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The Effect of Immersion Period on the Dezincification Behavior of α-Brass Alloy Waste

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***Abstract* - Dezincification of alpha-brass, which is one of the most prominent cases of selective corrosion, has been investigated by the corrosion -polarization scheme (Tafel) and Atomic Absorption Spectrophotometer (AAS) methods. The dezincification behavior of brass alloy waste (Zn-35.4 %) was studied at different pH (1, 7, and 10) and immersion periods (1, 3, and 10 days). The loss of zinc/copper ratio at the surface of specimens revealed an increase with increasing immersion period, 10 days, was found to be ΔW/g=0.0149, 0.0029, and 0.0015 for a pH=1, 7, and 10 respectively. The corrosion results showed that the corrosion rate was increased to 6.672 mm/y for the dezincification solution with pH 10 compared with 2.11 and 3.866 mm/y for pH (1 and 7) respectively. The concentrations of Cu2+ and Zn2+ ions in solution, produced by the dezincification of brass, were determined by atomic absorption spectrometry (ASS). AAS analysis illustrated a clear improvement in the dezincification yield (Zn 112.6 ppm) for pH1 rather than Zn 5.714 ppm and Zn 1.828 ppm for pH (10 and 7) respectively. The purity of zinc produce was determined by XRF analysis and we can note the highest value in hydrochloric solution with PH1 was 20.9% and 18.28%, 12.4% for pH10 and pH7 respectively.**

Keywords - Atomic Absorption Spectrophotometer, Brass, Corrosion, Dezincification.

INTRODUCTION

Corrosion is chemical or electrochemical reaction with the surrounding environment, resulting in a gradual deterioration, destruction, or in extreme cases structural failure of the metal [1, 2, 3, 4]. Corrosion is highly destructive and occurs in practically every given environment which includes the atmosphere, air and water mixture, industrial atmosphere (gases, alkali, acids, etc.), fresh and salty water, and other organic and inorganic solutions or media [5, 6]. The most prominent case of selective corrosion is the dezincification of copper-zinc alloy systems. Dezincification is one type of selective corrosion which removes zinc from the alloy, leaving behind a porous, copper-rich structure that has little mechanical strength. Copper-zinc alloys containing more than 15% zinc are susceptible to dezincification [7]. Zinc is a highly reactive metal, as seen in its galvanic series ranking. This reactivity stems from the fact that zinc has a very weak atomic bond relative to other metals. Simply, zinc atoms are easily given up to solutions with certain aggressive characteristics. During dezincification, the more active zinc is selectively removed from the brass, leaving behind a weak deposit of the porous, nobler copper-rich metal. Dezincification usually occurs in relatively mild conditions when Contact with slightly acidic or alkaline water and if the flow rates of the circulating liquid were low, Soft low pH and low mineral water combined with oxygen, which forms zinc oxide (uniform attack) at room temperature (uniform attack) Dezincification may be visible to the naked eye, as the characteristically yellow brass turns into pink [8]. Dezincified brass retains the original shape and dimensions of the metal component before corrosion, but the residue is porous and has very little strength [9, 10]. Mild dezincification may simply cause a cosmetic change, namely, De zincified brass retains the original shape and dimensions of the metal component before corrosion, but the residue is porous and has very little strength but severe dezincification can lead to the weakening of brass and even its perforation [11]. There are three actual mechanisms of dezincification but is still not completely agreed upon, In one, the zinc preferentially corrodes and is removed from the alloy, leaving the copper behind. On the other, both the copper and zinc corrode and are removed from the alloy, but the copper ions in the solution plate back onto the surface. The metal should become porous after dezincification but, otherwise, should not change [12, 13]. More recently, a third mechanism has been gaining support [14,15], In this mechanism, the zinc dissolves out of the brass, leaving behind the copper, and then the copper rearranges on the surface of the metal, leading to the formation of copper crystals. This rearrangement is possible because the copper on the surface is attracted by negative ions in the solution. The attraction is not enough to dissolve the copper, but it does weaken the binding of the copper to the surface, allowing the copper to move around more rapidly [16]. Brass is widely used in various industries due to its stability in aggressive environments. The environment in which chloride ions are present is one of these [17, 18], and corrosion processes in these environments are a major problem [19]. In this paper, the dezincification phenomenon of α-Brass alloy waste has been studied in the present experiment by losing weight, corrosion characteristics, x-ray fluorescence (XRF) and Atomic Absorption Spectrophotometry.

EXPERIMENTAL PART

The specimens of scrap material (brass waste) with dimensions of 4cm as width and 8cm as length were employed for dezincification process. Samples were smoothed with a polishing paper composed of silicon carbide with a granular size of 500 microns. The specimens were rolled to a thickness of about l mm. Samples were washed with 96% ethanol using an ultrasound bath for 10 minutes and twice, after which the samples were washed. With distilled water using an ultrasound basin for 10 minutes once. Table (1) explains the chemical analysis of these specimens using PMI-Master Pro OES spectrometer, showed 35.4 % zinc content. It is the precipitation experiment by losing weight by immersing the specimens in three solutions of different concentrations or three basic media with a 3.5% NaCl + NaOH, acidic media 0.1M HCl and neutral solution 3.5% NaCl for varying period (1day, 3 day, 10 day). Weighing the samples before immersion with using a German-made Sartorius sensor with accuracy (±0.0001g), after which corrosion tests were conducted in the different solutions The corrosion characteristics were examined to determine the polarization scheme (Tafel) to determine the annual corrosion rate using a device (PARSTAT 2273, USA) by using solutions 3.5% NaCl + NaOH, acidic media 0.1M HCL and neutral solution 3.5% NaCl (dezincification solution). The concentration of Cu^{2+} and Zn^{2+} in the solutions after the various exposure periods was determined with an atomic absorption spectrometer model phenix986 –Japanese. The pH values were measured with a Meterlab portable pH meter, model pHM201. The purity of zinc deposited was determine with X-ray fluorescence model XEPOS – Type 76004814.

TABLE 1
THE CHEMICAL ANALYSIS OF ALPHA-BRASS

Continent	Percentages %
cu	64
Zn	35
pb	0.08
Sn	0.007
Mn	0.008
Fe	0.04
Ni	0.02
Si	0. 03
Mg	0.0021
Cr	0.01
Al	0.008
Ag	0.01
Be	0.0019
Co	0.154
Cd	0. 11
Zr	0.008
Se	0.02
Ti	0.001
Bi	0.005

RESULT AND DISCUSSION

1. Weight Loss

The weight loss on brass waste specimens immersed in three solutions of different concentrations or three basic media with a 3.5% NaCl + NaOH, acidic media 0.1M HCL, and neutral solution 3.5% NaCl for the varying period (1day, 3 days, 10 days) is shown in Table 2. There is variation in weight loss for three solutions of different concentrations and increases up to 0.0149 with 0.1M HCl, the highest weight loss is noticed in 10day.

TABLE 2
WEIGHT LOSS ON BRASS PANELS IMMERSED AT DIFFERENT PERIOD TIME

Δ W/g	Weight after immersion one day/g	Weight before immersion/g	Sample number	corrosive medium
0.0149	7.5516	7.5665	1	acidic medium /PH1
0.0049	7.1553	7.1602	2	brine medium/PH7
0.0006	7.0351	7.0357	3	basic medium /PH10

Δ W/g	Weight after immersion 3 days/g	Weight before immersion/g	Sample number	corrosive medium
0.0108	7.6219	7.6327	4	acidic medium /PH1
0.0042	7.5934	7.5976	5	brine medium /PH7
0.0038	7.4360	7.4398	6	basic medium /PH10

Δ W/g	Weight after immersion 10 days/g	Weight before immersion/g	Sample number	corrosive medium
0.0149	7.4410	7.4559	7	acidic medium /PH1
0.0029	7.7169	7.7198	8	brine medium /PH7
0.0015	7.6178	7.6193	9	basic medium /PH10

We noticed that the most corrosive medium in which weight was lost is the acidic medium because it contains chlorine ions, which increase the susceptibility to corrosion, and the most medium in which zinc and copper were precipitated in the solution, according to the atomic absorption assay, is also the acidic medium. The weight loss curve is a measure of the electrochemical reaction occurring under the fouling and scale [6].

Figure 1 shows the brass strip control was not immersed and other three strips immersed in 0.1 M hydrochloric acid, were immersed for varying lengths of period 1, 3 10 days. The dezincification occurred mainly in the first few hours, and there was much change after few days.

FIGURE 1
DEZINCIFICATION PROGRESSES WITH IMMERSION TIME

2. Corrosion Characteristics (Electrochemical Polarization)

Fig. 2 and Table 3 illustrate the potentiodynamic polarization curves of the brass sample immersed in three solutions of different concentrations with neutral solution 3.5% NaCl, acidic media 0.1M HCl and 3.5% NaCl + NaOH. The corrosion potential (Ecorr) and corrosion current density (icorr), calculated using the Tafel extrapolation method are given in Table 2. It's a clear increasing in corrosion rate from 2.144mm/y to 6.672 mm/y for neutral solution 3.5% NaCl and acidic media 0.1M HCl respectively. As shown in fig (4) which represents the comparison of polarization curves for samples of brass sample immersed in acidic media 0.1M HCl. We observed also the change in passivation region been narrower (i.e more corrosion) as shown in table (3) for corrosion test results. It is evident that, the brass samples immersed in acidic media 0.1M HCl shifts the Ecorr towards more negative values and increases the icorr. The extent of shift in Ecorr and the increase in icorr is found to be a function of the concentration. Mansfield et al. (1994) concluded that the increase of corrosion rate of copper alloys with increasing mass transport at constant Ecorr is due to acceleration of both anodic and cathodic reactions.

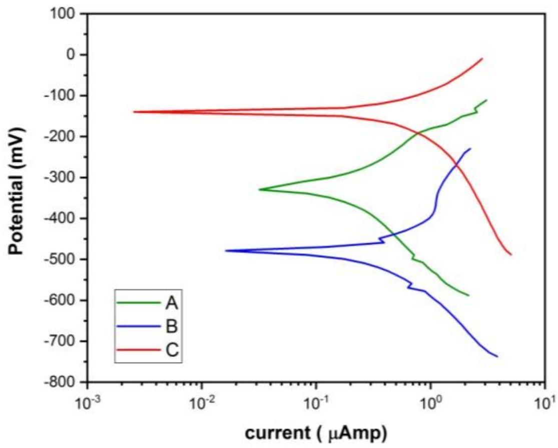

FIGURE 2

POLARIZATION CURVES (TAFEL) FOR BRASS WASTE IMMERSED IN THREE SOLUTIONS OF DIFFERENT CONCENTRATIONS WITH (A) NEUTRAL SOLUTION 3.5% NACL, (B) ACIDIC MEDIA 0.1M HCL AND (C) 3.5% NACL + NAOH

TABLE 3

CORROSION MEASUREMENTS FOR BRASS WASTE IMMERSED IN THREE SOLUTIONS OF DIFFERENT CONCENTRATIONS

ITEM	E corr. (mV)	I corr. (µAmp)	Corr. rate (mmpy)
A	-480.6	185.84	3.866
B	-134.9	320.74	6.672
C	-323.9	103.06	2.144

3. Atomic Absorption Analysis

The concentration of Cu^{2+} and Zn^{2+} ions in PH1/ 0.1MHCl solution produced by the dezincification of brass, are given in Table 4. It is evident from the results that both the copper and zinc are leached into the solution. The ratio of copper to zinc in the solution was found to be much smaller than in the alloy .After 10 days of exposure the concentration of Zn2+ was about 700 times more than of Cu^{2+}. Copper is less leached in the solution than zinc, because E° (Cu^{2+}/Cu) for copper is positive with a value of +0.34 V against the value for zinc whose E° (Zn^{2+}/Zn) is 0.76 and also diffusion depends on the size of the ion, and zinc (II) ion having an atomic radius of 0.074 nm diffuses faster than the copper (II) ion which has atomic radius of 0.096 nm.

TABLE 4

CONCENTRATIONS OF CU2+, ZN2+ OF BRASS DEZINCIFICATION IN THE DIFFERENT SOLUTIONS

Measurements	Solution
Cu 2.4074 ppm % 0.000240 Zn 50.6 ppm % 0.005060	PH1/ 0.1M HCl
Cu 0.777 ppm % 0.000077 Zn 1.828 ppm % 0.00018	PH7/3.5% NaCl
Cu 2.148 ppm % 0.00021 Zn 5.714 ppm % 0.00057	PH10/ 3.5% NaCl + NaOH

4. X-ray Fluorescence (XRF) Analysis

The purity of Zn in different media produced by the dezincification of brass, are given in Table 4, We find that the largest value for purity was in the acidic medium, reaching 20.89%, alkaline and neutral media (18.28, 11.65) respectively After 10 days of exposure.

CONCLUSION

The dezincification behavior of brass waste exposed in different pH solutions for 1, 3 and 10 days were studied. 0.1M HCl causes a significant increase in the extent of corrosion products on brass and observed in potential E_{corr} and current I_{cor} characteristics.

The purity and the concentration of Cu and Zn by dezincification using different solutions was confirmed by AAS analysis and the ratio of copper to zinc in the solution was found to be much smaller than in the alloy.

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