

Effect of Acetic Acid on Mass Transfer of Copper Corrosion Products in Fossil Power Plant Cycle

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One of the basic reasons for equipment failures at fossil power plants is presence of corrosive impurities in water and steam. Presently copper-based alloys are widely used at fossil power plants for manufacture of condensers and low-pressure heaters. Brass corrosion products (copper and zinc oxides) go to water. This intensifies corrosion of carbon steel. Corrosion of copper-based alloys is influenced by different factors: temperature, oxygen concentration, chloride, sulfate, organics etc. Recently a lot of attention in utility industry has been attributed to the effect of organic impurities (acetic, formic, and lactic acids, in particular) on corrosion of construction materials. Of abovementioned acids, concentration of acetic acid in the power plant cycle is significantly higher. Therefore, it is important to study the effect of acetic acid on brass corrosion rate and release of copper corrosion products from metal surface. This paper presents results of experimental study aimed to investigate effect of acetic acid on contamination of water with corrosion products of copper-based alloys at two chemistries – all-volatile (AVT) and “no-addition” (NA) at temperatures up to 100 °C. It was found that at the studied chemistries the corrosion rate of brass was higher with increase in concentration of acetic acid up to 300 ppb. Release of copper corrosion products from metal surface also increased with acetic acid concentration in water. It was shown that use of surface-active substance octadecylamine (ODA) with NA chemistry significantly decreases the corrosion rate of copper-based alloys.

1. Introduction

At the present copper-based alloys are widely used at fossil power plants for manufacture of condensers and low-pressure heaters. These alloys have higher thermal conductivity as compared to steel that reduces size of heat transfer surface. In addition, copper-based alloys (e.g. brass) are more technologically effective than steel [1].

Corrosion failures of brass condenser tubes are mainly in a form of dezincing and corrosion cracking [2]. Pattern of corrosion processes largely depends on composition and properties of working fluid [3]. For example, brass cracking is found predominantly during simultaneous presence in steam of oxygen (typical for vacuum systems) and ammonia. As a result, tube metal becomes brittle and easily fractures. Brass corrosion products (copper and zinc oxides) go to water and intensify carbon steel corrosion [4]. Among the factors that exert an influence on the brass corrosion rate are the following ones:

concentration in water of carbon dioxide, oxidants (oxygen, hydrogen peroxide), reducing agents (hydroxylamine, hydrazine), chloride, fluoride, and hydrogen. For example, carbon dioxide intensifies corrosion processes (carbon dioxide corrosion); oxygen also increases corrosion of copper-based alloys, especially in the presence of ammonia [5].

It is known that copper corrosion rate ambiguously depends on oxygen concentration (Fig. 1): in the oxygen concentration range in water of 10-300 ppb the corrosion rate increases, further increase in oxygen level up to 1000 ppb results in reduction of the corrosion rate. Such a pattern is explained by different composition of oxides formed on copper surface: at oxygen concentration >300 ppb the oxygen film consists of protective CuO [6].

Oxygen also exerts an influence on release of copper corrosion products from metal surface in

both pure water and water with different impurities. It was found that feed of oxygen into water with dissolved carbon dioxide at temperature of 60 °C resulted in ca. 10 times increase in release of copper corrosion products as compared to the case when there was no carbon dioxide in water (Fig. 2).

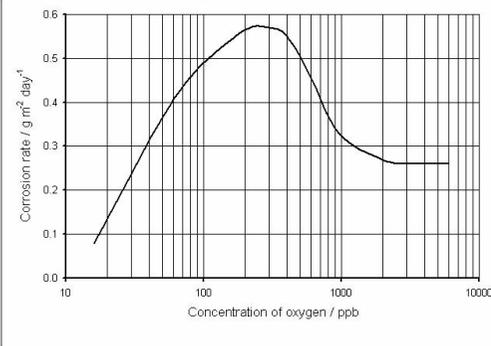


Fig. 1. Copper corrosion rate vs. oxygen level in water (pH=7.0, $sc=0.06-0.11 \mu\text{S cm}^{-1}$, $t=40^\circ\text{C}$).

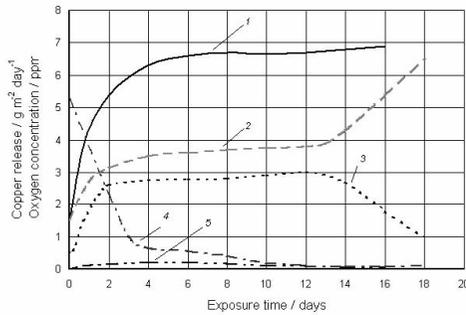


Fig. 2. Behavior of copper corrosion products in water with oxygen and carbon dioxide at temperature of 40 °C.

1 – total release of copper corrosion products; 2 – concentration of copper corrosion products on metal surface; 3 – content of copper corrosion products in solution; 4 – concentration of oxygen; 5 – content of copper corrosion products in deposits

Copper corrosion depends not only on composition of impurities in water, but also on its temperature. Maximum corrosion rate at different flow velocities of water after Na-column was found to be at temperature of about 80 °C (Fig. 3) [6]. It was also found that flow velocity of water being in contact with copper also exerts an effect on corrosion. Increase in flow velocity from 0.5 to 4.0 m/s at temperature of 10-27 °C resulted in ca.

6 times increase in copper corrosion rate. In the temperature range of 10-43 °C the effect of flow velocity on corrosion rate was insignificant (Fig. 3).

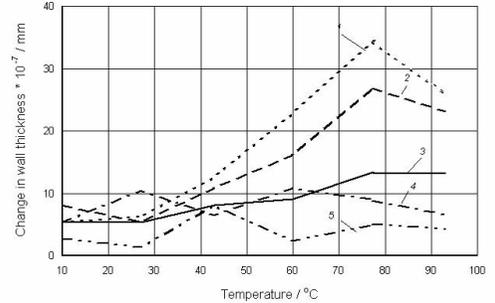


Fig. 3. Effect of temperature on change in thickness of copper specimen in water after Na-column.

Flow velocities: 1 – 3.2 m s⁻¹; 2 – 2.0 m s⁻¹; 3 – 1.0 m s⁻¹; 4 – 0.6 m s⁻¹; 5 – 0.4 m s⁻¹.

Thus, available literature data show that copper corrosion rate depends on many factors; water purity is one of them.

Recently a lot of attention in utility industry has been attributed to the effect of organic impurities on corrosion of construction materials. Negative impact of organic acids (acetic and formic acids, in particular) on corrosion of water-steam cycle at power plants is mentioned [7]. Elevated levels of these acids in the cycle could result in intensification of corrosion processes in condensers, turbines, and other power plant equipment. For example, presence of these compounds in condensing steam at Kendal Power Plant (RSA) resulted in condenser tube failures [8]. There is a limited amount of data on the effect of organic acids on brass corrosion rate. Therefore, the basic aim of this work was to study the effect of acetic acid on corrosion of brass at two different chemistries and temperatures up to 100 °C. This temperature range from 25 to 100 °C is typical for operation of condenser and LP heaters equipped with copper-based tubes.

2. Test Rig and Procedures

A test rig was assembled to perform these experiments. It includes: cell loaded with L65 (65% Cu and 35% Zn) brass specimens, system

for preparation of demineralized and deaerated water, and thermostat. The measures were taken to prevent ingress of oxygen into the cell during its filling with water. The oxygen level in water being in contact with specimens did not exceed 10 ppb.

The tests were performed in static conditions at temperatures up to 100 °C and two chemistries: AVT (pH = 9.0±0.1) and NA (pH = 7.0±0.1). The concentration of acetic acid varied from 0 to 300 ppb. Also, the effect of ODA on the brass corrosion rate with NA and different acetic acid levels at 25 °C was studied. Needed ammonia or acetic acid concentrations were maintained by injection of these chemicals into the cell.

Upon a certain period of time the specimens were removed from the cell and weighed. The corrosion rate W_{corr} , g m⁻² day⁻¹, was calculated with the following equation:

$$W_{\text{corr}} = \frac{\Delta m}{S \cdot \tau}, \quad (1)$$

where Δm is the difference in specimen's weight before and after the test, g; S is the area of the specimen, m²; τ is the time of specimen exposure in the test solution, days.

During the tests portion of copper corrosion products was released from the specimens to the test solution. Determination of copper concentration in the solution provided estimation of copper release rate from the brass surface. The release rate W_r , g m⁻² day⁻¹, was determined with the following equation:

$$W_r = \frac{C_{\text{Cu}} \cdot V}{S \cdot \tau} \cdot 10^{-5}, \quad (2)$$

where C_{Cu} is the copper concentration in the test solution, ppb; V is the cell volume, m³; S is the area of the specimen, m²; τ is the time of specimen exposure in the test solution, days.

3. Results and Discussion

The test data indicate that the brass corrosion rate depends on chemistry: at all studied temperatures the brass corrosion rate was higher with AVT as compared to NA: in both cases acetic acid was not added into test solution (Table 1).

The release of copper corrosion products was also higher at AVT over the studied temperature range (Table 2).

Presence of acetic acid in the test solution resulted in increased brass corrosion rates with both AVT and NA (Table 1, Figs 4 and 5). An increase in acetic acid level from 0 to 300 ppb and temperature of 25 °C resulted in an increase in the brass corrosion rate from 0.129 to 0.396 g m⁻² day⁻¹ with NA chemistry and from 0.135 to 0.277 g m⁻² day⁻¹ with AVT chemistry. An increase in temperature prompted higher brass corrosion rates for all studied concentrations of acetic acid (Figs 4 and 5).

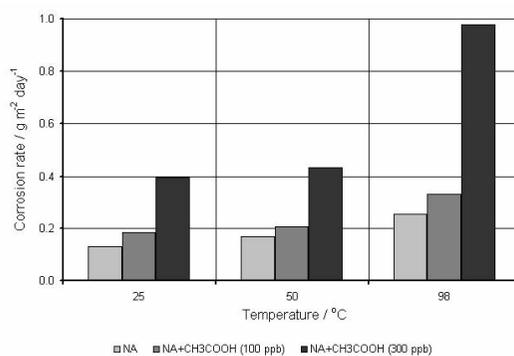


Fig. 4. Brass corrosion rate at NA chemistry and different temperatures (time of exposure 100 h).

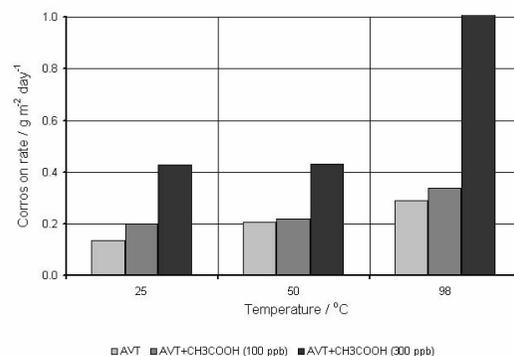


Fig. 5. Brass corrosion rate at AVT chemistry and different temperatures (time of exposure 100 h).

The data produced indicate that higher levels of acetic acid increased the release rate of copper corrosion products from specimen surface at all studied temperatures and chemistries (Table 2,

Figs 6 and 7). The release rate with AVT was much higher than with NA.

The brass corrosion rate also depended on the exposure time of specimens in the test solution: for both studied chemistries it decreased with an increase in the exposure time (Table 3, Fig. 8).

The tests with addition of ODA into the test solution revealed that in this case the brass corrosion rate was reduced. For example, at 100 ppb of acetic acid in the test solution the brass

corrosion rate was almost 3.5 times lower with ODA as compared to the condition without ODA (Table 3, Fig. 8). This is explained by the fact that ODA produces solid protective film on metal surface. This film decreases the brass corrosion rate. Therefore, ODA could be used as corrosion inhibitor of copper-based alloys.

Table 1. Brass corrosion rate at different temperatures and chemistries.

Chemistry	$W_{\text{corr}} / \text{g m}^{-2} \text{ day}^{-1}$		
	$t=25^{\circ} \text{C}$	$t=50^{\circ} \text{C}$	$t=98^{\circ} \text{C}$
NA	0.129	0.169	0.253
NA+CH ₃ COOH (100 ppb)	0.184	0.205	0.331
NA+CH ₃ COOH (300 ppb)	0.396	0.433	0.977
AVT	0.135	0.205	0.289
AVT+CH ₃ COOH (100 ppb)	0.199	0.217	0.336
AVT+CH ₃ COOH (300 ppb)	0.428	0.434	1.026

Table 2. Copper release rate from brass surface at different temperatures and chemistries.

Chemistry	$W_r / \text{g m}^{-2} \text{ day}^{-1}$		
	$t=25^{\circ} \text{C}$	$t=50^{\circ} \text{C}$	$t=98^{\circ} \text{C}$
NA	0.00041	0.00097	0.00180
NA+CH ₃ COOH (100 ppb)	0.00049	0.00126	0.00205
NA+CH ₃ COOH (300 ppb)	0.00151	0.00174	0.00359
AVT	0.00133	0.00232	0.00237
AVT+CH ₃ COOH (100 ppb)	0.00147	0.00252	0.00277
AVT+CH ₃ COOH (300 ppb)	0.00164	0.00412	0.00482

Table 3. Brass corrosion rate with and without ODA at different levels of acetic acid and exposure times.

Exposure time / days	Chemistry	Concentration of CH ₃ COOH / ppb				
		0	50	100	200	300
		$W_{\text{corr}} / \text{g m}^{-2} \text{ day}^{-1}$				
5	NA	0.129	-	0.184	0.314	0.396
16	NA	0.113	-	0.159	0.263	0.308
21	NA	0.060	-	0.125	0.146	0.143
31	NA+ODA	0.030	0.034	0.044	-	0.047

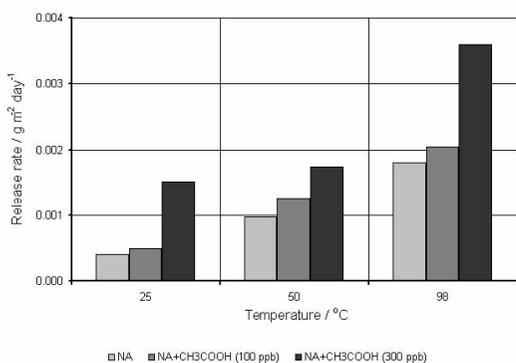


Fig. 6. Copper release rate from brass surface at NA chemistry and different temperatures (time of exposure 100 h).

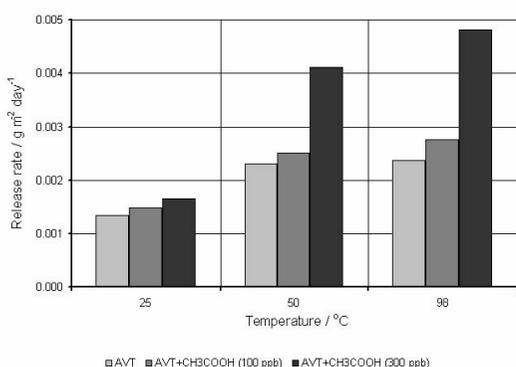


Fig. 7. Copper release rate from brass surface at AVT chemistry and different temperatures (time of exposure 100 h).

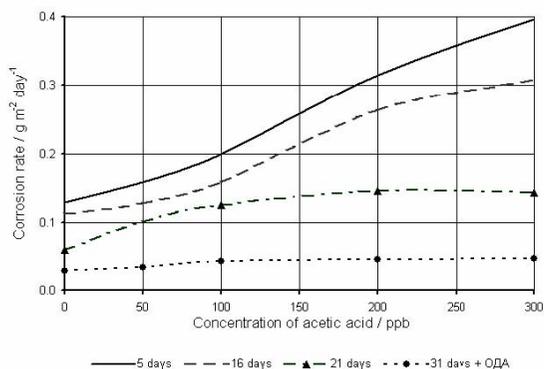


Fig. 8. Brass corrosion rate at different concentrations of acetic acid and time of exposure (t=25 °C)

It is known that corrosion rate of any metal depends on type of surface oxide film. The latter, in turn, depends on composition of impurities in aqueous medium in contact with metal surface. The most complete characterization of existence of different forms of copper can be given by pH-Potential (Pourbaix) Diagrams [9]. It is evident that copper is the most stable in reducing environment, i.e. at negative values of oxidation-reduction potential (ORP) over the wide pH range.

The test results show that at NA chemistry (pH~6.75) ORP was 0.36 V. Under these conditions, according to Pourbaix Diagram [9], copper was found to be predominantly as Cu²⁺ ions, i.e. oxide film on metal surface in this case should dissolve with formation of Cu²⁺ ions in water (Fig. 9). When acetic acid was added into water (pH~5.5), ORP was equal to 0.445 V; in this case copper was also in Cu²⁺ form, i.e. oxide film on metal surface should also dissolve. Elevated copper concentrations in water (copper release rate) and brass corrosion rate with acetic acid present in water may be explained by higher rate of dissolution of oxide film.

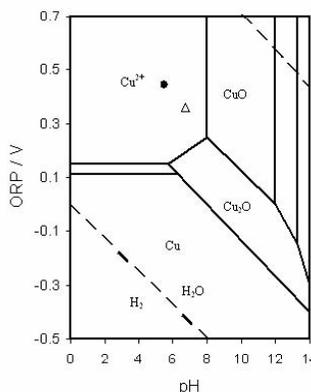


Fig. 9. Pourbaix Diagram for copper compounds at t=25 °C. Δ is the test point for NA chemistry ■ is the test point for NA+CH₃COOH chemistry

At AVT chemistry (pH~9.0) ORP was 0.242 V. In this case, according to Pourbaix Diagram [7], copper was in the region of formation of complex cuprous ions [Cu(NH₃)₂]⁺, i.e. it was also dissolved (Fig.10). When acetic acid was added into water (pH~8.7), ORP became 0.260 V, and the copper was also in the form of complex

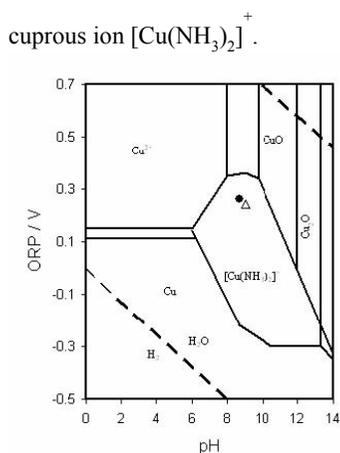


Fig. 10. Pourbaix Diagram for copper compounds in presence of ammonia at $t=25\text{ }^{\circ}\text{C}$

Δ is the test point for AVT chemistry

\blacksquare is the test point for AVT+ CH_3COOH chemistry

Therefore, the study performed shows that at both chemistries (AVT and NA) presence of acetic acid in water increases the brass corrosion rate. Measures should be undertaken aimed at removal of acetic acid from the power plant cycle.

4. Conclusions

- Higher levels of acetic acid increase corrosion rate and release rate of copper from brass surface over studied temperature range at all studied chemistries.
- Brass corrosion rate at NA chemistry is slightly lower than that at AVT; the maximum brass corrosion rate is observed with presence of acetic acid at concentration of 300 ppb.

- Feed of ODA into test solution reduces brass corrosion rate: at NA with 100 ppb of acetic acid the brass corrosion rate is ~ 3.5 times lower than that without ODA feed.
- The test data produced are confirmed by Pourbaix Diagrams for copper compounds.

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