

Control of Corrosion of Copper-Alloy Condenser Tubes by Chemical Treatment

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Received on: 25/4/2011 & Accepted on: 3/11/2011

ABSTRACT

The present work deals with the study of the factors that affect the corrosion resistance and heat transfer resistance of treated condenser tubes by surface filming with ferrous sulfate solution. The reduction of corrosion rate on the filmed surfaces was determined under dynamic conditions using weight loss method. The variation of the corrosion rate at different exposure time and different fluid velocities of the filming solution were studied throughout the laboratory corrosion system. While the effect of surface filming on depression of heat transfer process in term of increasing the heat transfers resistance was studied throughout the laboratory thermal system. The results indicated that the filming solution reduced the corrosion rate of copper alloy to 52.7%, but the heat transfer resistance increased from 12.88 to $18.73 \times 10^{-4} \text{ m}^2 \text{ K/W}$. Moreover, the metallurgical investigation clearly revealed the feature and nature of the film formed on the metal surface.

Keywords: condenser tubes, copper alloys, ferrous sulfate

السيطرة على تآكل أنابيب مكثفات سبيكة النحاس بالمعاملة الكيميائية

الخلاصة

البحث الحالي يتعلق بدراسة العوامل المؤثرة على مقاومة التآكل ومقاومة انتقال الحرارة لأنابيب المكثفات المعاملة بطبقة سطحية من محلول كبريتات الحديدوز . تم تعيين مقدار التناقص في معدل التآكل للسطح المعامل تحت ظروف حركية باستخدام طريقة فقدان الوزن كذلك تمت دراسة التغير في معدل التآكل عند أزمان غمر مختلفة وسرع جريان مختلفة باستخدام منظومة قياس التآكل المختبرية. كما انتاثير الطبقة المتكونة على السطح في تقليل انتقال الحرارة بدلالا لزيادة مقاومة انتقال الحرارة قد تمت دراسته من خلال استخدام المنظومة الحرارية المختبرية. أظهرت النتائج بأن الطبقة المتكونة على السطح تقلل معدل تآكل سبيكة النحاس بنسبة 52.7%، ولكن لوحظ ان تلك الطبقة تزيد مقاومة انتقال الحرارة من 12.88 الى $18.73 \times 10^{-4} \text{ m}^2 \text{ K/W}$. اضافة الى ذلك أشارت الاختبارات الميتالورجية بوضوح الى طبيعة وخصائص الغشاء المتكون على سطح المعدن.

INTRODUCTION

One method of the anticorrosion protection of copper alloys condenser tubes used in thermal power plant and other industries- is the dosing of ferrous sulfate FeSO_4 solution which produce film consisting of ferrous oxide hydroxide (FeO.OH). This film reduced oxygen transport to the metal surface and acts as cathodic inhibitor increasing cathodic polarization [1].

Rapid film formation is achieved if the cooling water shows temperature of $\sim 20^\circ\text{C}$ and pH value of ~ 8.0 . Lower temperature and lower pH slow down considerably the development of protective film [2].

Ferrous sulfate treatment and chlorination treatment should not be carried out simultaneously because chlorine reacts with ferrous sulfate to form ferric sulfate. Since ferrous sulfate is consumed, it is not available to contribute to the development of protective film [3]. The remaining ferric sulfate provides no beneficial effect. The protective film formed by ferrous sulfate dosing has inadequate resistance against the attack by turbulent flow caused around foreign bodies lodged in a tube from coolant water. So the FeSO_4 treatment can be repeated as often as required to renew the production of the protective film [4].

The present study aimed to investigate the parametric conditions and their effect on the treatment by ferrous sulfate on reducing the corrosion of brass condenser tubes – Hartha power plant, relevant to heat transfer process.

EXPERIMENTAL

Sample preparation: A condenser tube segment of 1m length (outer diameter 25.4 mm, thickness 1.25mm) was taken from "Hartha Power station-Basra". These samples were cut by means of electric cutter into 9 pieces each 10 cm length and used for treatment by ferrous sulfate in order to be tested for corrosion rate.

The experimental work includes the following steps:

1) Treatment by ferrous sulfate, 2) Measurements of corrosion rate, 3) Measurements contributed to the heat transfer resistance and 4) Metallurgical examination.

Treatment by ferrous sulfate

The system for the treatment of a brass tube samples by ferrous sulfate solution was shown in Fig. (1). The tubes samples were combined to each other by flexible tubes. The solution of ferrous sulfate was pumped by means of small centrifugal pump $Q=45$ l/min. The recirculation flow velocity was adjusted to produce 1.6m/s, and run for 5 hours each day within a duration extended from 1st – 12th, January, 2009. The experiment was conducted at temperature of $23\pm 2^\circ\text{C}$. Three runs were carried out 4 days each [5], the solution after the first run was rejected. Freshly prepared Fe^{2+} solution for the second and third runs were used. Then the same procedure was repeated on a separate tube sample of 1m length.

Measurements of the corrosion rate

The corrosion rates were determined by weight loss method under different parametric environmental conditions of the exposure time and fluid velocity using the following equation:

$$CR = K_w / TAD \quad \dots\dots(1)$$

Where CR is the corrosion rate(mpy),K is constant(3.45x106) ,w is the weight loss(g),T is the time of exposure ,A is the surface area(cm2) and D is the density of brass(g/cm3)[ASTM G10-70].The corrosion inhibition or protection efficiency conferred by ferrous can be calculated from the following formula:

$$\%Efficiency = [1 - CR_i / CR_o] \quad \dots\dots(2)$$

Where CR_o is the corrosion rate of untreated sample and CR_i is the corrosion rate of treated sample at specified time and velocity.

Effect of exposure time

The corrosion rates of the samples were tested in filtered water as a function of exposure time. The recirculation water velocity was adjusted to 1.6m/s, after test period which extended for 7days[5]; the samples set were taken out for cleaning from adherent depositing emery paper and cotton cloth. The weight loss was used to calculate the corrosion rate according to the above equation. Then the experiment was repeated for another 7 days period. All the tests were conducted at temperature of 25±2 °C.

Effect of fluid velocity

The corrosion rate was determined at four different velocities (0.8, 1.2, 1.6 & 1.8) m/s. The fluid velocity was calculated as follow:

$$Q_t = V_m / t \quad \dots\dots (3)$$

Where: Q_t is the volumetric flow rate (m³/s),V_m volume of vessel (m³) and t is the time(s).

$$u = Q_t / a \quad \dots\dots (4)$$

Where u is velocity (m/s) and a is cross section area (m²). The flow rate was changed by means of the controlled valve to verify the specified velocity required in each case.

Each test velocity was carried out for 7days in rate of (5hrs) in day; the corrosion rate was calculated from weight loss resulted data. The experiment was conducted at temperature of 27±2°C.

Measurements relevant to the heat transfer resistance

A heat transfer resistance (HTR) test rig assembled in the "Metallurgical Engineering Laboratory" shown in Fig. (2) and consisted from the following parts:

Heating Element: A coil resistance placed inside an electric insulator and wound on exterior surface of each test tube at a distance of 12 cm, three types of coil resistance were used to produce different energies. The heating element was isolated from outside, so that when energized practically all of heat (power) generated was transferred through the tube wall and into a stream of flowing water recirculated through the tube from a reservoir.

Thermocouples: Three thermocouples were embedded under heating element for measuring the temperature of the heated surface (Ts), and other two thermocouples were placed in the inlet and outlet of the test tube to measure the bulk water temperature (Tb).

Cooling System: It is a closed loop; contains one cooling water reservoir, two small centrifugal pumps and cooler device. The cooling water flow to the test section was adjusted manually using a bypass return to the associated reservoir. After water was passing through the test section, the water flows through the cooler, this cooler was used to maintain desired cooling water temperature, before return to the reservoir.

The requirements of the thermal procedure can be explained as follows:

Surface preparation : all the tested tubes sections were abraded, using silicon carbide paper grad 400µ to remove the tarnish films to attain smooth and clean surface finish. This was accomplished to assure that the HTR measurement would related to the inner diameter surfaces, and not be confounded by tarnish films present on the outer diameter.

Temperature Measurements: The temperatures of the heated surface (Ts) were determined by taking the average of temperature readings of three thermocouples embedded under heating element. The bulk water temperature (Tb) was determined by taking the average temperature readings of inlet and outlet water temperature.

Applied Heat Flux: A heat flux of 880W, 726 W and 628 W, was applied by the coil resistance of heating element, through the external surface of the tube under test. Digital multimeter recorder was used to measure coil resistance with accuracy of (±0.001mΩ), and digital clamp meter used to measure the current with accuracy of (±0.001 A). The power input to heating element equal to V*I or I²*R.

Adjusted Velocity: The water was recirculated through the tested tube section at a known velocity from the reservoir.

The heat transfer resistance HTR for each run was calculated from the following equation [4]:

$$HTR = A (T_s - T_b) / Q \dots\dots(5)$$

HTR: heat transfer resistance m²K/W, A: surface area of heated surface.

Ts: average surface temperature.

Tb: Bulk water temperature.

For each tube, the HTR values were determined from data obtained in separate test run at four different velocities (0.8, 1.2, 1.6 & 1.8) m/s. Each test run took approximately 2 hours duration in order to reach the steady state.

Metallurgical examination

The objective of the present investigation was to examine the nature and characteristic of barrier film formed on the metal surface by the treatment with ferrous sulfate solution, and to gain information for the morphology and appearance of the film formed using optical microscope.

Specimens preparation

The specimens of (1.9x1.5x 0.2)cm were cut from the same tube sample of brass . The specimens were ground to 1200 μ followed by polishing with velvet cloth using alumina powder –water suspension. Another specimens were cleaned only by cotton cloth, then the specimens immersed in prepared solution of 5 mg/l of ferrous sulfate for a periods of 4, 8 & 12 days respectively. Also another set of specimens were immersed in filtered water for the same period at temperature of $25\pm 2^{\circ}\text{C}$ for the sake of comparison.

RESULTS AND DISCUSSION

Corrosion rate measurements

The corrosion rate results observed to be affected by the a) exposure time and b) velocity of solution under dynamic test condition, both at specified experimental temperature.

Effect of exposure time on corrosion rate

The comparison between the corrosion rates values of untreated and treated admiralty brass with ferrous sulfate are shown in Figure (3). The corrosion rates at a test period of 35 days are 2.832 and 1.312 mpy for untreated and treated samples showed increase in corrosion rate as exposure time to recirculation water increased, while the corrosion rate of treated sample showed slight increase from 0.51 to 0.53 mpy within the period of 7 to 14 days of experiment. The surface film of ferrous sulfate acts as barrier which counteract and deaccelerate the corrosion rate [6,7]. Then the corrosion rate was found to be remarkably increased to 1.312 mpy at a test period of 35 days, this may be due to damage of ferrous sulfate film formed on metal surface [8]. The efficiency of ferrous sulfate film in reduction of the corrosion rate as compared with untreated samples was found 52.7% at maximum exposure time of 35 days.

Effect of velocity on corrosion rate

The results of the corrosion rate of untreated and treated brass with ferrous sulfate in filtered water at four different velocities (0.8, 1.2, 1.6 & 1.8) m/s are shown in Figure (4). It can be seen that the corrosion rate of untreated sample was remarkably increased as the water velocity increased, while treated sample showed slight increase in corrosion rate from 0.312- 0.516 mpy with velocity range 0.8-1.6 m/s ,this because that the presence of ferrous sulfate film had a beneficial effect on copper alloy surface, thus improving the alloy resistance to flow induced corrosion [7,9]. But when velocity

increased to 1.8 m/s the corrosion rate accordingly increased to 1.443mpy, where the film of ferrous sulfate seemed to be affected by recirculation velocity i.e. high velocity led to destruction of the protective film [10]. It was found that the efficiency of ferrous sulfate film in reduction the corrosion rate at maximum velocity used was 52.7%.

Heat Transfer Resistance Results

The variation of heat transfer resistance (HTR) with velocity of treated and untreated brass tube samples are shown in Figures (5&6) respectively. The comparison of the HTR results between treated and untreated at various amount of applied heat (880, 726 and 628) W showed that increasing applied heat led to reduction in HTR, the higher applied heat during the experiment of 880W showed minimum HTR when compared with the HTR at applied heat of 726 & 628 W respectively. The results indicated that the HTR at 880W with 1.8m/s are $(12.88 \text{ \& } 16.12) \times 10^{-4} \text{ m}^2 \cdot \text{K/W}$ for untreated and treated samples respectively. The treated tube with ferrous sulfate exhibited minimum HTR when compared to that of untreated tube; the surface film thickness of ferrous sulfate is just of some microns (3μ) indicating that there is no remarkable depression on the heat transfer resistance [2].

Results of Microscopic Examination

The results of the microscopic examination including the following:

Examination of as-received specimens

As- received Specimens in Filtered Water

Figure (7 a) showed the appearance black isolated regions that refer to the oxidation products of metal surface [12]. Specimens immersed in filtered water for a period of 4, 8&12 days are shown in **Fig.(7b,c,d)** indicated that the oxidation profile followed the same profile of as-received specimen, the appearance showed dark brown and green coloration resulted from cupric oxide and carbonate imposed by the effect of dissolved oxygen and dissolved solid in water containing carbon dioxide [11]. Prolonged immersion time of 8, 12 days showed increasing the darkness which can be attributed to further oxidation and corrosion.

As- received Specimens Treated With Ferrous Sulfate Solution

Figures (8 b,c&d) showed the surface feature of specimens immersed in ferrous sulfate for a period of 4, 8&12 days. The predominated coloration was dark brown mixed with black appearance indicating formation of cupric oxide and iron hydroxide $\text{Fe}(\text{OH})_3$ from FeSO_4 . These results showed agreement with observation of Nagata [13] which showed that the treated tubes covered with a light brown film typical of iron hydroxide.

Prolonged immersion time in ferrous sulfate led to a thicker film that was clear from increasing surface shielding with dark brown film.

MICROSCOPIC EXAMINATION OF FRESHLY POLISHED SPECIMENS

Polished Specimens in Filtered Water

Figure (9 a) shows the appearance of freshly bright yellowish polished surface. Polished specimens immersed in filtered water for a period of 4, 8&12 days are shown

in Figure (9b,c,d), the entire surface showed yellowish green color indicate the effect of salts derived from plain water. Prolonged immersion for 8, 12 days, clearly showed increasing of the darkness with red and green coloration resulted from the presence of dissolved oxygen and carbonate salts.

Polished Specimens Treated With Ferrous Sulfate Solution

The polished metal specimens immersed in ferrous sulfate for a period of 4, 8 & 12 days are shown in Figure (10)b,c,d, apparently ferrous sulfate act as etching solution; α brass grains were visible associated with the presence of twinning [12]. Ferric film (brown) shielded the metal microstructure partially, which revealed evidence to ferrous sulfate film formation. Prolonged immersion time of 8 & 12 in ferrous sulfate solution showed film thickening see Figure (10) c,d.

Comparison between as-received and Polished Specimens in Filtered Water

It was observed that the oxidation profile of as-received specimens showed dark brown color resulted from originally black oxidation CuO mixed with red cuprous oxide Cu_2O and green corrosion product of copper carbonate CuCO_3 . While polished specimens showed corrosion of brass with red cuprous oxide Cu_2O and green copper carbonate CuCO_3 . Apparently prolonged immersion time increased the amount of the corrosion product on metal surface.

Comparison between as-received and Polished Specimens in Ferrous Sulfate Solution

The same microstructure profile was observed in each polished and as-received specimens, the only difference was in color darkness. The polished specimen showed red brown color refer to ferric hydroxide formed by ferrous sulfate, while as-received specimen showed dark-brown mixed with black coloration of originally present oxidation products.

The treatment of as-received specimens were more practically accepted, because it represent the actual situation observed in power plant, as the condenser tubes internally treated with ferrous sulfate.

CONCLUSIONS

The following conclusions can be drawn from the present investigation:

1. The presence of ferrous sulfate film had a beneficial effect on brass surface by improving the resistance to flow induced corrosion. It was found that the filming of ferrous sulfate reduced the corrosion rate from 2.721 to 1.443 mpy to confer a protection efficiency of ~52.7%.
2. The heat transfer resistance of treated brass samples with ferrous sulfate increased from 12.88×10^{-4} to $16.12 \times 10^{-4} \text{ m}^2 \cdot \text{K/W}$ (i.e. film resistance of $3 \times 10^{-4} \text{ m}^2 \cdot \text{K/W}$) compared to bare metal sample.

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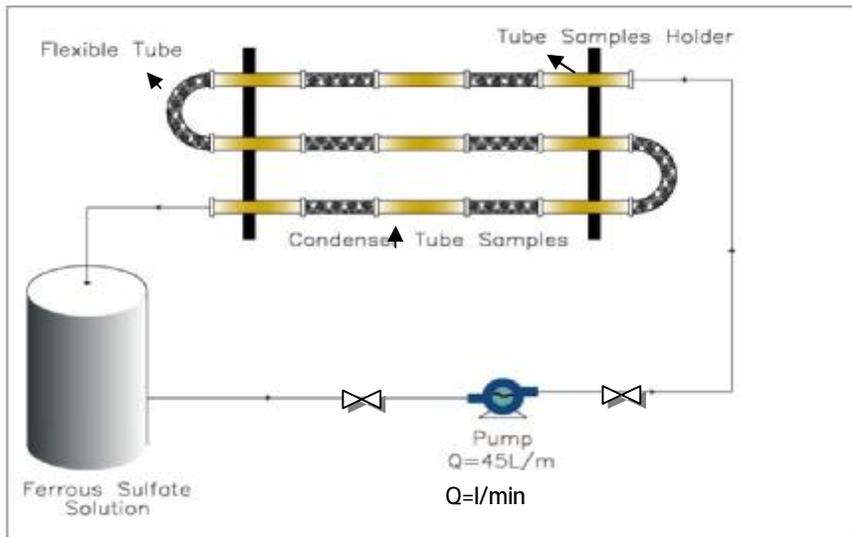


Figure (1) Ferrous sulfate treatment system.

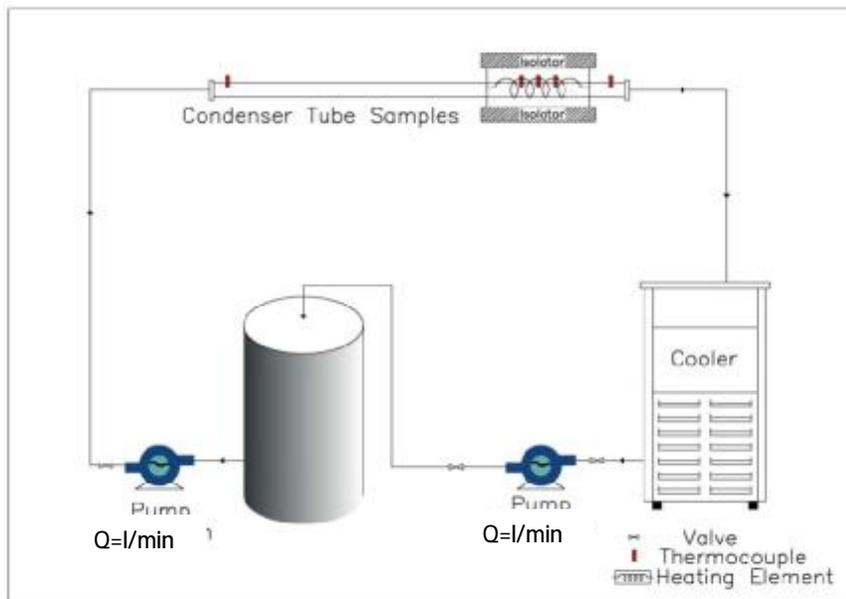


Figure (2) Thermal measurements System.

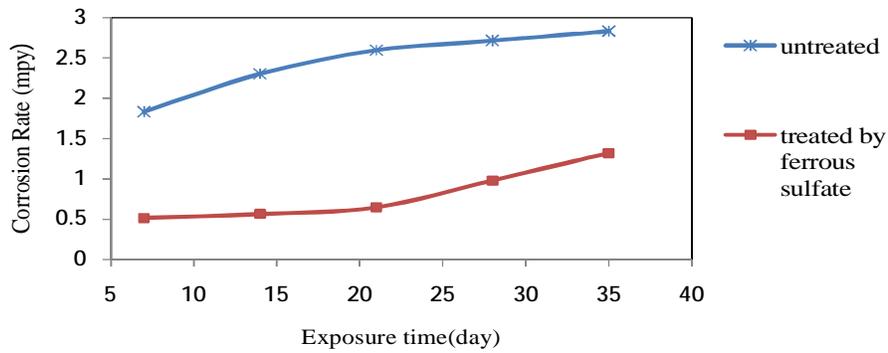


Figure (3) Variation of corrosion rate with time for treated and untreated brass with ferrous sulfate and filtered water (pH 7.6) respectively, velocity 1.6 m/s, at 25°C.

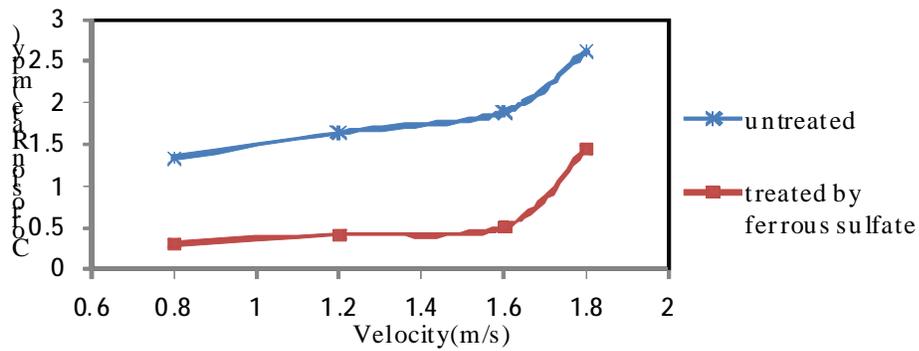


Figure (4) Variation of corrosion rate with velocity of treated and untreated brass with ferrous sulfate and filtered water (pH 7.6) respectively for 7 days, at 27°C.

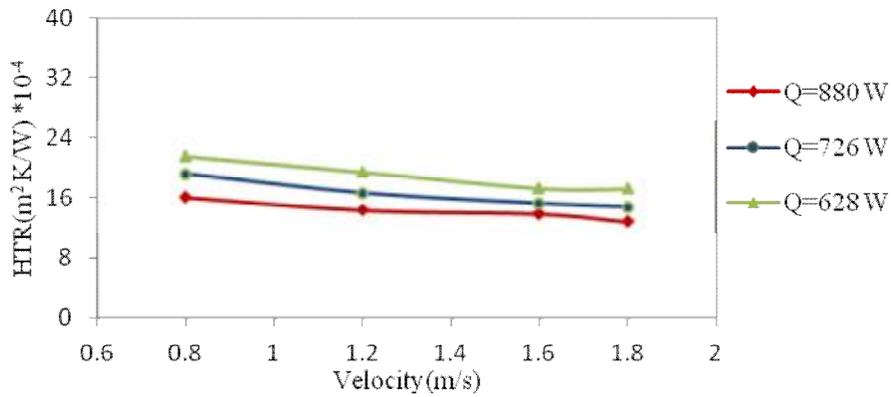


Figure (5) Variation of heat transfer resistance with velocity for untreated brass tubes at different applied heat, at 30°C.

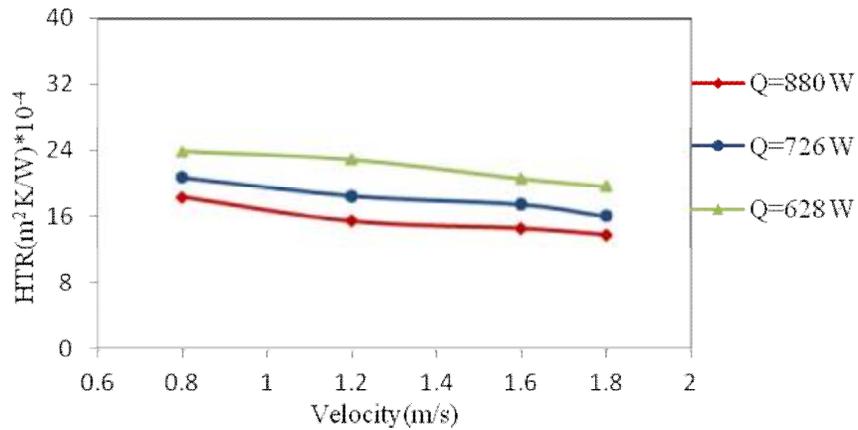
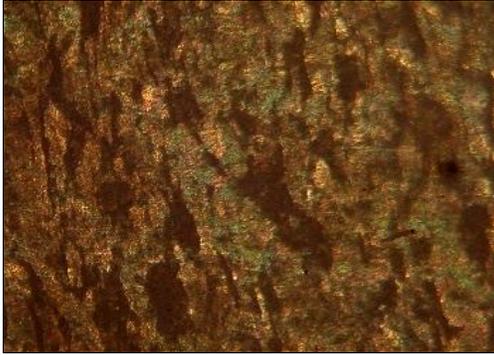


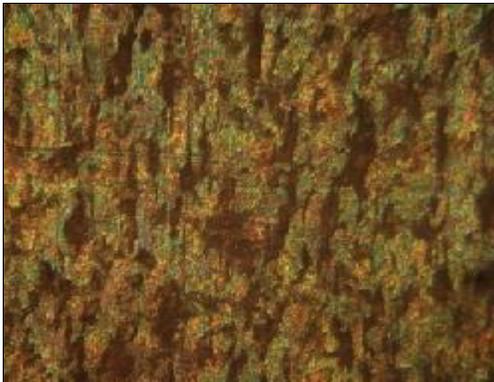
Figure (6) Variation of heat transfer resistance with velocity for treated brass with ferrous sulfate at different applied heat, at 30°C.



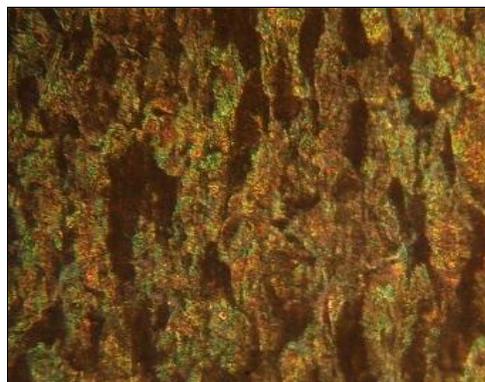
(a) As received specimen



(a) As received specimen

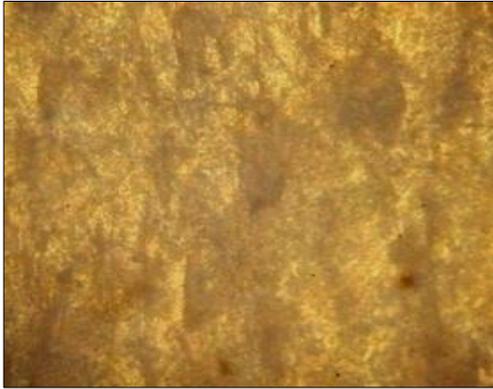


(b) 8 Days immersion

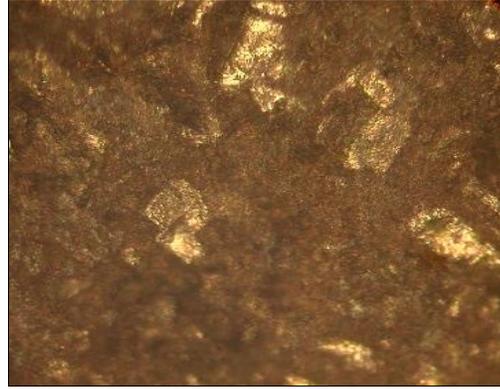


(c) 12Daysimmersion

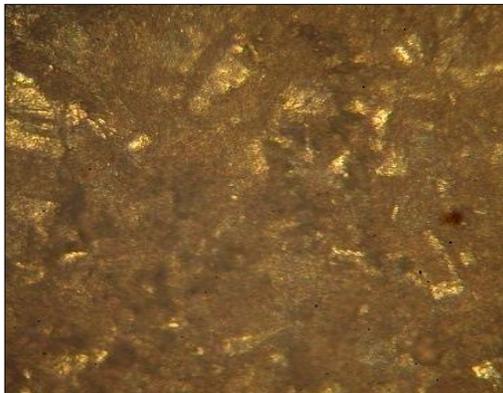
**Figure (7) Surface feature of as-received specimens with and without
Immersion in filtered water, 200X.**



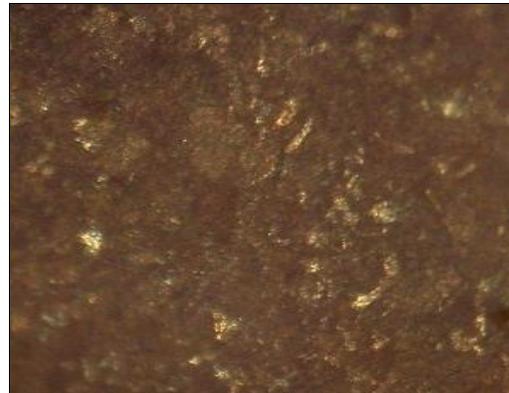
(a) As received specimen



(b) 4 Days immersion



(c) 8 Days immersion



(d) 12 Days immersion

**Figure (8) Surface feature of as-received specimens with
and without immersion in ferrous sulfate solution, 200X.**



(a) Polished specimen



(b) 4 Days immersion

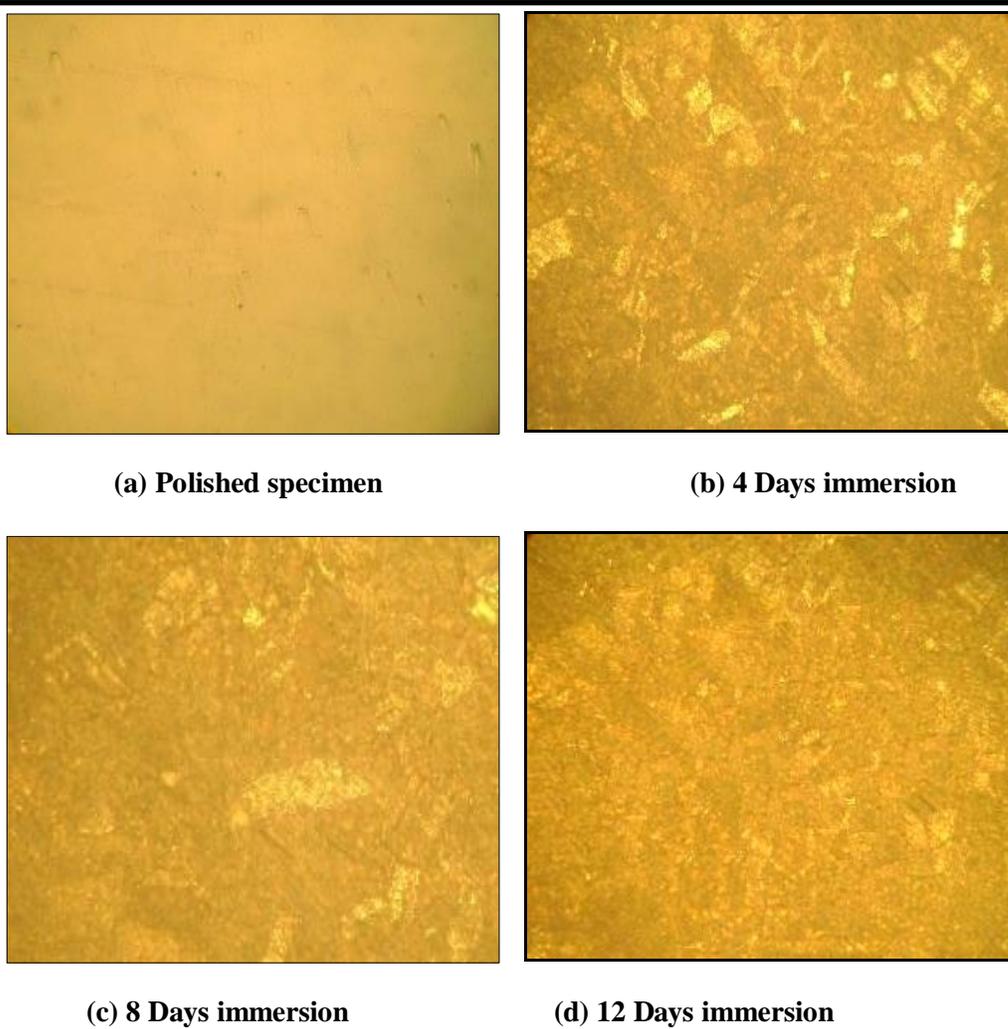


(c) 8 Days immersion



(d) 12 Days immersion

**Figure (9) Surface feature of polished specimens with and
Without immersion in filtered water, 200X.**



**Figure (10) Surface feature of polished specimens with and
Without immersion in ferrous sulfate solution, 200X.**