

# Corrosive protection of metal materials in cooling water

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## Abstract

The work deals with the study on the influence of the inhibitor based on phosphonates (S-fp) on corrosion protection of metal materials in cooling water. The specimens, in a form of corrosive coupons, have been placed in an open circulating system of the cooling water for one month. The protective effect of S-fp inhibitor is based on production of insoluble salts with  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  ions present in the cooling water and on forming a protection layer on the surface of exposed metal coupons. The corrosion rate in cooling water with and without inhibitor was determined by measuring of weight change of exposed coupons. The analysis of samples surface was carried out, too. After one month exposure, the coupons were removed from the corrosion slings of the cooling system. The highest inhibitor efficiency was observed on coupons from brass. The addition of inhibitor to cooling water increases corrosion resistance of metal materials by formation a high quality protective layer on their surface.

## Keywords

Corrosion, Inhibitor, Cooling Water System, Corrosion Coupons

## 1. Introduction

Cooling water systems (open or closed) are parts of industrial operations, in which the cooling water must be permanently treated and its required quality observed and controlled [1 - 3]. Functionality and service life of the cooling system equipment is ensured by selecting a suitable material and water of required quality. The practice shows that this is not always sufficient [4].

The cooling systems contain several types of metals including carbon steel, stainless steel, galvanized steel, mild steel, copper alloys. This material can offer 20 years or more life expectancy when maintained properly [5].

Corrosion resistance of metals in open cooling systems has an important economic impact. Several problems of cooling water systems are corrosion scale formation and fouling by micro-organisms. Protection against corrosive degradation of metals is based on both the literary sources and laboratory analysis which result in effective practical applications [4 - 6].

Degradation of metal materials which are part of the open cooling system is caused mostly by oxygen dissolved in water at concentrations higher than 30  $\mu\text{g/l}$ . This results in a local corrosion attack on metal surface in the form of concave porous membrane of corrosion products above anodic site which can grow into a tubercle form [7]. The magnitude of the corrosion attack on the internal surface of pipes suffering from oxygen corrosion per unit time can be expressed as weight loss  $\Delta m$  [g/year] [8, 9].

One addition of the ways of decelerating the corrosion process is addition of inhibitors into the flowing cooling water. The inhibitory substance, the so-called inhibitor, forms an insoluble layer on the metal surface protecting the metal against aggressive environment [10, 11].

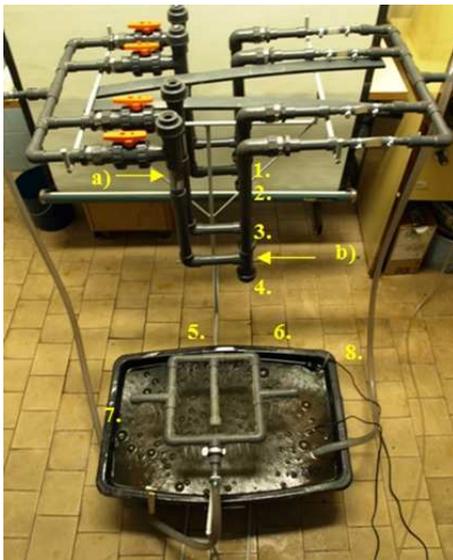
When selecting a suitable regimen of chemical water treatment, one should consider the type and character of operation, quality of additional water and operation conditions. The current trends in chemical treatment of cooling water are mostly oriented on improvement of the recommended chemical regimen. This involves particularly securing of more effective checking up of the specified

parameters of the treated water and the cooling system as a whole (automation, more effective monitoring, rapid response to changing conditions and similar) [12].

The present work aims to study precipitation inhibitor effectiveness to improve corrosion resistance of the materials commonly used for construction of cooling water system.

## 2. Experimental Materials and Methods

Determination of corrosion rate of selected materials during their exposure in an open cooling system, presented in Fig. 1, was carried out for one month. The examined samples presented in Fig. 2, were in the form of corrosion coupons: carbon steel (C-steel); zinc-coated steel (Zn-steel); copper (Cu); and brass (Cu-Zn). In the pipe cooling system, the cooling water of volume 2.5 l circulated at the rate of 1m/s. The total volume of the tank holding the test circulation system was 90 l.



**Fig 1.** Open circulation cooling system: 1.- 4. Corrosion slings; 5. Water jets; 6. Water heater; 7. Cooling water reservoir; 8. Water pump; a) b) Location of corrosion coupons.



**Fig 2.** Corrosions coupons: a) C-steel; b) Zn-steel; c) Cu; d) Cu-Zn.

Dimensions of corrosion standard coupons from C-steel, Zn-steel and Cu, placed in corrosion slings of the cooling system marked 1-3 presented in Fig. 1, were 72×10×1.5 mm. The standard brass coupons Cu-Zn were placed in corrosion sling 4 of the cooling system as presented in Fig. 1. Their dimensions were 49.7×18.6×1.1 mm. Before introducing them into the cooling system the corrosion coupons were degreased with ethyl alcohol, dried and weighed at ± 0.00001 g accuracy. Two samples of each material were used for our experiment. As it is shown the first and second one were placed in the upper (location a) and the lower part (location b) of the cooling system, respectively. When starting up with the coupon exposure, we added 5 ml of the S-fp inhibitor based on phosphonates into flowing water in the described system. The chemical composition of the S-fp inhibitor is shown in Table 1 [13]. Throughout the experimental period the additional water was added into the cooling tank. Chemical composition of additional as well as water circulating in the system corresponded to drinking water.

**Table 1.** Precipitation inhibitor added to the cooling water system [13].

Inhibitor type	Composition
S-fp	phosphonate + (polymer, tolyltriazol, PBTC*, zinc, orthophosphate)

\* PBTC – phosphonobutanetricarbonic acid

The protective effect of S-fp inhibitor is based on production of insoluble salts with  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  ions present in the cooling water and on forming a protection layer on the surface [13].

The corrosion rate of coupons in the cooling water environment containing S-fp inhibitor was determined by an indirect method, namely by determination of weight change  $\Delta m$  according to the formula (1):

$$V_{CORR} = \frac{\Delta m}{S \cdot t} \quad (1)$$

where  $V_{CORR}$  is corrosion rate [ $\text{mg}/\text{m}^2/\text{day}$ ],  $\Delta m$  is weight change [ $\text{g}/\text{m}$ ],  $S$  is coupon surface [ $\text{m}^2$ ] and  $t$  is exposure time [ $\text{day}$ ].

## 3. Results and Discussion

### 3.1. Corrosion Coupons Surface Analysis

After one month exposure, the coupons were removed from the corrosion slings of the cooling system, Fig. 3, and corrosion products were removed from their surface by chemical solution (15% HCl + 0.5% IBIT 2S). For final cleaning we used a nylon brush. Then the coupons were rinsed with water and ethyl alcohol, dried and weighed at ± 0.00001 g accuracy. The surface of selected types of coupons before and after surface cleaning is shown in Fig. 4 and Fig. 5, respectively.

Fig. 5 shows that the surface of coupons from Zn-steel, Cu

and Cu-Zn did not change considerably after removal of corrosion products. On the contrary, visible changes were observed on the surface of C-steel (arrow).



Fig 3. Detail of corrosion slings of the cooling system.



Fig 4. Surface of corrosion coupons: a) C-steel; b) Zn-steel; c) Cu; d) Cu-Zn with corrosion products after exposure in the cooling system water.



Fig 5. Surface of corrosion coupons: a) C-steel; b) Zn-steel; c) Cu; d) Cu-Zn after removing corrosion products.

### 3.2. Corrosion Rate Determination of Corrosion Coupons

The measured and calculated [formula (1)] corrosion rates are presented in Table 2 and graphically illustrated in Fig. 6.

Table 2. Weight losses and corrosion rates of materials after one month exposure to cooling water with inhibitor S-fp.

Material	$\Delta m$ [g.m <sup>-2</sup> ]	$V_{\text{corr}}$ [mg.m <sup>-2</sup> .day <sup>-1</sup> ]
C-steel	0.08126	15.18
C-steel	0.06601	12.33
Zn-steel	0.03151	6.08
Zn-steel	0.02002	3.86
Cu	0.00219	0.42
Cu	0.00257	0.50
Cu-Zn	0.0084	0.16
Cu-Zn	0.00054	0.10

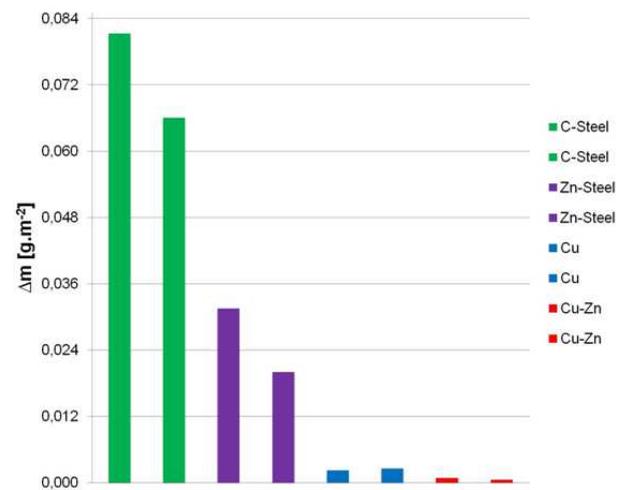


Fig 6. Corrosion losses  $\Delta m$  of corrosion coupons after one month exposure to cooling water with inhibitor S-fp.

The highest efficiency of the S-fp inhibitor was observed on coupons from brass. Their weight change  $\Delta m$  was the lowest (0.00054 g/m<sup>2</sup>). On the other hand, the lowest inhibitor efficiency was observed on coupons from C-steel. The weight loss  $\Delta m$  reached 0.08126 g/m<sup>2</sup>.

The efficiency of this type of inhibitor is based on the production of a thicker protective film consisting of two different layers. The bottom phosphate-iron layer and the upper phosphate-calcium layer [14]. A disadvantage of this type of inhibitors is higher porosity and lower uniformity of the upper layer [15].

Corrosion protection of metal materials depends on both the efficiency of the applied S-fp inhibitor and favourable chemical composition of water. For this reason it was necessary to analyse the additional and circulating water.

### 3.3. Analysis of Water in Open Cooling Circuit System

The principal goal of chemical treatment of water is

effective anti-corrosion protection of metal materials used in the cooling systems, protection from lime stone deposits, dirt, etc. The simplest way of deceleration of corrosion process is based on the favourable action of  $\text{Ca}^{2+}$  ions in the cooling system. This involves presence of cations of an inhibitory substance capable of depositing on metal surfaces in the form of insoluble compounds. In general, application of precipitation types of inhibitors results in production of insoluble compounds on the cathodic sites of metal materials thus decreasing the rates of cathodic oxygen reduction and at the same time the rates of corrosion [15]. The following water parameters such as temperature, pH, m-alkalinity,  $T_H$ , content of Fe and concentration of relevant inhibitor were regularly monitored during one month exposure: [16].

Parameters of additional and circulating cooling water are presented in Tab. 3. Their values were compared with recommended levels [16].

According to the literature [17-19], the corrosion rate is affected by temperature after reaching 60 °C. Below and above this temperature the corrosion rates are not affected. In our case the temperature of the additional and circulating water as well as water of the circulation system was  $22 \pm 3$  °C. Another monitored parameter was the Fe level in the circulating water which complied with the requirements.

**Table 3.** Parameters of additional and circulating water in the cooling system.

Parameter	Value	Recommended values / ranges
T [°C]	21	*
pH	7.81	8.2 – 9.3
m-alkalinity (KNK4.5) [mg.l <sup>-1</sup> ]	85	>150
$T_H$ [mg.l <sup>-1</sup> CaCO <sub>3</sub> ]	170	>250
Fe [mg.l <sup>-1</sup> Fe]	0	<1
Inhibitor S-fp [mg.l <sup>-1</sup> ]	**	50-100

\* recommended value derives from the technical solution of the cooling system: [14]

\*\*changes in concentration are shown in Table 4.

**Table 4.** Parameters of treated cooling water.

Parameter	1st wk	2nd wk	3rd wk	4th wk
pH [-]	7.18	6.98	7.17	8.77
m-alkalinity [mg/l]	175	175	195	250
$T_H$ [mg/l CaCO <sub>3</sub> ]	310	370	480	510
Fe [mg/l Fe]	0.12	0.14	0.34	0.85
inhibitor [mg/l]	88.8	78.8	39.2	62

Results of water analysis, presented in Tab. 4, pointed out the decrease in inhibitor concentration to the level of 39.2 mg/l after 3 weeks of exposure of samples. Therefore there was a need to add 2 ml of inhibitor to the circulating water.

Analysis of water showed that the content of salts in water at concurrent action of the used inhibitor ensures surface protection of selected metal materials except for C-steel.

## 4. Conclusion

Presence of inhibitors and favourable chemical composition of water should ensure corrosion degradation of metal materials in cooling systems. Results of our experiments allowed us to state the following:

After one month exposure of metal materials to the conditions in the cooling system with inhibitor added corrosion products deposited on the surface samples. The highest efficiency of inhibitor based on phosphonates + polymers was observed on the brass samples. Weight changes  $\Delta m$  after one month corrosion test amounted to 0.00054 g/m<sup>2</sup>.

The lowest efficiency of the selected inhibitor was observed on the steel samples that showed the highest weight changes  $\Delta m$ , reaching 0.08126 g/m<sup>2</sup>.

The additional and cooling water had lower content of salts compared to the recommended values with respect to m-alkalinity and total hardness, which could ensure a high quality protective layer on the surface of metals consisting of insoluble calcium and zinc salts.

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