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EVALUATION OF PEROXIDE BASED BIOCIDES FOR INHIBITION AND BIOCIDAL EFFICIENCIES

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Microbially induced corrosion can be controlled through biocides that eliminate the deleterious microorganisms. However, the electrochemical properties of such biocides and their role on the corrosion process is not very well understood. The present investigation is focused ,on the evaluation of peroxide based biocides viz. sodium peroxide, sodium perborate, sodium dithionite and sodium chlorite for their efficiency from corrosion as well as biocidal point of view. The biocides investigated were found to alter the corrosion tendency of mild steel. Sodium peroxide was proved to be the ideal choice both as biocide and as corrosion inhibitor.

Keywords: **Mild steel, peroxides, weight loss, impedance, bacterial count and inhibition efficiency.**

INTRODUCTION

Uncontrolled microbiological growth in re-circulating water cooling systems results in biofouling and sludge formation. To reduce the maintenance cost and control biofouling, a wide range of chemicals are used [1]. One of the biocides which has been studied as a potential algicide is hydrogen peroxide. Hydrogen peroxide is a good oxidizing agent, generally used to oxidize organic materials in water treatment plants. It has a short persistence in natural waters and its breakdown products are water and oxygen. Although it is toxic to higher plants, hydrogen peroxide kills algae at much lower concentrations [2-4]. But its limiting factors are stability and difficulty of storage.

Biocides are classified as either oxidizing or non-oxidizing toxicants. The selection and application of suitable biocide treatment depends on the broad spectrum activity, *p*H, economics and compatibility with the other chemicals used for treatment and most importantly suitability with the materials of construction from the corrosion point of view.

Ozone is also a strong oxidizing type biocide like peroxides and has attracted a great deal of interest for its application as a biocide. However, two to three fold increase in the corrosion rate with increasing ozone concentration has been reported for carbon steel [5]. This raises the question whether peroxides also as a class will enhance corrosion.

In the present study four algicide peroxide compounds have been evaluated for their inhibition and biocidal efficiencies.

EXPERIMENTAL PROCEDURE

Weight loss method

The mild steel test specimens were polished successively in 1/0 to 4/0 emery papers and degreased with trichloroethylene. Specimens of 1 x 4 x 0.2 cm size in triplicate were immersed in 100 ml of the test solution for a period of seven days. The changes in weight (with an accuracy of ± 5%) were measured and the loss in weight due to corrosion was calculated.

Impedance measurements

A three electrode cell assembly was used for impedance measurement. A mild steel test specimen as the working electrode; a large platinum foil as counter electrode and a saturated calomel electrode as reference electrode were used. A.C impedance studies were carried out using computer controlled EG & G PAR system model M 6310 with software M 398.

X-ray diffraction analysis

Computer controlled X-ray powder diffraction system JEOL JOX-8030 with CuK_{α} (Ni filtered) radiation at a rating of 40 kV, 20 mA was used to study the surface of mild steel. XRD study had been undertaken to examine the nature of the protective barrier formed on the M.S. surface after exposure to sodium peroxide solution at different intervals. The scan rate was 0.05 - 20^0 per step and the measuring time was 1 second per step. Observations were made on duplicate samples.

Water and bacterial analysis

The pond water used for the investigation was analyzed by standard analytical procedures [6]. Bacteria were enumerated from water sample as well as metal surface by using Zobell medium by pour plate technique. After 24 hours the bacteria count was enumerated.

RESULTS AND DISCUSSION

The chemical composition of the water used for this study is given in Table I. It can be seen that the water sample is having a moderate calcium hardness but chloride content is quiet significant. The dissolved solid content is quite considerable. The suitable content is on the lower side.

The bacterial activity of the pond water has been analyzed by using zobell medium by pour plate technique and bacterial count of 4.2 x 10^6 to 3.6 x 10^7 CFU/ml measured is quite significant.

Generally, the efficiency of inhibitors on corrosion control and efficiency of biocides are evaluated separately. But it is quite essential to consider the influence of inhibitors on bacterial growth and that of biocides on corrosion.

The weight loss data are given in Table II. The variations of the change in weight for mild steel at different concentrations of peroxide based biocide are given in Fig. 1. It can be seen that the pond water without any biocide has a corrosion rate of 3 mpy. It can also be seen that by addition of biocides like sodium perborate, sodium dithionite and sodium chlorite, the corrosion rate is doubled (6.5 mpy). Concentration has no effect in the case of sodium chlorite and it has the maximum aggressivity. Next to sodium chlorite, sodium dithionite is aggressive, eventhough the aggressivity is brought down at 500 ppm. Sodium perborate is also almost similar to sodium dithionite. So, the most interesting observation comes from the behaviour of sodium peroxide. The corrosion rate is significantly reduced at a concentration of 400 ,ppm and it is further brought down at 500 ppm and an inhibition efficiency of 80% has been obtained at 500 ppm of sodium peroxide. This is quite appreciable for a peroxide based biocide.

To substantiate the weight loss data instantaneous corrosion rate measurements have been carried out using impedance technique and the results are given in Table III. The Bode diagrams obtained from the AC impedance measurements are presented in Fig. 2 for the sodium peroxide system. Because of the advantage of the Bode plots over the Nyquist plots in the low frequency range, the R_{ct} values obtained from the Bode plots were taken into account for the analysis.

It can be seen that R_{ct} values for the control system lie in the range of 2-3 kohm.cm^2 for a period of 0 to 7 days and an increase in corrosion rate with time is observed.

In the case of the most aggressive system sodium perchlorite, the R_{ct} value is drastically reduced at 300 ppm concentration. An initial value of 0.09 kohm.cm^2 increases to 0.5 kohm.cm^2 at the end of 7th day. Similarly at 400 ppm an initial value of 0.13 kohm.cm^2 increases to 0.24 kohm.cm^2 on the 7th day. At 500 ppm it increases from 0.22 to 0.55 kohm.cm^2 on the 7th day. On the whole an average R_{ct} value of 0.5 kohm.cm^2 irrespective of concentration can be considered.

Both sodium perborate and sodium dithionite behave more or less similarly and R_{ct} values decrease with time and an

TABLE I: Chemical composition of pond water

Parameter	Concentration
pH	6.8
Dissolved oxygen	6.2 mg/l
Chloride	160 ppm
Sulphate	67 ppm
Calcium	130 ppm
Magnesium	86 ppm
Total hardness	216 ppm
Dissolved solids	539 mg/l
Suspended solids	197 mg/l
Total solids	736 mg/l
Total alkalinity	250
Conductivity	980 umhos/cm^2

TABLE II: Corrosion rate of mild steel in water containing various peroxide based biocides

Biocide	Conc (ppm)	Corrosion rate (mpy)	I E %
Control	—	3.03	—
Sodium	300	6.54	-117
chlorite	400	6.54	-117
	500	6.52	-115
Sodium	300	5.88	-94
dithionite	400	6.20	-104
	500	4.25	-40
Sodium	300	5.64	-86
perborate	400	5.01	-65
	500	4.01	-32
Sodium	300	2.74	10
peroxide	400	1.29	57
	500	0.61	80

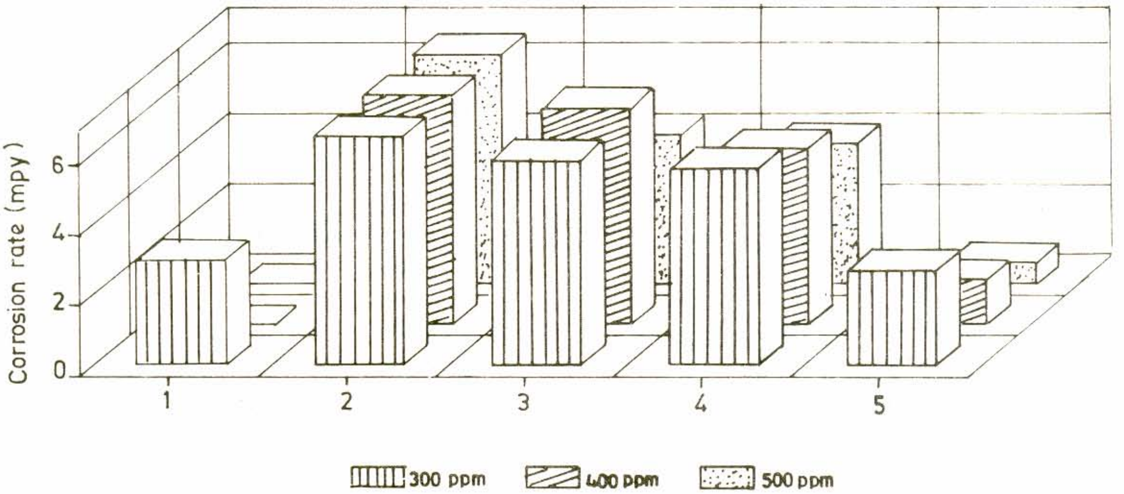

Fig. 1: The effect of various biocides on the corrosion rate of mild steel
(1) Conttrol (2) Sodium chlorite (3) Sodium dithionite (4) Sodium perborate (5) Sodium peroxide

TABLE III: The effects of various biocides on the electrochemical parameters of mild steel in pond water

Biocide investigated	Conc ppm	Period in days	Rct k ohm cm^2	I E %
Control	—	0	2.00	
	—	3	2.84	
	—	7	3.01	
Sodium chlorite	300	0	0.09	-21
		3	0.23	-11
		7	0.50	-5
	400	0	0.13	-14
		3	0.18	-15
		7	0.24	-12
	500	0	0.22	-8
		3	0.24	-11
		7	0.55	-4
Sodium dithionite	300	0	0.47	-3
		3	0.14	-19
		7	0.12	-24
	400	0	0.47	-3
		3	0.20	-13
		7	0.09	-32
	500	0	0.23	-8
		3	0.22	-12
		7	0.10	-29
Sodium perborate	300	0	0.79	-2
		3	0.21	-13
		7	0.09	-32
	400	0	0.14	-13
		3	0.10	-27
		7	0.05	-59
	500	0	4.24	53
		3	0.41	-6
		7	0.11	-26
Sodium peroxide	300	0	2.99	33
		3	0.29	-9
		7	0.15	-19
	400	0	5.11	61
		3	0.26	-10
		7	0.14	-21
	500	0	9.66	79
		3	0.27	-10
		7	0.18	-16

average value of 0.1 kohm.cm^2 is observable at the end of 7th day and this is independent of the concentration.

Again the most interesting observation comes from the behaviour of sodium peroxide. The system shows a high R_{ct} value initially which decreases quite steeply with time. For example at 500 ppm concentration a R_{ct} value of 9.66 kohm.cm^2 dips to 0.27 kohm.cm^2 during third day and gets further reduced to 0.18 kohm.cm^2 during 7th day. An average R_{ct} value of 0.16 kohm.cm^2 is observed irrespective of the concentration.

When the average R_{ct} values are compared, it is seen that corrosion is significantly increased in presence of biocides including sodium peroxide. This abnormal behavior observed through impedance measurements is difficult to understand. However, it can be explained that the protective film may be disturbed by the impedance technique, the initial values in the case of sodium peroxide is quite high, indicative of a resistive film of the corrosion product.

Comparing Tables II and III it can be clearly seen that sodium chlorite, sodium dithionite and sodium perborate enhance the corrosion rate of mild steel in the pond water under study. Impedance measurements being instantaneous obviously give corrosion rate on the higher side compared to weight loss data, (i.e. nearly six times the control).

The variation of the bacterial count at different concentrations of various peroxide based biocides are given in Fig. 3. Compared to control, bacterial count is reduced in presence of biocides. It is also seen that the bacterial count decreases significantly when the concentration is increased. Here again the behaviour of three biocides sodium chlorite, sodium dithionite, sodium perborate is more or less similar.

Behaviour of sodium peroxide is quite different and it has acted as a very efficient biocide particularly at 500 ppm of concentration.

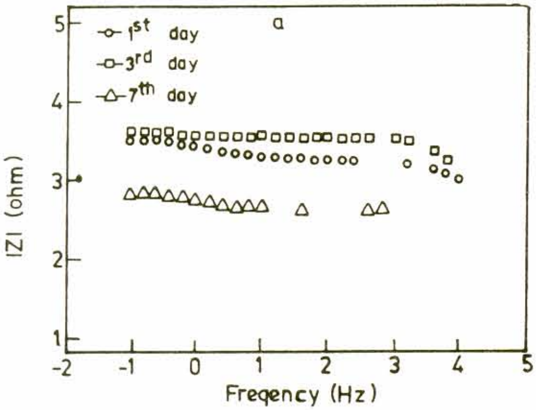

Fig. 2a: control

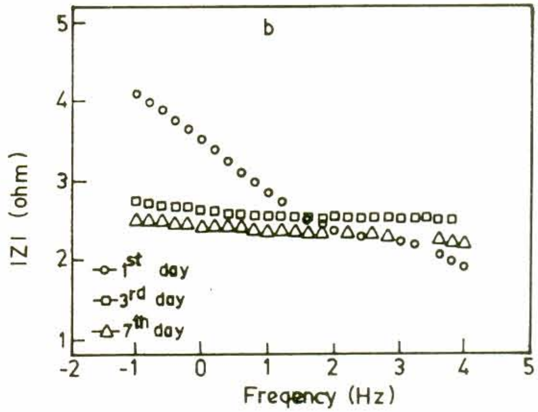

Fig. 2b: 300 ppm

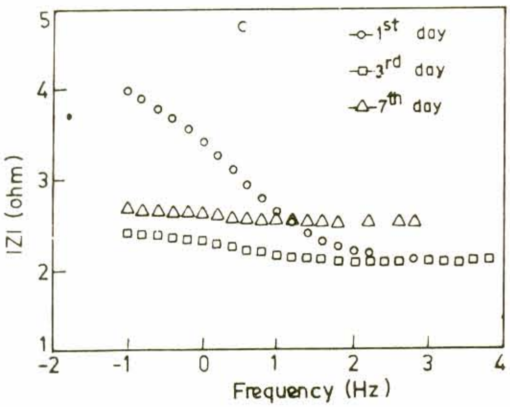

Fig. 2c: 400 ppm

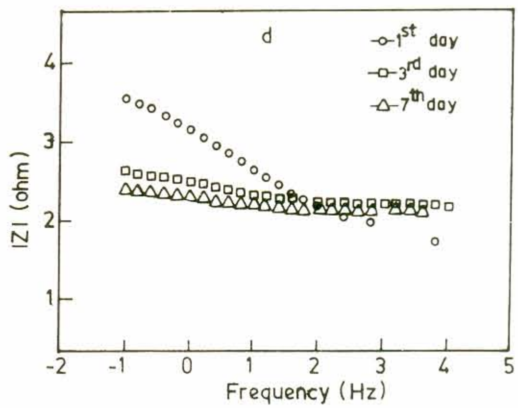

Fig. 2d: 500 ppm

Fig. 2: Bode plots for mild steel in the sodium perodixe biocide

So, this investigation has clearly established sodium peroxide as an efficient biocide and at the same time it has also functioned as efficient inhibitor in terms of weight loss data.

The XRD analysis of the M.S. specimens in sodium peroxide system at different time intervals are given in Fig. 4 $Fe(OH)_2$, and γ FeO(OH) (2θ = 33.0^0, 46.8^0, 59.8^0, 61.7^0) peaks [7-9] were noted on the metal surface within 24 hours

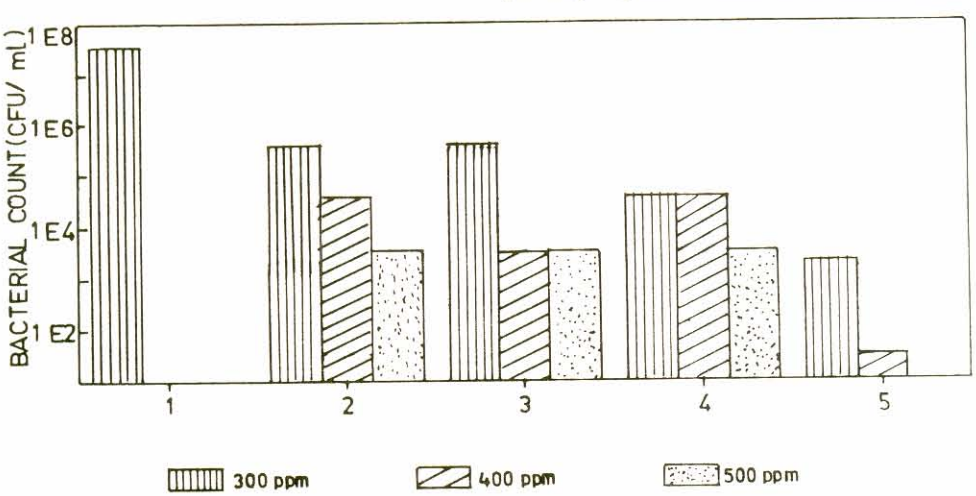

Fig. 3: The killing efficiency of various biocides against the heterotrophic bacteria
(1) Control (2) Sodium chlorite (3) Sodium dithionite (4) Sodium perborate (5) Sodium peroxide

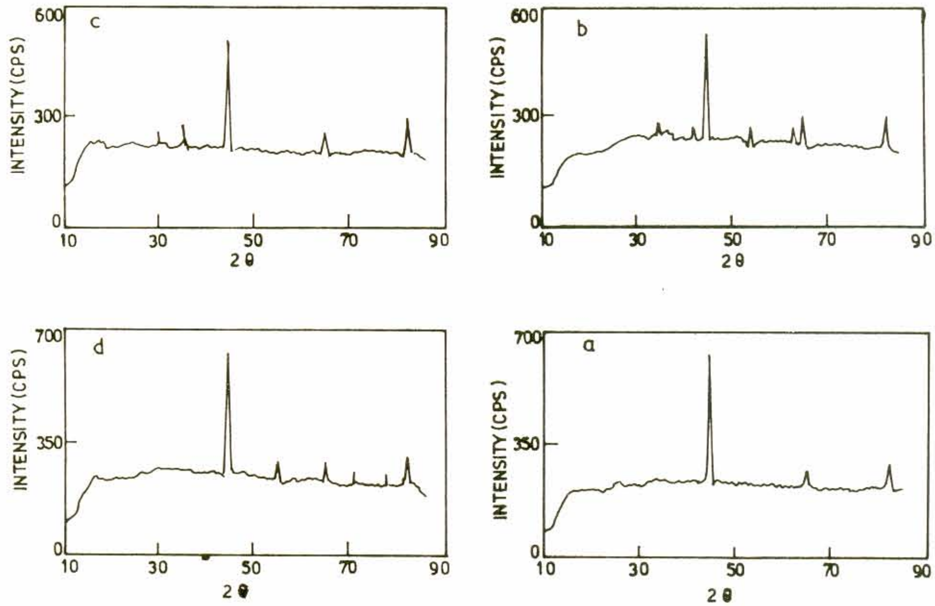

Fig. 4: XRD analysis of mild steel immersed in sodium peroxide solutions surface at different time intervals (1) Control (2) Sodium chlorite (3) Sodium dithionite (4) Sodium perborate (5) Sodium peroxide

of immersion in sodium peroxide system. But in the case of specimens exposed for 3 days and 7 days, peaks for Fe_2O_3 and Fe_3O_4 (20 = 30.1°, 35.5°, 57.1°, 62.5°) have been observed.

In the light of the XRD analysis, the following sequential reactions are visualised for sodium peroxide system.

$$Na_2O_2 + 2H_2O \longrightarrow 2H_2O_2 + 2NaOH \quad (1)$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \quad (2)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (3)$$

$$Fe(OH)_2 + H_2O + [0] \longrightarrow Fe(OH)_3 \quad (4)$$

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O \quad (5)$$

In the initial stages, the sodium peroxide dissociates into hydrogen peroxide and sodium hydroxide. The sodium hydroxide thus produced increases the alkalinity of the system. Due to the increase in alkalinity, the OH^- ion is adsorbed on the metal surface and forms $Fe(OH)_2$ which acts as protective barrier in the initial stage. With passage of time, the hydrogen peroxide dissociates into water and oxygen. Due to the increase in the oxygen concentration the $Fe(OH)_2$ gets oxidized and the protective barrier gets stabilised as Fe_2O_3 and Fe_3O_4.

CONCLUSIONS

1. Four types of peroxide based biocides, namely sodium peroxide, sodium dithionite, sodium perborate and sodium chlorite have been evaluated for biocidal and inhibition efficiencies. The three biocides namely sodium dithionite, sodium perborate and sodium chlorite enhance the corrosion rate by a factor of two and are not suitable.
2. Sodium peroxide has been found to be an efficient biocide with a better inhibition efficiency of 80%.
3. All the four biocides have the capability to reduce the bacterial activity, however sodium peroxide stands out as the best biocide, with 100% efficiency at a concentration of 500 ppm. Hence sodium peroxide is an ideal choice both as biocide and corrosion inhibitor.

REFERENCES

1. C Bennett, *Control of microbial problems and corrosion in closed systems, Paper Technology and Industry,* (1985) p 331
2. P C Quimby, *Journal of Aquatic Plants Management,* **19** (1981) 53
3. S H Kay, P C Quimby and J D Ouzts, *Journal of Aquatic Plant Management,* **22** (1984) p 25
4. M C Fowler and Battett, *Proceedings EWRS 7th Symposium on aquatic weeds,* (1986) p 113
5. M Matsudaira, M Suzuki and Y Sato, *Dissolved ozone effect on corrosion of metals in water,* Material performance, NACE, November (1981)
6. *Standard methods for the examination of water and waste, Seventeenth Edition,* APHA-AWWA-WPCF, (1989)
7. M Yamashita, H Miyuki, Y Matsuda, H Nagamo and T Misawa, *Corr Sci,* **36** (1994) 283
8. M Favre and D Landolt, *Corr Sci,* **34** (1993) 1481
9. S Mohan, S Maruthamuthu, A Mani and G Venkatachari, *Anti-corrosion methods and materials,* 43-5 (1996) 2