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Some Data on the Dynamics of Corrosion Processes in Water Circulation Cooling Systems

Todor Peev[1], **Vanya Taseva**[2,*], **Ivan Mitov**[3], **Bogdan Kunev**[3], **Daniela Paneva**[3], and **Bogdan Bonev**[2]

[1] South-West University "Neophit Rilski", Department of Chemistry, BG-2700 Blagoevgrad, Bulgaria
[2] University "Prof. Dr. As. Zlatarov", Department of Water Technology, BG-8010 Bourgas, Bulgaria
[3] Institute of Catalysis, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Summary. Both origin and changes in phase composition of corrosion products deposited on Standard Carbon Steel during 313 days of exposure were monitored by X-ray diffraction analysis. The corrosion was caused by water from industrial cooling systems in the presence as well as in the absence an inhibitor. The predominant components of the corrosion products were initially found to be carbonates such as $CaCO_3$ as well as hydroxycarbonates like $Fe_2(OH)_2CO_3$; they were followed by the appearance of other products such as γ-FeOOH, Fe_3O_4, and α-FeOOH. The corresponding chemical reactions were found to comply with first-order kinetics. The rate constants were calculated from changes in the relative intensities of the corresponding X-ray patterns of Standard Carbon Steel samples. In absence of the inhibitor the rate of the corrosion processes were found to be 2.3 to 3 times higher than in its presence.

Keywords. Corrosion products; Industrial cooling systems; X-Ray diffraction; *Mößbauer* spectroscopy.

Introduction

The corrosion of iron and its alloys in water or aqueous electrolyte solutions is known to proceed in accordance with specific mechanisms depending on a number of factors such as nature of the material subjected to corrosion, salt composition and *pH* of the medium, temperature, flow dynamics, presence of inhibitors, *etc*. The basic components of the corrosion products such as oxyhydroxides and iron oxides undergo various transformations [1, 2] the overall scheme of which has been previously discussed [3].

Studies on the kinetics of corrosion processes is usually based on the determination of the corrosion weight loss by gravimetric analysis or by electrochemical potentiostatic methods. Furthermore, the complexity of the corrosion process requires the application of phase and structure analytic techniques. The objective of the present work was to utilize such an approach with the implementation of

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[*] Corresponding author

laboratory experiments aiming at investigating the formation of corrosion products and the kinetics of corrosion processes as well as on the effect of an inhibitor.

Results and Discussion

The samples (coupons) obtained in the presence of the corrosion inhibitor were marked as **A**, whereas those obtained without inhibitor were designated as **B**. On the whole, 28 X-ray diffractograms were evaluated, *i.e.* 14 for each of the coupons, at 0 (initial measurement), 1, 2, 5, 9, 20, 28, 37, 50, 70, 93, 110, 187, and 313 days. Some of these scans are presented in Fig. 1. The phases were identified and marked according to the published powder diffraction file [5]. Figure 1 shows the occurrence of the basic components in the corrosion product as a function of time. Two principal observations are obvious: first, the intensities of the X-ray patterns for Standard Carbon Steel at $d = 0.203$, 0.1430, and 0.1168 nm change in the two series of samples; second, the deposits and the corrosion products in absence of the inhibitor (samples **B**) appear sooner than in its presence. The first X-ray patterns at $d = 0.3095$ and 0.303 nm for samples **B** were observed one day after the beginning of the experiment and were assigned to $CaCO_3$ and $Fe_2(OH)_2CO_3$. It is supposed that the appearance of these products is caused by the presence of hard water in the system. However, in the presence of the inhibitor, these phenomena were not observed before the ninth day of the experiment. Products such as γ-FeOOH ($d = 0.627$, 0.248, 0.193, and 0.1724 nm) and Fe_3O_4 ($d = 0.418$, 0.252, 0.210, and 0.613 nm) in samples **B** were detected after 9 and 20 days, whereas for samples **A** this happened after 28 and 70 days. α-FeOOH ($d = 0.418$ and 0.247 nm) can be detected in both cases after *ca.* 70 days. Some shoulders or humps in the X-ray scans, detected between $\theta = 5°$ and $\theta = 10°$ indicated the probable formation of X-ray amorphous products the amount of which was higher in **A** than in **B**.

A comparison of the changes in the intensities of the X-ray patterns at $d = 0.1430$ and 0.1168 nm, characteristic for Standard Carbon steel, shows that these changes occur at a higher rate in the absence of the inhibitor (Fig. 2, curves II) than in its presence (Fig. 2, curves I). The extrapolation of curves II indicated that the carbon steel coupon would be completely destroyed and transformed into corrosion products after 220 to 230 days. The coupon treated in a medium containing the inhibitor, however, was not completely corroded even after 313 days. This fact reflects the retardation of the corrosion process in the presence of the inhibitor.

The analysis of the intensities of the X-ray patterns at $d = 0.309$ nm (Fig. 3) indicated that a non-uniform formation of carbonates took place. The amount of the latter was lower in the samples of series **A**. In both cases, a pronounced maximum in the intensity was observed within the period from 70 to 110 days.

The data obtained from the kinetic curves in Fig. 3 can serve as an instrument for studying the kinetics of corrosion processes. This is facilitated by the fact that all measurements concerning X-ray diffraction scans were carried out with metal plates of the same thickness and the same surface area using a special device (the so-called collimator). The percentage of iron in the samples was evaluated by the relative intensities of the X-ray patterns expressed as the intensity ratio I/I_0. The intensity for each X-ray pattern was normalized with respect to its own initial intensity. The

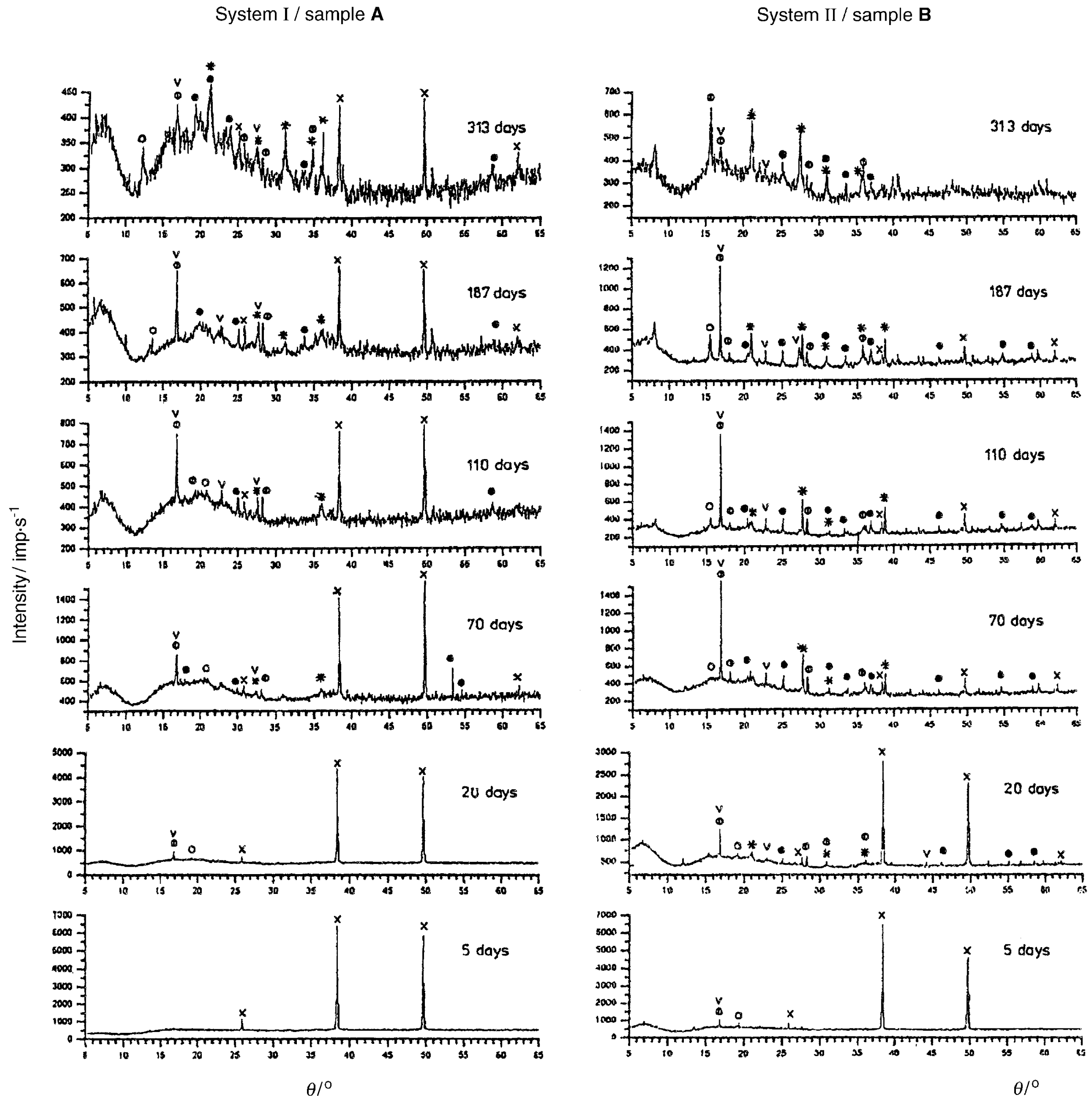

Fig. 1. X-Ray scans of samples with identified phases marked; x: Standard Carbon Steel, v: $CaCO_3$, ○: α-FeOOH, ●: Fe_3O_4, ✻: γ-FeOOH, ⦶: $Fe_2(OH)_2CO_3$

values obtained for different periods of time were practically the same; the average values are shown in Fig. 3 and confirm a first-order kinetics according to the following equation:

$$\frac{d(I/I_0)}{dt} = -k \cdot \frac{I}{I_0}$$

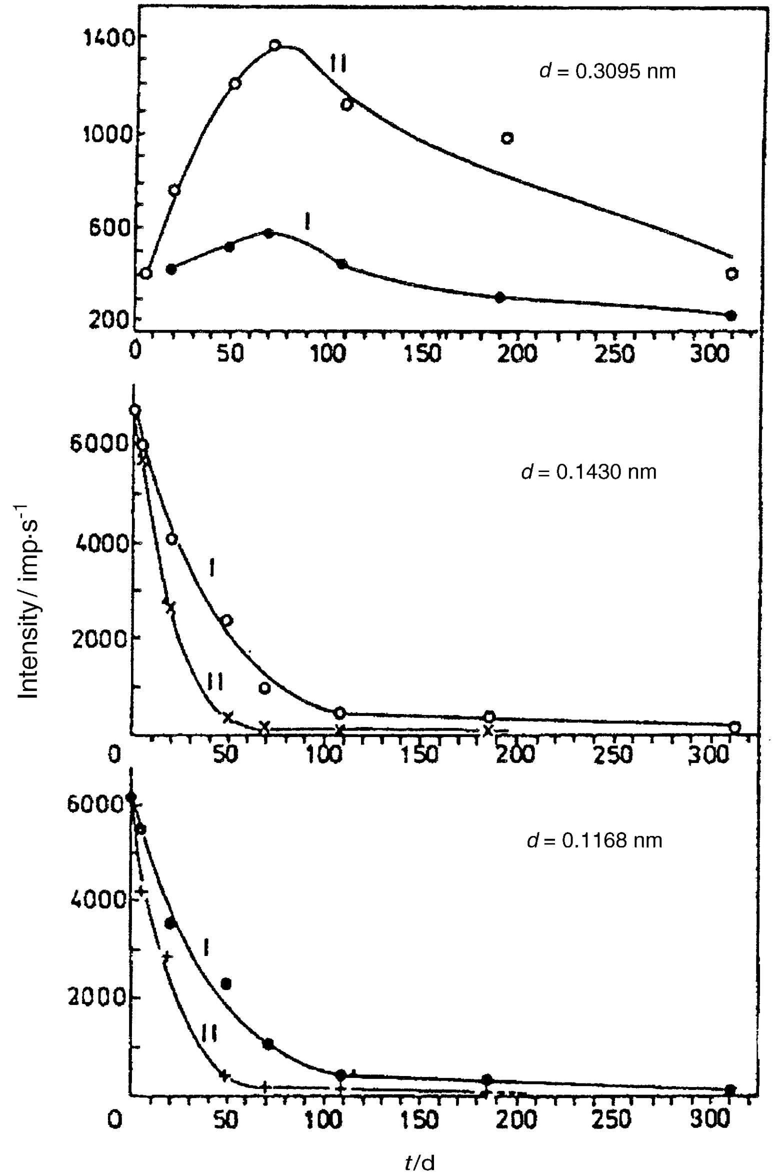

Fig. 2. Changes in the intensities of some characteristic X-ray patterns; I: system with inhibitor, II: system without inhibitor

Such a behaviour is known to be characteristic for heterogeneous reactions taking place under diffusion control and at low concentrations. After a certain period, the slopes changed; the time at which this change occurred was found to correspond to the observed maximum in the kinetic curves obtained on the basis of the X-ray pattern at $d = 0.303$ nm for the carbonates (Fig. 2). This is presumably caused by the decrease in the diffusion coefficient of the aggressive medium towards the metal surface originating from the formation of a surface layer containing corrosion products and deposits: the reaction order remains the same, but the rate constants decrease.

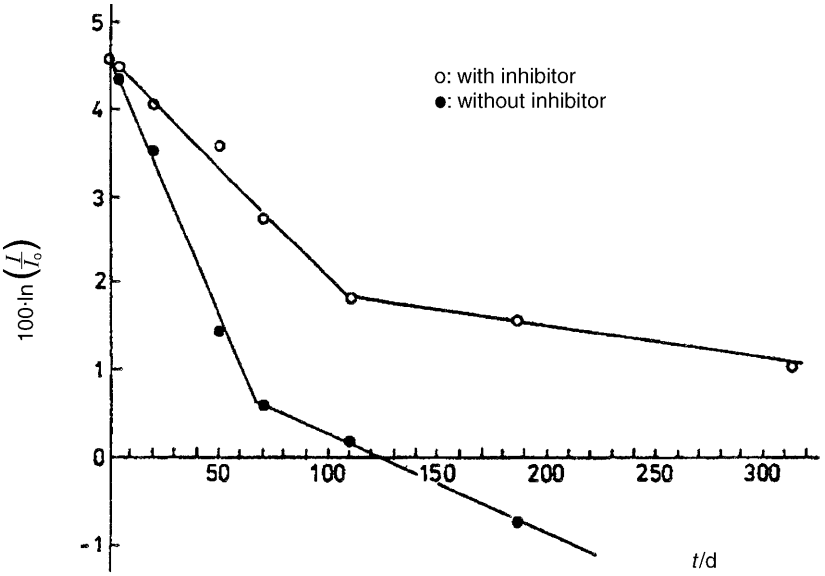

Fig. 3. Experimental data complying with first-order kinetics; ○: system I (with inhibitor), ●: system II (without inhibitor)

The percentage of the inhibitor effect was calculated as follows:

$$IE = \frac{k_B - k_A}{k_B} \cdot 100\ (\%)$$

The rate constants and the inhibitor effects accompanying the corrosion processes were calculated from the experimental data by the least squares method; the results are shown in Table 1.

During the first period (*i.e.* preceding the sharp change in the slope of the kinetic curves), the decrease in the presence of inhibitor (2.37) was lower than that for the second period (2.94). This is believed to result from the formation of a protecting surface layer with prolonged time of sample treatment.

A number of factors such as the mechanical destruction of the corrosion layer, changes in the composition of the corrosion medium which might occur under the

Table 1. Rate constants

Sample type	Period from 0 to 110 (**A**) and 70 (**B**) days of treatment (d^{-1})	Period exceeding 110 (**A**) and 70 (**B**) days of treatment (d^{-1})
A (obtained in the presence of inhibitor)	$k_A = (2.52 \pm 0.02) \cdot 10^{-2}$	$k_A = (3.91 \pm 0.02) \cdot 10^{-3}$
B (obtained in the absence of inhibitor)	$k_B = (5.97 \pm 0.01) \cdot 10^{-2}$	$k_B = (1.15 \pm 0.01) \cdot 10^{-2}$
Rate constants ratio k_B/k_A	2.37	2.94
Inhibitor effect *IE* (%)	62.8	65.6

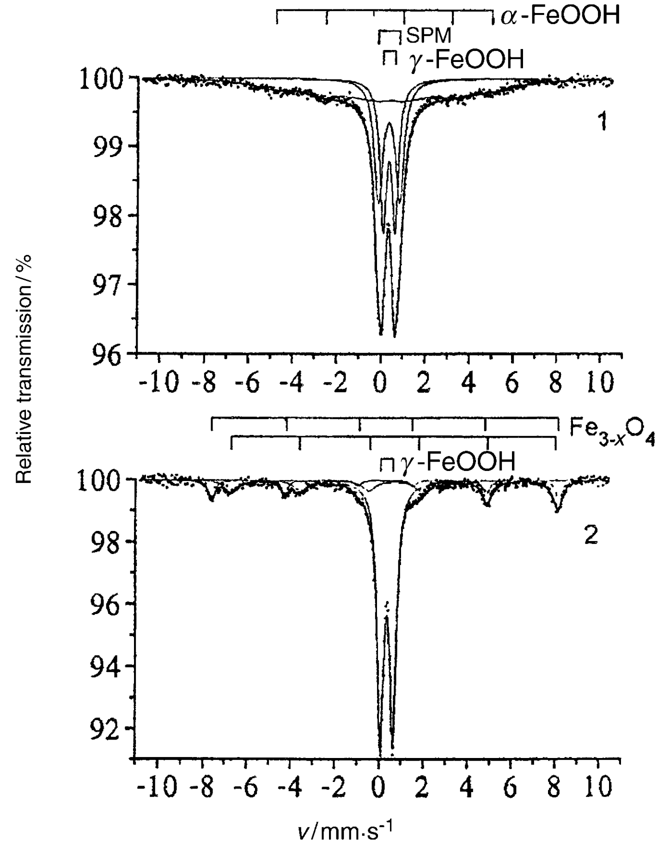

Fig. 4. *Mößbauer* spectra of corrosion products dispersed in the aqueous medium obtained after 313 days of treatment; 1: system I, 2: system II

static (batch) experimental conditions, changes in the mechanism of the corrosion due to internal phase transformations in the corrosion layer, *etc.* are likely to influence the kinetics of the corrosion processes. Mechanical separation of particles from the corrosion layer was proved by *Mößbauer* spectroscopy of samples taken by centrifugation of the aqueous medium after 313 days of treatment without affecting the surface of the coupons. Phases indicated on the corresponding bar diagram were identified in accordance with data from previous studies [2, 4] from the *Mößbauer* spectra (Fig. 4). The aqueous medium from the system with the inhibitor contained particles of α-FeOOH (42.5%), γ-FeOOH (25.5%), and the superparamagnetic component SPM (30%). On the other hand, the aqueous medium without inhibitor contained Fe_3O_4 (30%) and γ-FeOOH (70%). The percentage of the components was determined by evaluation of the corresponding areas of the partial spectra. The fact that the metal coupon from the samples of the series **B** was completely destroyed after 220–230 days of treatment explained the presence of Fe_3O_4 in the aqueous medium. On the other hand, no Fe_3O_4 was found in the aqueous medium containing the inhibitor; however, Fe_3O_4 was detected on the coupons of sample **A** by observation of the corresponding X-ray scans (Fig. 1). This product is supposed to remain tightly bonded to the non-completely destroyed metal surface of the coupon. The so called SPM component in sample **A** might be due to the presence of Fe(III) hydroxides and/or finely dispersed oxides, but the presence of inhibitor should also be taken into consideration. The inhibitor might affect the corrosion processes in two principal modes: first, influencing the mechanism of the corrosion and the transformation of the corresponding products, directing the latter towards the predominant formation of phases detected by evaluating spectrum **A**; second, by the formation of compounds between the inhibitor and the iron oxyhydroxides.

Conclusions

On the basis of X-ray diffraction studies it is found that the principal corrosion products and deposits on Standard Carbon Steel coupons in contact with industrial water from circulation cooling systems in the presence as well as in the absence of an inhibitor consist initially of $CaCO_3$ and $Fe_2(OH)_2CO_3$. At later stages of treatment with the aggressive medium, products such as γ-FeOOH, Fe_3O_4, and α-FeOOH are formed. The processes take place by a similar mechanism; the presence of the inhibitor retards the corrosion.

Based on the relative intensities of the X-ray patterns for the coupons, the corrosion processes are found to comply with first-order kinetics. After a certain time of contact with the corrosion medium, the reaction rate changes, probably, due to the formation of a surface layer consisting of corrosion products. The corresponding rate constants are also calculated. The presence of inhibitor decreases the corrosion rate by a factor of 2.3 for the first stage of the process; later on, the corrosion takes place almost 3 times slower than the non-inhibited process.

The results obtained as well as the adopted approach for the evaluation of corrosion can be useful for future studies of the corrosion resistance of materials tested under both laboratory and industrial conditions.

Experimental

The laboratory experiments were carried out with water from two industrial circulation cooling systems at the Chimko company (Vratsa, Bulgaria). The basic data concerning the characteristics of water from these systems do not significantly differ from those published previously [4]. Several chemical parameters of the circulated cooling water from the first and the second system were determined and are presented in Table 2.

The first system is known to operate in the presence of the corrosion inhibitor Betz Dearborn-AEG 3189 (a water-soluble product based on alkylepoxycarboxylate); the second system operates in the absence of inhibitor.

The corresponding samples (called coupons) were made of carbon steel of a composition according to the Russian State Standards (RSS) or the Bulgarian State Standards (BSS): C: 0.14–0.22%, Si: 0.12–0.30%, Mn: 0.40–0.65%, P: $< 0.04\%$, S: $< 0.05\%$, dimensions: $60 \times 10 \times 1$ mm. The coupons were placed into vessels of 5 dm^3 capacity and were kept there for 313 days. At certain periods of time, the samples were removed, X-ray patterns were recorded, and the coupons were immersed in the corrosion medium again. To avoid changes in the composition of the corrosion products caused by air oxidation, the same procedures as published previously were employed [4]. The X-ray diffractograms were recorded on a TUR-M62 instrument equipped with a cobalt anode. The profile of the X-ray patterns was analyzed and decoded. After 313 days of treatment, the samples were analyzed by *Mößbauer* spectroscopy according to a procedure described elsewhere [4].

Table 2. Characteristics of cooling water in systems I and II

	Standard	Circulating cooling water	
		System I	System II
pH	7–8.5	8.5	7.9
Electroconductivity (μs/cm)	<1300	882	802
Total hardness (mmol/dm^3)	<8.00	5.96	6.30
Alkalinity (mmol/dm^3)	>1.2	1.75	1.32
Nitrates (mg/dm^3)	<300	80	166
Ammonium ions (mg/dm^3)	<1.0	0.21	0.51
Total iron content (mg/dm^3)	<1.0	0.62	0.09
Sulfates (mg/dm^3)	<350	203	133
Salt concentration coefficient	none	2.26	1.20

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