of corroded materials. Between the anaerobic microorganisms, sulphate reducing bacteria (SRB) are one of the most important groups commonly associated with microbial corrosion.

Microorganisms tend to form biofilms consisting of cells embedded in a highly hydrated, extracellular polymeric matrix (Costerton et al. 1981). Biofilms mediate the interaction between metal surfaces and the aqueous solution leading to modifications of the metal/solution interface. Traditionally, the strategies for controlling biofouling in industrial systems include the application of biocides. However, it is now recognized that the effectiveness of biocides is much lower when bacteria are incorporated into a biofilm rather than when suspended (Boulangé-Petermann 1996). Several laboratory studies have shown that the organisms embedded within the biofilm are protected from biocides, largely due to the diffusion barriers generated by the exopolymeric substances (EPS) matrix that hinder the chemical penetration of the entire thickness of the deposits (Gordon et al. 1988; Nichols et al. 1989). Moreover, it was postulated that bacteria within the biofilm are physiologically altered and more resistant to the disinfection (Boulangé-Petermann 1996; Kajdasz et al. 1984).

The resistance of bacteria to biocides depends on the nature of the chemical used. Traditionally, biocides can be classified as either oxidizing or non-oxidizing (McCoy 1987). Apart from ozone and hydrogen peroxide, all the oxidizing agents used as biocides contain halogens. The non-oxidizers are relatively non-reactive chemicals and, therefore, compatible with strong reducing agents in water treatment application (McCoy 1987). Typical biocides of this later type are formaldehyde, glutaraldehyde, isothiazolones and quaternary ammonia compounds. Non-oxidizing biocides are often used in combination with dispersants and surfactants to stimulate full biocides penetration into the biofilm.

Laboratory studies on the control of microbially influenced corrosion (MIC) are widely conducted, however, often they do not succeed in stimulating the conditions observed in industrial systems. In fact, although biocides and antimicrobials are efficiently used in man-made systems, when they are subsequently implemented into industrial systems, less successful results are often obtained (Watkins & Costerton 1987). The present study was carried out *in situ* in a metallurgic factory and the main objective was to evaluate the efficacy of an industrial biocide and a corrosion inhibitor against the corrosion of a circulating pipe in a cooling tower. In recirculating water systems the evaporating losses of water lead to a concentration of nutrients which, along with lengthy residence times, high water temperature and surface/volume ratios, result in the formation of high microbial cell numbers in the circuit which promotes corrosion (Videla 1996). It is particularly important in these systems that corrosion and biofouling hazards are kept under control.

Materials and methods

The studies presented here were performed on a recirculating pipe of a metallurgic industry cooling tower in a metallurgic factory. Four different experiments were carried out in order to study the corrosion in the circuit: (i) in the absence of any type of control; (ii) on the application of biocide; (iii) on the application of biodispersant; and (iv) with corrosion inhibitor treatment.

(i) Corrosion in the absence of control mechanisms

Thirteen mild steel (ST33) coupons with a dimension of $70 \times 10 \times 1$ mm were installed in a bypass of the recirculation pipe of a cooling tower as shown in Figure 1. The mild steel used had the same composition as the recirculation pipe. Holders were specially constructed to keep the coupons rigidly in position and allow easy access during sampling.

The coupons were initially polished and weighed by Betz Dearborn. Subsequently, they were submitted to a water flow-rate in the pipe of 10–15 L/min, a water temperature of 30–45° C and a water pH of 8.0–8.2. The coupons were kept in the circuit for different duration and the corrosion was then evaluated by weight-loss determinations following the procedure described below.

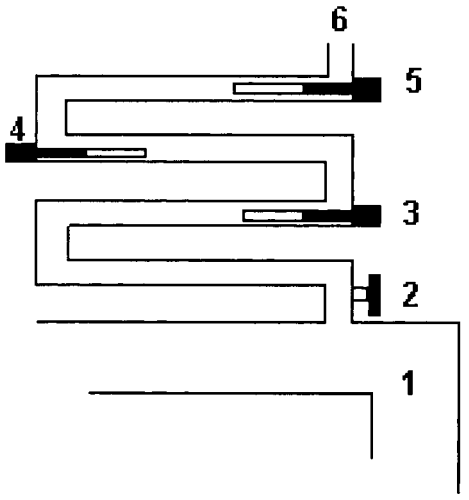

Figure 1. Experimental set-up: (1) cooling tower circuit; (2) valve for flux control; (3–5) mild steel coupons holders; and (6) outlet.

(ii) Corrosion control using a biocide

The efficiency of a biocide based on 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothianzolin-3-one (7% v/v) and glutaraldehyde (15% v/v) (Biomate 5792 supplied by Betz Dearborn) was tested at a concentration of 120 mg/L.

These assays were carried out using mild steel (ST33) tube portions of 12 cm in length and 2.54 cm in diameter, externally protected with cellulose paint and installed in a bypass of the recirculation pipe. A scheme of the experimental set-up is shown in Figure 2.

The biocide was continuously injected into the second part of the system. Therefore, only tubes 6, 7 and 8 were exposed to its action. The tube portions were submitted to running conditions identical to those described above in (i).

(iii) Corrosion control combining a biocide and a biodispersant

The efficiency of the same concentration of biocide (120 mg/l) was tested while simultaneously adding a biodispersant (Biomate 5651 supplied by Betz Dearborn) based on *bis*-(2-methyl hexyl)-sodium sulfosuccinate (20% v/v) in a concentration of 24 mg/L. The combined additives were injected into the system under the conditions described in (ii).

In both assays (ii) and (iii), a control test was run with no biocide addition.

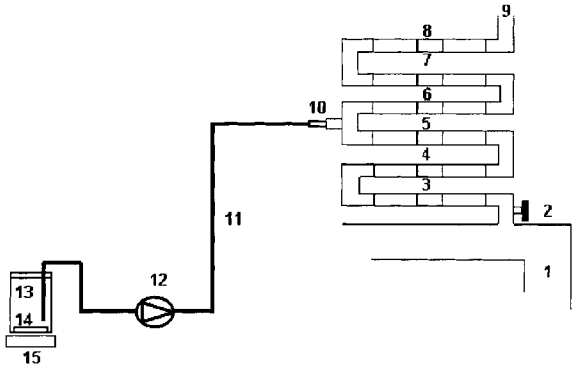

Figure 2. Experimental set-up used in the biocide (Iso Biomate 5792, Betz Dearborn) and biodispersant (Biomate 5651, Betz Dearborn) corrosion control study: (1) cooling tower circuit; (2) valve for flux control; (3–8) mild steel tube portions (each one constituted by two pieces – light areas in the scheme); (9) outlet; (10) biocide and biodispersant injection point; (11) silicone tubing; (12) peristaltic pump; (13) biocide and biodispersant vessel; and (14, 15) stirring.

(iv) Corrosion control using a corrosion inhibitor

A zinc chloride-based corrosion inhibitor (Flomate 5495 supplied by Betz Dearborn) was pumped through the bypass system at a concentration of 150 mg/L for the first 10 days and then reduced to 60 mg/L for the rest of the assay. The conditions and the experimental set-up were identical to those described above.

Sampling and preparation of mild steel samples

After their removal from the circuit, the tube portions were taken (under aseptic conditions) to the laboratory for processing. Each tube portion constituted two pieces as shown in Figure 2. One section piece of the tube was used to evaluate the cell numbers in the biofilm (total and viable counts) and weight-loss determinations. The second section was used for biofilm and surface analysis by a Scanning Electron Microscope (SEM). The analysis of the corrosion products was carried out using an Energy Dispersive X-ray Spectrometre (EDS).

Analysis of weight loss

The samples taken from the circuit at different exposure times were washed in a detergent solution (6 g/L) at 70° C to remove any organic matter. After rinsing twice with distilled water, they were washed in a hexamine solution (30 g/L) in 50% (v/v) hydrochloric acid in order to remove corrosion products. They were rinsed again with distilled water, then with ethanol and finally dried in a dessiccator. The dried mild steel was weighed using an analytical balance and the weight loss was determined by comparison with the weight recorded prior to exposure.

Cell counts in the biofilm

The biofilm was scrapped from the tube portion under aseptic conditions and the total microorganism count was determined using a Neubauer Counting Chamber and an optical microscope (Nikon Labophot). The viable aerobes were counted by plating out on to Petri dishes with a Tryptic Soy Agar (TSA) medium, and the viable SRB were determined by plating out on to petri dishes with Postgate medium E (Postgate 1993) after incubation at 37° C in an anaerobic jar for 1 week.

Preparation of samples for SEM

For the surface analysis, a 1-cm^2 sample was cut from the tube portion after the treatment described above for weight-loss analysis.

The samples for biofilm analysis were submerged, washed for 30 minutes at 4° C in a 0.5% (v/v) glutaraldehyde solution in phosphate buffer 0.1 M; rinsed in phosphate buffer 0.1 M and fixed for 4 hours at 4° C in a 2.5% (v/v) glutaraldehyde solution. The samples were then dehydrated by 20-minute long immersions in a series of ethanol–water solutions with concentrations ranging from 50 to 100% (v/v). After this treatment, a 1-cm^2 sample was cut from the tube and rapidly frozen in liquid nitrogen prior to overnight freeze drying. The samples were then carbon coated and imaged with a JOEL JSM 35C Scanning Electron Microscopy. The corrosion products were analyzed using the SEM coupled to a Noran Voyger EDS with a Si (Li) detector and a Be window.

Results and discussion

Evolution of corrosion in the absence of control mechanisms

The aim of the first part of this study was to evaluate corrosion as a function of time in the cooling tower circuit. The variation in weight loss and the corrosion rate observed for the mild steel coupons introduced in the bypass of the system are shown in Table 1 and Figure 3. The weight loss of the coupons increased during the first 30 days of exposure and reached a plateau after this period. The maximum value of the weight loss

Table 1. Weight loss and corrosion rates of mild steel coupons as a function of exposure time in the cooling tower circuit

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Weight loss (%)	Corrosion rate (mm/year)
1	8.9245	8.8737	0.0508	0.569	0.848
4	8.6638	8.5067	0.1571	1.813	0.656
7	8.6719	8.3596	0.3123	3.601	0.745
7	8.7145	8.3590	0.3555	4.079	0.848
13	8.9831	8.6946	0.2885	3.212	0.371
16	8.9622	8.5539	0.4083	4.556	0.426
20	9.0159	8.6057	0.4102	4.550	0.343
28	8.8734	8.2157	0.6577	7.412	0.392
32	8.6147	8.0252	0.5895	6.843	0.308
46	8.9419	8.1511	0.7980	8.844	0.290
50	8.8185	8.3281	0.4904	5.561	0.164
59	8.9916	8.4216	0.5700	6.339	0.161
74	8.4083	7.4802	0.9281	11.04	0.209

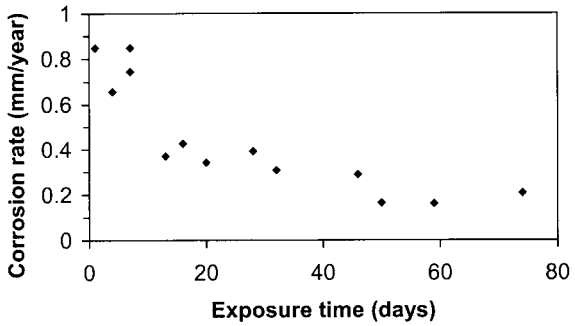

Figure 3. Evolution of the corrosion rate of mild steel coupons installed in the cooling tower circuit without corrosion control over exposure time.

determined was 0.92 g (after 74 days exposure) which corresponds to about 11% of the coupon initial weight.

The values of the corrosion rate presented in Figure 3 were calculated using an equation proposed by the ASTM standard D 2688-94 for coupons:

$$R = (W/dat)3650, \qquad (1)$$

where R = corrosion rate (mm/year); a = coupon area (cm^2); W = coupon weight loss (g); d = density of metal (g/cm^3); and t = exposure time (days). The density of steel was 7.86 g/cm^3 (determined by Betz Dearborn).

The corrosion rate decreased strongly during the first 30-day period and to reach a constant value of around 0.3 mm/year. Corrosion rates of 0.2 mm/year were observed in a heat exchange system consisting

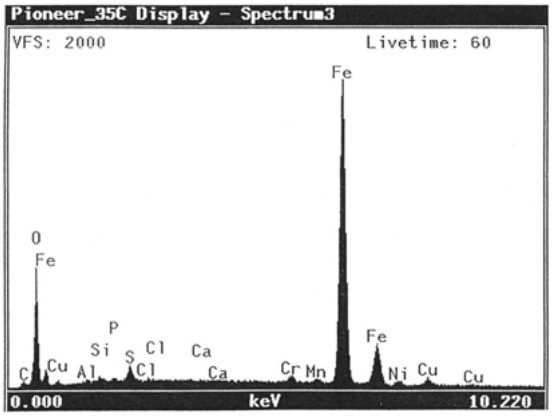

Figure 4. EDS spectra analysis of the coupon surface installed in the cooling circuit for 50 days.

of mild steel (AISI 304) used in a petrochemical industry in Brazil (Gaylarde 1995). The stabilization of the corrosion rate in the present study could probably be related to the development of a passivation film on the metal surface mainly due to iron oxides. In fact, the EDS spectra analysis showed oxygen (O) and iron (Fe) peaks (Figure 4).

A visual inspection of the coupons after removal from the circuit revealed a well-developed film on the surface, and the SEM analysis (data not shown) revealed a very irregular surface with well-developed pits in which the size and depth had increased with exposure time.

Corrosion control using a biocide

The aim of this experiment was to evaluate the effect of a biocide on biofilm development and the corrosion of the metallic surfaces exposed in the circuit of the cooling tower. An illustration of the experimental set-up is shown in Figure 2.

The tube portions used were not efficiently protected externally and a considerable degree of a visible corrosion could be observed on the outer surface. Consequently, the weight-loss determinations included both the internal and external sides. For this reason, only the results from the SEM analysis are shown.

The SEM micrograph images of the biofilm developed on the surface exposed to the biocide action during 54 days, and the biofilm developed in a tube where no biocide was added and was kept in the circuit for the same length of time, are shown in Figures 5 and 6, respectively. It could be observed that the biofilms

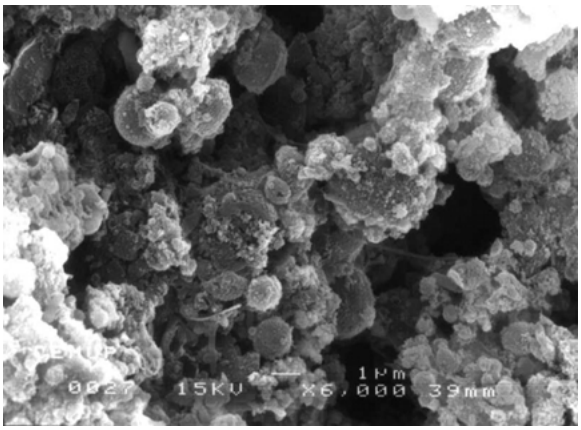

Figure 5. SEM micrograph obtained from the biofilm exposed for 54 days to the biocide.

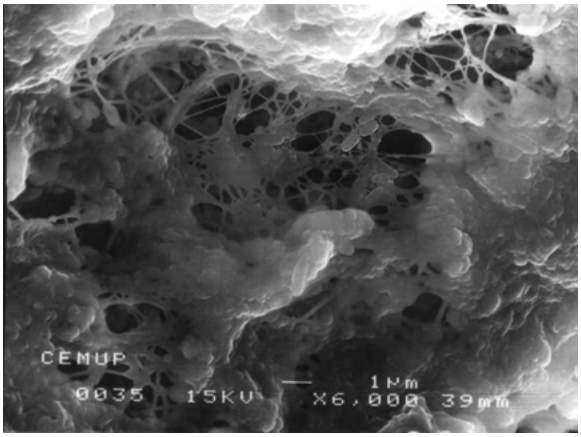

Figure 6. SEM micrograph showing the biofilm developed for 54 days without biocide.

consist of a wide variety of microbial cells embedded in a matrix of viscous biopolymer.

Although a thick biofilm could be observed on both the treated and control surfaces, the tube portion exposed to biocide action showed a lower level of bacterial colonization. Figure 7 shows the SEM micrograph of the tube surface exposed to the biocide. The general deterioration with areas of severe pitting corrosion can be observed.

This biocide (generally classified in the category of "non-oxidizing" biocides) is a mixture of organonitrogen–sulfur with an aldehyde (glutaraldehyde). The biocide concentration used (120 mg/L) was previously tested in the laboratory against planktonic bacteria obtained from the cooling circuit. This concentration resulted in a complete inhibition of bacterial activity and growth. When used *in situ*, however, the biocide showed a low effectiveness against

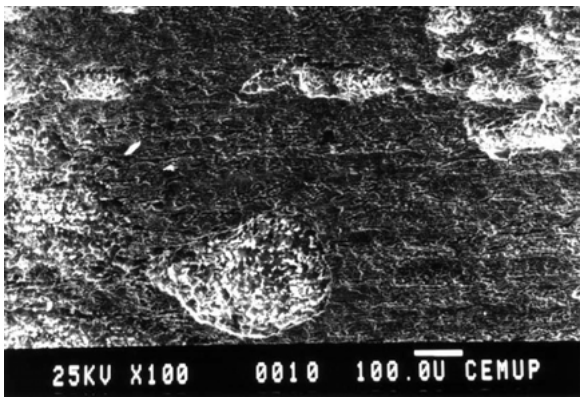

Figure 7. SEM micrograph of the tube surface exposed for 54 days to the biocide.

the biofilm development. The low biocide efficacy over corrosion control in the present situation could be explained either by the hindered biocide penetration into the biofilm, because the exopolimeric matrix constitutes a diffusion barrier, and/or by the great resistance of the planktonic cells against the biocide (Boulangé-Petermann 1996; Kajdasz et al. 1984).

Corrosion control using a biocide and biodispersant

In order to improve the biocide diffusion through the biofilm, a biodispersant which has the capacity to solubilize the exopolimeric matrix, was simultaneously injected with the biocide. The first three sections of the experimental system (tube portions number 3, 4 and 5 in Figure 2) were used as controls and, consequently, they were not submitted to biocide and biodispersant action. The biocide and biodispersant were injected into tube portions numbers 6, 7 and 8.

The results of the weight-loss measurements over the exposure time are shown in Table 2 and Figure 8. The tube weight loss increased drastically during the 37 days of exposure reaching a steady state after this period. Similar results had been obtained when mild steel coupons were used to evaluate the degree of corrosion in this system. The corrosion rates were calculated using the Equation (1) where a is the internal tube area. As mentioned above, each value of the corrosion rate was calculated from the weight loss of just one tube portion. For practical reasons it was not possible to use more than one tube for each contact time.

The values of the corrosion rate determined were very similar for the tube used as the control and the tubes receiving the biocide and biodispersant treatment. After 23 days of exposure, the corrosion rate

Table 2. Weight loss and corrosion rates of mild steel tube portions submitted to the biocide and dispersant and to the corrosion inhibitor and without corrosion control

Exposure time (days)	Type of treatment	Initial weight (g)	Final weight (g)	Weight loss (g)	Weight loss (%)	Corrosion rate (mm/year)
23	Biocide and dispersant	283.587	282.052	1.535	0.541	0.324
23	None	283.927	282.243	1.684	0.593	0.356
23	Corrosion inhibitor	282.299	282.186	0.113	0.040	0.024
37	Biocide and dispersant	283.740	281.523	2.217	0.781	0.291
37	None	282.566	279.849	2.717	0.962	0.359
37	Corrosion inhibitor	282.689	282.559	0.131	0.046	0.017
54	Biocide and dispersant	283.905	281.351	2.554	0.900	0.230
54	None	284.569	281.494	3.075	1.087	0.277
54	Corrosion inhibitor	282.905	282.740	0.165	0.058	0.015

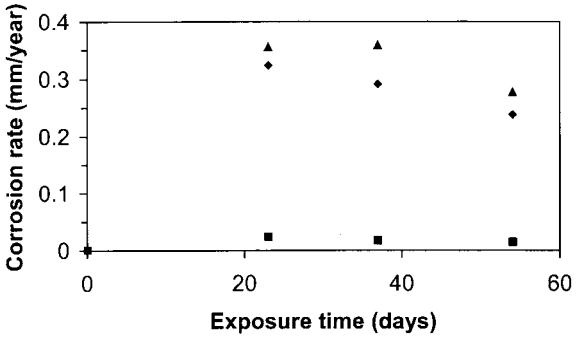

Figure 8. Evolution of the corrosion rate of mild steel tube portions over exposure time to biocide and biodispersant influence (♦), to corrosion inhibitor influence (■); and without any corrosion control (▲).

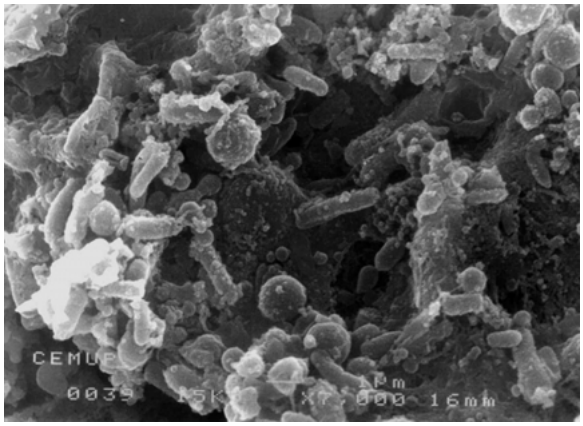

Figure 9. SEM micrograph of the biofilm developed on the tube surface treated with biocide and biodispersant.

reached a stable value of about 0.3 mm/year which, again, was similar to the value determined for the coupons where identical flux conditions were used (Figure 3). These results show that the corrosion was independent of the shape of the specimen used providing that the mild steel had the same composition. Moreover, the biocide and biodispersant failed to prevent corrosion in this industrial system.

The SEM analysis of samples (Figures 9 and 10) showed that in both situations a thick biofilm developed on the internal surface of the tube. However, in the tubes where the biocide and biodispersant were used, the biofilm consisted of numerous bacteria embedded within an extensive but not very dense polymeric matrix. It appears that although the dispersant minimized the formation of a compact polymeric structure in the biofilm, this it was not sufficient to avoid the biofilm development and consequent corrosion

The biofilm contained many varieties of cell morphologies, including filamentous and rod- and spiral-shaped organisms. The number of cultivable sulphate-reducing bacteria present in the biofilm was very low (10–20 CFU/cm^2) compared to the total amount of microorganisms (2–3 $\times$ 10^8 cell/cm^2). Therefore, the observed corrosion in this system could not be attributed to the presence of cultivable sulphate-reducing bacteria, implying that other groups of microorganisms may have a relevant role in the process. The high corrosion rates in systems containing relatively low SBR concentration were also observed by Gubner and Beech (1996).

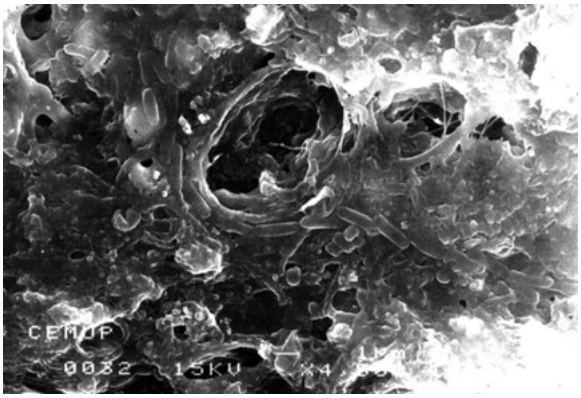

Figure 10. SEM micrograph of the biofilm developed on the tube surface in the absence of biocide and biodispersant.

Corrosion control using a corrosion inhibitor

The final part of this work was performed by replacing the biocide with a zinc chloride-based corrosion inhibitor. The set-up used was the same as that shown in Figure 2 and the results are presented in Table 2 and Figure 8.

The weight loss and corrosion rates obtained were very low compared with those obtained when biocide and biodispersant were used. The maximum value recorded with the inhibitor was 0.024 mm/year, whereas this value was 0.324 mm/year in the case where the biocide and biodispersant were supplied. The low value registered for the corrosion rate of the tube portions exposed to the corrosion inhibitor can be related to the zinc–phosphate compound formed, which functions as a barrier preventing access of microorganisms and degradation products to the metallic surface, thus inhibiting biofilm formation. In fact, the biofilm developed under these conditions was thinner than those in the presence or absence of biocide.

Conclusions

The results show that the simultaneous use of a biocide and dispersant failed to control the corrosion in a cooling tower of a metallurgic industry system. Although the biological activity of isothiozolone against planktonic cells was proven in the laboratory studies, it was unable to inactivate sessile bacteria and hence did not avoid the biofilm development on the tube surface of the industrial system. The SEM analysis revealed that the biofilm was composed of many varieties of cell morphologies embedded within an extensive polymeric matrix. It can be postulated that either the complex matrix created a diffusion barrier, which prevented the penetration of the biocide through the biofilm, and/or that the sessile cells were more resistant to the biocides than the planktonic cells.

The corrosion rates in the absence and presence of biocide were comparable and quite high (0.3 mm/year). This confirms the inefficacy of the biocide to control corrosion.

The corrosion control was successfully achieved by using a corrosion inhibitor, and was accomplished because of the formation of a zinc–phosphate protective layer on the tube surface preventing the direct access of bacteria, their metabolic products and other compounds to the surface.

The results presented here show that the biofilm formation on the surface of metallic tubes plays an important role in the corrosion process. The direct contribution of bacteria embedded in the dense matrix of the biofilm on the corrosion rates could not be determined due to the complexity of the process. In fact, the many varieties of mechanisms resulting from the interaction of different physical/chemical, and the biological phenomena occurring during the biofilm formation, may be responsible for the global process of corrosion.

The results obtained in the present work allowed the metallurgic factory to improve the treatment programme currently used to control corrosion in the cooling tower.

Acknowledgments

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