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Assessment and Control of Microbial Induced Corrosion in Sea Water in Nuclear Power Plant Materials

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ABSTRACT

Microbial-induced corrosion (MIC) can occur due to the long building timeframes connected with nuclear facilities and the huge number of redundant or standby systems where water is permitted to remain stagnant for long periods of time. MIC affects carbine and low-alloy steels, stainless steels and copper alloys are all susceptible to MIC in raw water applications. Visual examination is especially helpful in performing preliminary assessments of MIC. If properly diagnosed, MIC can be effectively treated during plant development, operation and brief shutdowns. The main aim of this work is directed to investigate some methods for evaluating and controlling one of the most important economic problems arose from the presence of some microorganisms which are responsible for promoting corrosion process of metals and/or their mixtures (alloys) in cooling water systems and those in different Egyptian industrial fields such as power stations, oil fields and power plants. The study concentrated on finding applicable treatment methods for controlling *Thiobacillus*bacteria which represent one of the important active members of microbiologically induced corrosion (MIC) group found in seawater, through recording their growth and reducing their activities, and consequently reducing the harmful impact of its presence in different industries as mentioned above.The current research is also concerned with the scales formation studies for water and the effect of scales inhibitors on the scales formed during cooling processes. Moreover, this research includes and discusses the results of using some special biocides as a chemical method applied for reducing microbial counts and its efficiencies on *Thiobacillus* bacteria.

Benzalkonium bromide, Sodium hypochlorite and Gluteraldehyde were chosen for the present study because of their broad spectrum and biodegradability. A strategy is developed for inhibiting *Thiobacillus* bacterial colonization and aerobic corrosion in biofilms on mild steel. The most effective biocide was gluteraldehyde that has been used as a reference biocide, its addition firstly prior to *Thiobacillus* bacterial colonization considered a valuable approach to reduce *Thiobacillus* bacterial induced corrosion. Gluteraldehyde form biocide which has wide a range of biocidal effects and also inhibiting *Thiobacillus* bacteria as shown in this study. The results indicated that 50 (mg/L) of Glutaraldehyde was sufficient to eliminate all bacterial counts, but 2.5 (mg/L) of Benzalkonium bromide and 8 (mg/L) of sodium hypochlorite were also required to achieve the same result. The results also demonstrated that high biocide concentration inhibit *Thiobacillus* bacteria growth more than the low biocide concentration. Finally, the findings support the construction of nuclear power plants in order to prevent aerobic bacteria from causing bio corrosion and to provide media for the growth of anaerobic bacteria such as sulphate reducing bacteria which were previously thought to be the most important bacterial group involved in bio corrosion.

1. INTRODUCTION

Corrosion measurements use a range of methods to detect how corrosive the environment is and how quickly metal is being lost. Corrosion measurements are quantitative methods for evaluating the effectiveness of corrosion control and prevention procedures and providing the feedback for improving corrosion control and prevention methods. Surface corrosion caused by *Thiobacillus* bacteria was investigated using the coupon weight loss method on various alloys similar to those used in cooling system equipment.

Microbial biofilm and corrosion in cooling systems whether in power stations or in nuclear power plants are the most typical issues resulting in costly equipment damage, production loss, and increased maintenance costs. The major bacterial group associated with metals in the terrestrial and aquatic habitats involved in the microbiological influence corrosion (MIC) process are

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Sulfate- iron- reducing bacteria, iron oxidizing bacteria (1), and acid producing bacteria (2). Different categories of biocides are used as chemical control of MIC. The widely used in oil field are oxidizing biocides such as chlorine, chlorine dioxide and bromine, non-oxidizing biocides such as Glutaraldehyde as well as tetrakis hydroxymethyl phosphonium sulfate (THPS), quaternary ammonium compounds (QAC), bromo-nitropropanediol (BNPD), etc.(2).

According to a previous study (3), corrosion costs the oil industry millions of dollars each year. Corrosion has an impact on every phase of exploration and production, from offshore rigs to casing, and the importance of corrosion agents such as drilling and production fluids is discussed.

Despite the corrosion that aerobic microorganisms appear to inflict on metals surfaces, bacteria can adjust a variety of reaction pathways to influence the corrosion process (4).

Microbially induced corrosion (MIC) is expected to affect a variety of industries with severe economic effects, and is estimated to account for 20% of overall corrosive damage (5).

Corrosion induced by electrochemical processes linked with microorganisms is referred to as MIC. Due to the wide range of reactions in which microorganisms can participate, MIC mechanisms can either increase or limit corrosion by forming biofilms or chemical inhibitors (6).

Deterioration can occur as a result of the production of scales as well as the formation of biofilms as a results of bacterial activity. This section of the study is an attempt to find an applicable method for preventing bio deterioration of industrial materials –particularly in power plants- thereby preserving their structures and extending their use as long as possible in order to reduce costs, which is critical in large scale industrial projects such as nuclear power plants and oil industries (7) .

2. MATERIAL AND METHODS

Sampling preparations were conducted for detection and enumeration of *Thiobacillu*s growth

Collecting water samples

Water samples were obtained from several location along the north shore at various times; Samples were collected in sterile polypropylene bottles that were closed under aerobic conditions to maintain an optimal medium for *Thiobacillus* bacterial growth, until being investigated. Then the samples were stored in ice tank and transferred to the analytical laboratory at the NCRRT for analysis.(7).

Procedure for preparation of *Thiobacillus* bacterial growth suspension stock inoculum

Thiobacillus bacterial growth stock suspension was made by inoculating 10 ml of seawater into a liquidmodified Starkey's growth medium contained in an aerobic container (500 ml)and incubated for two days at 33°C under aerobic conditions. The *Thiobacillus* bacterial growth was stored at 4°C for further use. The *Thiobacillus* bacterial growth inoculum used in the tests was made by pouring one ml of stock culture suspension into 10 ml glass flask containing 9 ml of modified liquid Starkey's growth medium and incubated for 2 days at 33°C under aerobic conditions. These steps were repeated for all the tested seawater samples (7)

Microbiological Studies of *Thiobacillus* bacterial growth

Individually, the *Thiobacillus* bacterial growth was counted using water samples obtained from several locations around the North coast at various desired points. The method for detecting and counting *Thiobacillus* bacterial growth is demonstrated in this experiment. The medium utilized was theStarkey'smodified growth medium (8).

The enumeration of the *Thiobacillus* bacterial growth was carried out using the Most Probable Number (MPN) approach,according to earlier publications (9-10). The contents of modified Starkey growing medium were dissolved in 1000 ml of pre-boiled Mediterranean Sea water, pH was adjusted at 7.3, and 9 ml media per pre-washed and sterilized glass vials were distributed, subjected to aerobic conditions, and then sealed with a rubber stopper and capped with aluminum caps, autoclaved at 121°C for 15 minutes.

After sterilization, the bottles were classified into sets in triplicate. One ml of the corresponding water sample was added to the first triplicate and sequentially diluted up to 10^5 fold dilution, then incubated at 33 °C for 2days. *Thiobacillus* bacteria, which are found in both marine and fresh water were recorded, The *Thiobacillus*bacterial growth MPN count was compared to that of Cochran (11).

Biocides as a chemical method of controlling *the growth ofThiobacillus* bacteria

1. Evaluation of different biocides efficiency on controlling *Thiobacillus* bacterial growth present on different water samples

To restrict *Thiobacillus* bacterial growth, this study used three separate sets of biocides, each with two concentrations; sodium hypochlorite, benzalkonium bromide and Glutaraldehyde which were submitted as part of this project's evaluation of efficiency.

Each biocide was gradually added to a sterile vial-containing 100 ml of seawater sample until the desired concentration reached (100 ppm). One vial was left untreated as a control. All biocides were kept in contact with sea water at 30°C for two hours (12). After 24h,one ml of each biocide concentration bottle was injected into a Starkey modified medium with a sterilized syringe, at the conclusion of the contact time and incubated at 33°C for two days. The *Thiobacillus* bacterial growth was counted and the associated MPN values were computed. This experiment was repeated for water samples collected from several locations along the north coast at various study points. Each biocide's effectiveness was calculated as follows:

%Efficiency= (a-b/a) x 100

a: Count of Thiobacillus bacteria before using biocide
b: Count of Thiobacillus bacteria after applying biocide

2. Evaluation of different biocides concentrations on controlling*Thiobacillus* bacterial growth

The inhibitory effect of different concentration of biocides on *Thiobacillus* bacteria

The three different biocides with different concentrations were studied to evaluate the effect of their different concentrations on controlling *Thiobacillus* bacterial growth. Each biocide was added to a sterilized aerobic vial containing 100 ml of sea water sample. A vial with the same aerobic conditions must be left untreated to represent negative control vial. Each biocide concentration was kept with sea water at 30°C. At the end of contact time and by using a sterilized syringe, 1ml of each biocide' concentration was inoculated into a Starkey' modified medium, incubated at 33°C for two days under continuous observation. After introducing the biocide to the sea water, bacteria were counted, and this was repeated after 2hours and 24hours, and a particular amount of biocide was applied to each container to double the biocide concentration, after which residual chlorine and bacteria were sampled and analyzed (13)

The biocide concentration at which no growth was observed represented the most referable concentration to be used in subsequent trials, as well as the minimum inhibitory concentration of the biocide. Enumeration of *Thiobacillus* bacterial growth took place and MPN values were calculated. As previously stated, the efficiency of biocides was calculated. The technique was followed in the same way for the cooling sea water of the water samples under study.

The formation of scales and scales inhibitors

1. The formation of scales under various conditions

According to a previous work (14), 100ml of each filtered sea waters was poured into a beaker for each experiment of common sea water scales. The sea water samples were incubated for 48 hours at various temperatures of 25, 50, 100, 150 and 200°C with constant stirring by a mechanical stirrer before being filtered through filter paper. Following filtration, 5ml of the filtrate was placed into a 50ml volumetric flask, which was then filled to capacity with distilled water.

2. Jar test for determination of high scales at different seawater samples

The jar test was performed to investigate the number of scales in water samples obtained from several locations along the north coast at various desirable points. To remove any suspended impurities, the sea water samples are first pre-filtered. For 48 hours,the sample was incubated at the necessary test temperatures of 25, 50, 100, 150 and 200 degrees Celsius. The samples were incubated for one day before being filtered through filter paper to eliminate any precipitation.The precipitates were weighted after the filter sheets were dried. Based on the weight of the precipitates, the highest scaling amounts were established (7).

3. Evaluation of the effectiveness of scales inhibitors in preventing the formation of scales in various sea water samples.

According to an earlier publication (7), scales inhibitors with the trade names Gyptron SA860N were used in the jar test described above. Different concentrations of Gyptron were made separately and added to glass vials containing 50 ml of the *Thiobacillus* containing sea water sample sequentially to achieve the final required concentrations: 5, 10, 15, 20, 25 and 30 ppm. A negative control was made by adding 50 ml of sea water sample to a glass vial without any scale inhibitors, All test cells were exposed to aerobic conditions and agitated to thoroughly mix them (15).

For 48 hours,all test vials and blanks were immersed to 3/4 of their lengths in a water bath at 71°C. After 48 hours,the test vials were removed to avoid agitation. The test vials were cooled to 25°C and 5°C for a time not

exceeding 120 minutes. Following that, the samples were then kept for 24h before being filtered using filter paper to eliminate any precipitation. The filter papers were dried and the precipitates were then weighed (16).

Investigating the impact of biocides and scales inhibitors on bacterial growth

Gyptron SA860N was chosen as the most effective scales inhibitor in the investigation, resulting in the best scales inhibition outcomes (**7**). A solution with a final concentration 10 ppm was prepared in 100 ml of sea water sample present in a sterilized aerobic vial. This step was prepared before adding the desired biocide by 24 hours (Gluteraldehyde, Sodium hypochlorite and Benzalkonium Bromide under investigations in controlling *Thiobacillus* growth).

Gluteraldehyde was prepared to achieve the concentration of 100 ppm and was added to an aerobic vial. This step was repeated to sodium hypochlorite and Benzalkonium Bromide (with concentrations of 50,8,2.5g/l respectively) with a constant Gyptron SA860N concentration of 10 ppm, lifting one untreated vial as a negative control. Then the same steps achieved for evaluation of biocides were repeated, enumeration of *Thiobacllus* bacteria were calculated according to MPN technique. Results were recorded for sea water under investigation.

Corrosion evaluation in sea water alone and if associated with the*Thiobacllus* bacteria chemical controlling method (biocides) and scales inhibitor

In this part of study, the microbial corrosion of sea water samples was evaluated and the corrosion rate was estimated. In addition, the effects of using the minimum inhibitory concentration of the most efficient biocide Glutaraldhydeon corrosion process and also in the presence of both Glutaraldhyde and Gyptron SA860N were studied.

Coupon setting method was used to determine the corrosion rate using mild steel AISIC1018 coupon purchased from (EPRI) with dimensions of 3 x 1 x 0.2 cm^3 ,total exposed surface area of 7.6 cm^2 and coupon density of 7.87 g/cm^3 (17).

To investigate microbial corrosion in a Mediterranean salt water target sample, the corrosion rate was determined using the coupon setting method in water which was based on monitoring weight loss of the metal samples.

The following formula was used to calculate the corrosion rate of the samples.

A weighted sample of the metal (coupon) was introduced into the process, and then removed after a period of time. The coupon was then cleaned and reweighed to remove any corrosion products. Using the formula presented by Krisher (18), the weight loss was converted to a corrosion rate (CR) or metal loss (ML)

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (g)} * K}{\text{Density of the alloy :(gm/cm}^3\text{)} * \text{Area of exposure :(A)} * \text{Time of Exposure: (hr)}}$$

Where, Weight loss is the difference between MI: the Main weight of sample (g) and M2 the secondary weight of the sample(g).

Coupons preparation

According to A. B. Ramadan et al.(7),metal coupons were first polished according to ASTM G1-72,1993(19) before being used in the coupon setting process The metal coupons were cleaned with sterile distilled water after being degreased with acetone, and washed with sterile distilled water. Before being exposed to the experimental media, the coupons were dried in a current air and sterilized with ethanol (20)

The method for determining corrosion rate is based on the weight loss of metal samples.

$$\text{Metal Loss (ML)} = \frac{\text{Weight Loss (g)} * K}{\text{Alloy Density (g/cm}^3\text{)} * \text{Exposed Area (A)}}$$

Where, weight loss is the difference between M; primary weight of sample (g) and

M :Secondary sample weight (g)

4.RESULTS AND DISCUSSION

1. Detection and enumeration of aerobic bacteria in sea water used in cooling systems of power plants in Al Dabaa

Samples were collected from various locations along the north coast, including Sidiabdelrahman area that is a village on the coast of Mediterranean sea in Egypt (Marasi and Amwaj) which is 40km from Al Dabaa and located 132km west of Alexandria and some 30km west of Alamein as well as Marina,a village on the Mediterranean sea in Egypt located on Alamein city which is 65km from Al Dabaa and located 110 km west of Alexandria also from Ras el hekma which is 65km from Al Dabaa and located 200 km west of Alexandria in order to detect and enumerate aerobic bacteria and consequently to handle the problems they cause. The counts at different samples collection points had been calculated and given in Table (1).

Table (1): *Thiobacillus* bacterial counts of north coast samples

Sample No.	Sample Site	*Thiobacillus* bacterial count (cell/ml)
Sample A	Marasi	$2.2x10^4$
Sample B	Amwaj	$3.5x10^4$
Sample C	Marina	$1.6 x10^5$
Sample D	Ras el hekma	$3.4 x 10^3$

Generally the count (cfu/ml) ranged from $3.4 x 10^3$ to$1.6 x10^5$. It is clear that the minimum count was observed at sample D which recorded $3.4 x 10^3$ (cfu /ml), while the maximum bacterial count was $1.6x 10^5$ in sample C .

Results showed that bacterial counts differ from point to point in the same area. This data absolutely helped in selecting the most effective biocides and its minimum inhibitory concentrations,in fact these results are consistent with those reported by Ramadan et al.(7).

2. The effects of various biocides concentrations on *Thiobacillus* bacterial growth

Tables (2-5) summarized the data obtained as a result of using sodium hypochlorite ,benzalkonium bromide and Glutaraldehyde as well as theire efficacy on the log count of *Thiobacillus* found in four samples of the analysed sea water. The effect of different biocide concentrations on *Thiobacillus* bacterial growth for water samples were illustrated in Tables (2-5)

Table (2): The inhibitory effect of various biocides on *Thiobacillus* bacteria found on Marina water sample

Biocide	Concentration (mg/L)	Time (h) of exposure	*Thiobacillus*bacterialcount (cell/ml)	Log count
Seawater Blank	/	/	$160x 10^3$	5.20
Glutaraldehyde	25	0	$1.2 x 10^3$	5.08
		2	$4 x 10^3$	3.60
		24	/	/
		24(biocide is added again)	$3.8 x 10^3$	3.58
		48	/	/
	50	0	$8 x 10^3$	3.90
		2	$1.4 x 10^3$	3.0
		24	/	/
		24(biocide is added again)	$1.2 x 10^3$	3.15
		48	/	/
NaClO	4	0	$160x 10^3$	5.20
		2	$30 x 10^3$	4.48
		24	/	/
		24(biocide is added again)	$0.1x 10^3$	4.0
		48	/	/
	8	0	$140 x 10^3$	5.15
		2	$20 x 10^3$	4.30
		24	/	/
		24(biocide is added again)	$50x 10^3$	4.70
		48	/	/
Benzalkonium bromide	1.25	0	$160 x 10^3$	5.20
		2	$12 x 10^4$	5.07
		24	/	/
		24(biocide is added again)	$100x 10^3$	5.0
		48	/	/
	2.5	0	$160 x 10^3$	5.20
		2	$20 x 10^3$	4.30
		24	/	/
		24(biocide is added again)	$18 x 10^3$	4.26
		48	/	/

Table (3): The inhibitory effect of various biocides on Thiobacillus bacteria found on Marasiwater sample

Biocide	Concentration (mg/L)	Time (h) of exposure	*Thiobacillus* bacterial count (cell/ml)	Log count	Efficiency %
Seawater Blank	/	/	22 x 10^3	4.34	0.00
Glutaraldehyde	25	0	16 x 10^3	4.20	27.2
		2	1.3 x10^3	3.11	94.1
		24	/	/	100
		24(biocide is addedagain)	1.2x 10^3	3.08	94.55
		48	/	/	100
	50	0	6.0x10^3	3.78	72.73
		2	0.3 x 10^3	3.48	99.13
		24	/	/	100
		24(biocide is addedagain)	0.21 x10^3	2.32	99.05
		48	/	/	100
NaClO	4	0	22 x10^3	4.34	0.00
		2	5 x 10^3	3.70	77.27
		24	/	/	100
		24(biocide is addedagain)	4.3 x 10^3	3.63	80.45
		48	/	/	100
	8	0	19 x 10^3	4.28	13.6
		2	2.1 x 10^3	3.32	90.45
		24	/	/	100
		24(biocide is addedagain)	2.0 x 10^3	3.30	90.9
		48	/	/	100
Benzalkonium bromide	1.25	0	22 x 10^3	4.34	0.00
		2	8 x 10^3	3.90	63.64
		24	/	/	100
		24(biocide is addedagain)	7.5 x 10^3	3.88	65.91
		48	/	/	100
	2.5	0	22 x 10^3	4.34	0.00
		2	3.1x 10^3	3.49	85.91
		24	/	/	100
		24(biocide is addedagain)	3.0 x 10^3	3.48	98.64
		48	/	/	100

Table (4):The inhibitory effect of various biocides on Thiobacillus bacteria found on Amwajwater sample

Biocide	Concentration (mg/L)	Time (h) of exposure	*Thiobacillus* bacterial count (cell/ml)	Efficiency %
Seawater Blank	/	/	35×10^3	0.00
Glutaraldehyde	25	0	4.6×10^3	86.86
		2	0.13×10^3	99.63
		24	/	100
		24(biocide is added again)	0.12×10^3	99.66
		48	/	100
	50	0	0.7×10^3	98
		2	$0.09x\ 10^3$	99.74
		24	/	100
		24(biocide is added again)	0.1×10^3	99.71
		48	/	100
NaClO	4	0	35×10^3	0.00
		2	4.8×10^3	86.29
		24	/	100
		24(biocide is added again)	4.2×10^3	88
		48	/	100
	8	0	$9.8x\ 10^3$	72.0
		2	0.9×10^3	97.42
		24	/	100
		24(biocide is addedagain)	0.91×10^3	97.40
		48	/	100
Benzalkonium bromide	1.25	0	$35\ x10^3$	0.00
		2	9×10^3	74.29
		24	/	100
		24(biocide is added again)	9.3×10^3	73.43
		48	/	100
	2.5	0	35×10^3	0.00
		2	1.7×10^3	95.14
		24	/	100
		24(biocide is added again)	1.5×10^3	95.71
		48	/	100

Table (5): The inhibitory effect of various biocides on Thiobacillus bacteria found onRas el hekma water sample

Biocide	Concentration (mg/L)	Time (h) of exposure	*Thiobacillus*bacterialcount (cell/ml)	Efficiency %
Seawater Blank	/	/	3.4×10^3	0.00
Glutaraldehyde	25	0	1.6×10^3	52.94
		2	0.36×10^3	98.41
		24	/	100
		24(biocide is added again)	0.32×10^3	90.59
		48	/	100
	50	0	1.4×10^3	58.82
		2	0.18×10^3	94.71
		24	/	100
		24(biocide is added again)	0.16×10^3	95.29
		48	/	100
NaClO	4	0	3.4×10^3	0.00
		2	0.56×10^3	83.53
		24	/	100
		24(biocide is added again)	0.54×10^3	84.12
		48	/	100
	8	0	1.8×10^3	47.06
		2	0.19×10^3	94.41
		24	/	100
		24(biocide is added again)	0.15×10^3	95.59
		48	/	100
Benzalkonium bromide	1.25	0	3.4×10^3	0
		2	1.4×10^3	58.82
		24	/	100
		24(biocide is added again)	1.3×10^3	61.7
		48	/	100
	2.5	0	3.4×10^3	0.00
		2	0.21×10^3	93.82
		24	/	100
		24(biocide is added again)	0.22×10^3	93.53
		48	/	100

It was discovered that the concentration 50 (mg/L) of Glutaraldehyde was sufficient to eliminate all the bacterial count reported, as was 2.5 (mg/L) of Benzalkonium bromide and 8 (mg/L) of sodium hypochlorite.These findings are in line with those previously repoted (13).

Glutaraldehyde was also shown to be the most effective biocide across all types tested.This agrees with some authors (21)who acknowledged that glutaraldehyde is an effective and fast- acting biocide and that its reactivity prevent it from harming the environment which is also in agreement with some earlier investigations (22and 23).

The results also suggest that a high concentration of biocide inhibits *Thiobacillus* bacteria growth more than a low concentration, which is consistent with previous findings (7).

3. Scales formation and scale inhibitor

Scales formation at different conditions

Solubility of scales formation analysis in Mediterranean sea water is summarized in Table (6). The results showed that increasing the temperature,decreased the solubility of $CaCO_3$, $CaSO_4$, and $SrSO_4$, at various temperatures due to dissociation of $CaSO_4$and $SrSO_4$with exothermic process.

Table (6): Solubility of scales in Mediterranean sea water

Temp. Degree, °F	Temp. Degree, °C	$CACO_3$, mg/L	$CaSO_4$, mg/L	$SrsO_4$, mg/L
77	25	2015.6	2963.50	375.61
122	50	1255.74	1385.30	192.64
212	100	823.14	1091.62	103.78
302	150	730.21	415.06	66.23
392	200	610.68	95.45	40.65

The results showed that the relation between the concentrations of the common salts $CaCO_3$, $CaSO_4$, and $SrSO_4$ changed at different temperatures. According to the findings at various temperatures (25-150°C), the solubility of $CaCO_3$, $CaSO_4$, and $SrSO_4$, were reduced by increasing the temperature. The findings are consistent with the information gathered by Ramadan et al. (7).

The findings support the general trend in solubility dependence on temperature for common sea water scales. Using the software simulator Scale Chem 2.0, the number of scales precipitated under various temperature conditions was computed. This is the same outcome as reported before (24,25,26,27,28and 14).

4. Jar test for determining scales at sea water samples

Jar tests were frequently used in traditional water treatment process to supply water to cooling systems in the industrial power plants. The amount of scales formation in sea water samples was studied using the jar test. The results obtained are illustrated in Table (7) .The findings showed that when the temperature rise, the scales percentage grow.

Table (7): Jar test for scales formation in Mediterranean sea water

Temp. Degree, °F	Temp. Degree, °C	Amount of Scales mg/l
77	25	3.56
122	50	21.49
212	100	22.24
302	150	126.28
392	200	992.45

The amount of scales increased with increasing the temperature, possibly due to greater evaporation occurred as a result of higher temperatures, which raised the concentrations of various scales as well as the density of sea water. These findings are consistent with those of other studies (29 and 7).

5. Evaluation of some scales inhibitors on scales formation in Mediterranean sea water

Type of scales inhibitors with commercial names Gyptron SAS60N was studied to evaluate their efficiencies on the water samples under investigation.The jar test was carried out with quantities of 5, 10, 15, 20, 25 and 30 ppm added individually to duplicate500 ml flasks containing the sea water .

The effect of various scale inhibitor concentrations on the scales generated in sea water samples is summarized in Tables (8,9,10,11). The efficacy of scales inhibitors was determined using the formula previously established.

Table (8): Gyptron scale inhibitors evaluation for sea water of Marina

Scaleinhibitor conc.,ppm	Maximum scale formed mg/l	Scale inhibitor efficiency %
Control	9368.4	0.00
5.00	8219.69	12.26
10.00	6543.12	30.16
15,00	5078.42	45.79
20.00	4863.51	48.09
25.00	.4521.50	51.74
30.00	4409.58	52.93

Table (9): Gyptron scales inhibitors evaluation for sea water of Amwag

Scale inhibitor conc.,ppm	Maximum scale formed mg/l	Scale inhibitor efficiency %
Control	8650.5	0.00
5.00	7602.4	12.12
10.00	6089.6	29.6
15.00	5223.6	39.61
20.00	4750.6	45.08
25.00	4420.32	48.90
30.00	4355.42	49.65

Table (10): Gyptron scales inhibitors evaluation for sea water of Marasi

Scale inhibitor conc.,ppm	Maximum scale formed mg/l	Scale inhibitor efficiency %
Control	8312.56	0.00
5.00	7306.70	12.10
10.00	5915.6	28.84
15,00	4956.31	40.38
20.00	4680.38	43.70
25.00	4386.21	47.23
30.00	4156.92	49.99

Table (11): Gyptron scales inhibitors evaluation for sea water of Rasel hekma

Scale inhibitor conc.,ppm	Maximum scale formed mg/l	Scale inhibitor efficiency %
Control	8018.6	0.00
5.00	7019.58	12.46
10.00	5655.3	29.47
15,00	4870.21	39.26
20.00	4543.70	43.34
25.00	4196.34	47.67
30.00	4058.63	49.38

The findings showed that when the concentration of scale inhibitors grew, the efficiency increased progressively up to 15ppm and then began to differ slightly between the inhibitors efficiencies from 20 up to 30ppm.

At 25 ppm, the maximum efficiency was achieved. This result goes in parallel with the the results obtained by other investigators (29 and 7)

Gyptron SA860N exhibits significant scales inhibitor at recorded optimum concentration 20 ppm. These results agreed with previous ones (7and31).

6. The Effect of using scales inhibitors on biocides efficiency and correspond to *Thiobacillus* bacterial counts

Corrosion scaling and biofouling were two fetal problems that affected the performance of the recirculating cooling water systems, the most important part in most industries. To safeguard their systems from these challenges, most industrial projects used biocides and scales inhibitors in their cooling water systems. Biocides were added once and inhibitors were added permanently.

The current study explored the influence of the presence of the most efficient scales inhibitor – as indicated from the previous results Gyptron SA860N on the log *Thiobacillus* counts in the presence or absence of the most effective biocides independently glutaraldehyde and that in sea water samples collected as shown in Table (12)

Table (12): The effect of the biocides concentrations individually on the log *Thiobacillus* bacterial count in the presence or absence of 10 ppm of scales inhibitor

Biocide	Concentration (mg/L)	Log *Thiobacillus* Bacteria count	
		Without gyptron	With 10 ppm gyptron
Control	/	6.20	6.20
Glutaraldehyde	50	3.006	4.32
NaClO	8	5.30	6.12
Benzalkonium bromide	2.5	5.30	6.10

The effect of the two biocides concentrations on the log *Thiobacillus* bacterial count in the presence or absence of 10 ppm of scales inhibitor revealed that high biocide concentrations inhibit *Thiobacillus* bacterial growth more than low concentrations, but the efficiencies of the three biocides decreased when scale inhibitor was present , implying that the presence of scales inhibitor reduces the efficiencies of the three biocides on *Thiobacillus* bacteria count with small values. This result is in agreement wtih Ramadan et al. (7) and was parallel to what had been achieved by Maruthamthu et al.(32),who used Morpholine phosphate as biocide and found that when used it without scales inhibitor it acts as a good biocide, but when mixed with scales inhibitor the inhibitory effect decreased markably. This might explained that a sort of interference might occur which could affect the efficiencies of biocides.

7.1. Metal Corrosion Causing by *Thiobacillus* bacteria by coupon setting method

In the present study, a strategy is developed for inhibiting *Thiobacillus* bacteial colonization and aerobic corrosion in biofilms on mild steel. The commonly used biocide is the most efficient biocide found glutaraldehyde had been used as a reference biocide, its addition firstly prior to *Thiobacillus* bacteial colonization considered a valuable approach to reduce *Thiobacillus* bacterial induced corrosion. Glutaraldehyde form biocide which had wide range of biocidal effects and also on *Thiobacillus* bacteial count is shown in this study.

Moreover, the excellent scales inhibitor Gyptron SA860N was examined separately and mixed with Glutaraldehyde biocide to achieve a combined treatment for metal surface against microbial corrosion due to the presence of *Thiobacillus* bacteria in sea water. Mass loss from mild steel AISI C1018 coupon in sea water medium in the presence of Glutaraldehyde Gyptron SA860Nwas examined every 7 days and 30 days respectively in stationary batch cultures at 30°C.The presence of sulfate reducers was confirmed by detection of black iron sulphide in the culture media.

Data obtained from measuring the corrosion rate of the sea water for marina sea water sample using coupons method is illustrated in (Tables 13&14).

Table (13): corrosion rate of sea water for sea water of Marina after 7 days

Chemical additives	Initial weight (gm)	Secondary weight (gm)	loss of Weight (gm)	Setting period (day)	Density (gm/cm^3)	Rate of Corrosion (mm/y)
Control	5.6455	5.6349	0.0106	7	7.87	0.0092
Gyprton	5.6455	5.6358	0.0099	7	7.87	0.0086
Gluteraldehyde	5.6455	5.6356	0.0097	7	7.87	0.0084
Gyptron and Gluteraldehyde	5.6455	5.6347	0.0108	7	7.87	0.0094

Table (14): corrosion rate of seawater for Seawater of Marina after 30 days

Chemical additives	Initial weight (gm)	Secondary weight (gm)	loss of Weight (gm)	Setting period (day)	Density (gm/cm^3)	Rate of Corrosion (mm/y)
Control	5.6455	5.5538	0.0917	30	7.87	0.1865
Gyptron	5.6455	5.5587	0.0870	30	7.87	0.1769
Gluteraldehyde	5.6455	5.5585	0.0868	30	7.87	0.1766
Gypton and Glyteraldehyde	5.6455	5.5536	0.0919	30	7.87	0.1869

7.2. Metal loss of sea water

Metal loss of coupons using seawater of Marina after 7 days and 30 days were investigated as illustrated in Tables (15&16 respectively). The Weight method was used for measuring the metal loss. The batch experiments were examined in the presence of Gyptron SA860N as a scales inhibitor, Glutaldehyde as a biocide and Glutaldehyde biocide with Gyptron SA860N as scale inhibitor.

The resuts indicated that generally the metal loss deereased for sea water samples more than the control by using the chemical additives (Gyptron SA860N scale inhibitor and Gluteraldehyde biocide separately) and the biocide Gluteraldehyde is more effective in this case than Gyptron SA860N. Furthermor, the data showed that the scales inhibitor- biocide mixture had lowered the inhibition effect of biocide on the metal loss. It was remarkable that metal loss in the presence or absence of biocide and scale inhibitor in case of 30 days was higher than that of 7 days.The results showed that *Thiobacillus* bacteria play an important role in the corrosion process of the metal coupons.These results were consistent with those reported by other workers (7 and33) and disagree with Choudhary et al. (34) who found when studing MIC from *Acidothiobacillusferrooxidans* with 304 stainless steel(SS304)coupons that no weight loss was reported.

The data obtained was compatible with those found by several authors who studied methods of controlling microbial induced corrosion of SRB bacteria by metal weight loss method (35-36).

Table (15): Metal loss of sea water of Marina after 7 days

Chemical additives	Initial weight (gm)	Secondary weight (gm)	loss of Weight (gm)	Setting period (day)	Density (gm/cm^3)	Rate of Corrosion (mm/y)
Control	5.6455	5.6349	0.0106	7	7.87	0.00177
Gyprton	5.6455	5.6358	0.0097	7	7.87	0.00162
Gluteraldehyde	5.6455	5.6356	0.0099	7	7.87	0.00165
Gyptron and Gluteraldehyde	5.6455	5.6347	0.0108	7	7.87	0.00180

Table (16): Metal loss of sea water of Marina after 30 days

Chemical additives	Initial weight (gm)	Secondary weight (gm)	loss of Weight (gm)	Setting period (day)	Density (gm/cm^3)	Rate of Corrosion (mm/y)
Control	5.6455	5.5538	0.0917	30	7.87	0.01533
Gyptron	5.6455	5.5587	0.0868	30	7.87	0.01451
Gluteraldehyde	5.6455	5.5685	0.0870	30	7.87	0.01454
Gyptron and Gluteraldehyde	5.6455	5.5636	0.0919	30	7.87	0.01536

CONCLUSION

The results indicated that Glutaraldehyde is the most effective biocide for controlling Thiobacillus bacteria observed in water samples of all types.It was discovered that a biocide should be applied to bacteria first , followed by scale inhibitors , in order to achieve better outcomes. When scale inhibitors and biocides were combined in sea water cooling systems, an interaction process may occur.

The biocides must came into contact with the microbe to maximize its efficiency.

The results showed that a high biocide concentration inhibited *Thiobacillus* bacterial growth more than a low dosage. Finally, the findings supported the construction of nuclear power plants to prevent aerobic bacteria from causing bio corrosion as well as media for the growth of anaerobic bacteria such as sulphate reducing bacteria which was previously thought to be the most important bacterial group involved in bio corrosion.

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