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Corrosion Inhibition of a Gas Sparged Copper Cylinder in a Solution of NaCl and Na_2S by Using 4-Amino-4H-1,2,4-triazole as Corrosion Inhibitor

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Abstract: *Most of previous investigations for corrosion inhibition of copper using triazole derivatives were carried out in stagnant conditions and mainly in presence of either NaCl or* Na_2S*. The main aim of this work is to investigate the performance of one of triazole derivatives namely, 4-Amino-4H-1,2,4-triazole (AHT) on improving the corrosion resistance of gas sparged copper parts in a solution comprised of NaCl and* Na_2S *with different propotions. The potentiodynamic technique was used for investigating the effect of different variables on the corrosion rate of gas sparged copper such as gas velocity, initial* S^{-2} *concentration, gas sparged copper cylinder diameter, and initial AHT inhibitor concentration. The results show that the %improvement in corrosion resistance depends mainly on two main parameters, gas flow rate and amount of AHT inhibitor added. For lower gas velocities 0.07 cm/s the %improvement ranges from 6 to 22%, while for higher gas rate 0.35 cm/s it ranges from 2 to 7% depending on the amount of inhibitor added. The activation energy of the reaction was found to increase by approximately 20% by addition of the inhibitor up to 10ppm.*

Keywords: Corrosion, gas sparging, corrosion inhibitors, triazole derivatives, copper

1. INTRODUCTION

Presence of copper as part of a gas sparged system will enhance its corrosion especially in electrolytes where corrosion is controlled by diffusion step as the reduction of O2 at the cathode [1]. Many techniques are usually recommended for protection of copper against corrosion as using protective coating which comprises using either noble metals such as silver, gold and palladium or by using the so called passive metals such as tin and nickel [2]. The passive film is usually an oxide or nitride with a thickness of nanometers and inhibits deeper corrosion. Another method is the use of organic materials which can provide protection to the exposed surfaces by the formation of either thin or thick barrier layers. Thick barriers can be formed by using waxes or polymeric products [3-5] while thin films are formed by using corrosion inhibitors, [6-8]. Organic inhibitors are known to reduce the corrosion rate of metals by slowing down the anodic or cathodic reactions or both through the formation of very thin and persistent chemisorbed films on the metal surface [9]. In particular, it is well-known that on copper 1,2,3-benzotriazole (BTA) derivatives and other organic compounds offer a good protection against corrosion in different aggressive environments [10-15]. Azoles have been proved to inhibit corrosion of copper various media such as: NaCl [16], H_2SO_4 [17], NaOH [18], HNO_3[19], and HCl [20]. This study investigates the effect of using AHT with a formula $C_2H_2N_4$ and a molecular structure as shown in figure 1, for improving the corrosion resistance of a gas sparged copper rod in a solution comprised of 3.5%NaCl and Na_2S with different concentrations ranging from 2 to 10 ppm.

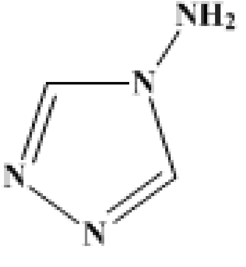

Figure 1. Molecular structure of AHT

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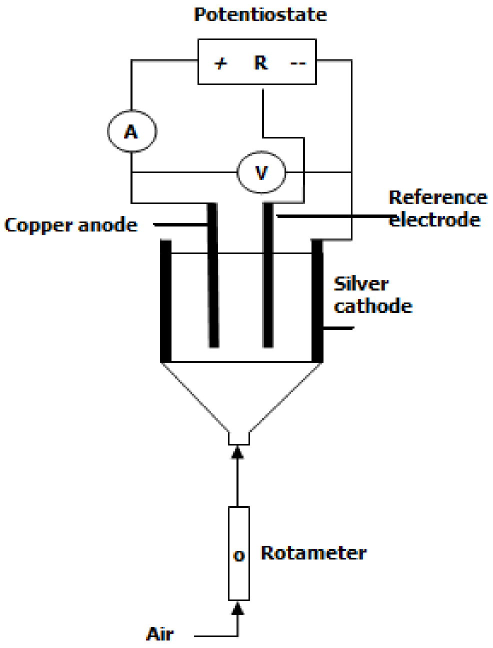

Figure 2. Experimental setup

The corrosion rate was calculated from Tafel parameters under different conditions such as gas velocity, Na_2S concentration, AHT concentration and anode diameter.

2. EXPERIMENTAL PART

As described in previous research of the authors [6] the main chemicals used were, AHT, HCl (32%), Na_2S as source of sulphide ions and NaCl as electrolyte. As shown in figure 2 an electrochemical cell composed of a copper cylinder anode and silver cathode, Ag/AgCl electrode (in saturated KCl) was used as reference electrodes. Corrosion rate was calculated using Tafel parameters of the Potentiodynamic test at different gas velocities ranged from 0.07 to 0.35 cm/s and measured using a gas rotameter, initial concentration of sulphide ion up to 10 ppm, different AHT concentrations up to 10 ppm, and different copper electrode diameter within the range from 0.6 to 1.2 cm were used. In all experiments 3.5% NaCl was used.

3. RESULTS AND DISCUSSIONS

3.1. Effect of gas velocity

Figures 3 and 4 show that by increasing gas sparging flow rate copper dissolution due to corrosion has been increased. Previous investigations showed that the nature of the reactions at the anode and/or the cathodic for this system are partially or totally controlled by the diffusion steps[21-23]:

Possible anode reactions:

$$Cu - e = Cu^{+}_{(ads)} \quad (1)$$

$$Cu^{+}_{(ads)} - e = Cu^{+2} \quad (2)$$

The second step is the slowest one where Cu^{+} is an adsorbed species at the copper surface and does not diffuse into the solution bulk [21,22]. The dissolution of copper is controlled by the diffusion of soluble Cu^{+2} species from the outer surface to the solution bulk which can be increased by increasing the gas flow rate.

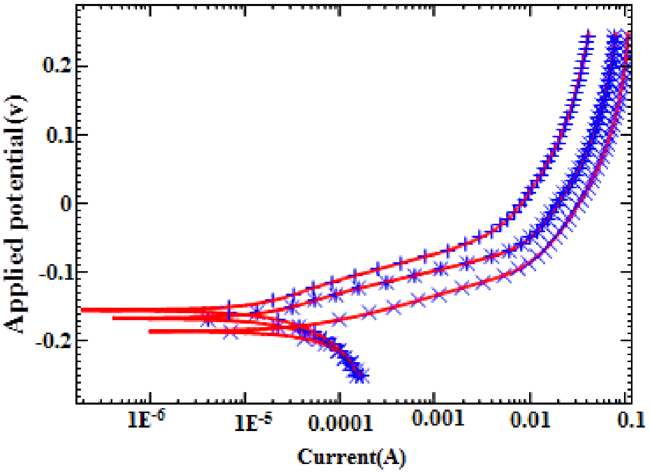

Figure 3. Applied potential vs current for at different gas velocity. Anode diameter=6cm, NaCl concentration=3.5%, S^{-2} concentration=0. (+ is 0.07, * is 0.21 and x is 0.35 cm/s).

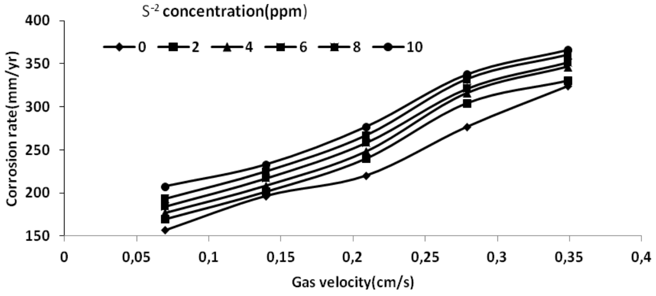

Figure 4. Corrosion rate vs gas velocity at different S^{-2} concentration. Anode diameter=6cm, NaCl concentration=3.5%, S^{-2} concentration=0.

Cathode reaction:

$$O_2 + 2H_2O + 4e = 4OH^{-} \quad (3)$$

Thus O_2 diffusion from the bulk of the solution to the surface of Cu anode is the limiting step for the cathodic reaction. The above reactions 1,2 and 3 show that the main limiting steps for copper dissolution are diffusion controlled where corrosion was increased by increasing the gas sparging flow rate.

3.2. Effect of S^{-2} concentration

figures 5 and 6 show that the copper corrosion rate was increased by increasing either the S^{-2} concentration and/or by increasing the gas velocity. The above results may be ascribed to the spontaneously formed cuprous sulfide that precipitates and clots on the surface of copper through the ionization of Cu metal followed by combination of cuprous ions and sulfide with the precipitation of a porous cuprous sulphide as a black-scale on the copper surface according to the following reactions[24]:

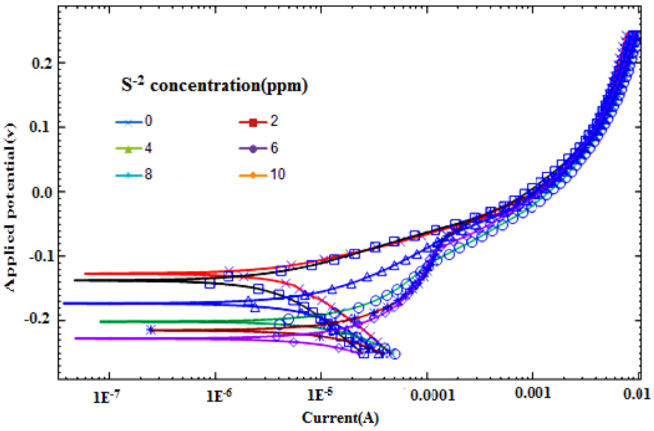

Figure 5. Applied potential vs current at different S^{-2} concentration. Anode diameter=6cm, NaCl concentration=3.5%, gas velocity 0.35 cm/s.

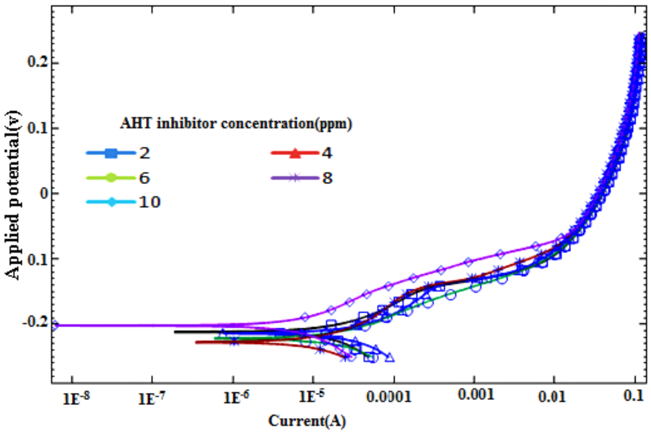

Figure 7. Applied Potential vs current at different AHT inhibitor concentration. Anode diameter=6cm, NaCl concentration=3.5%, gas velocity 0.35 cm/s and S^{-2} concentration=10 ppm.

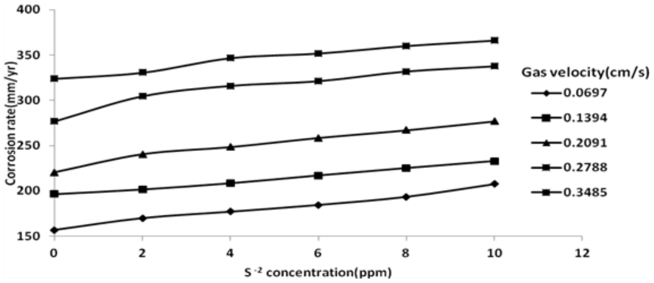

Figure 6. Corrosion rate vs S^{-2} concentration at different gas velocity. Anode diameter=6cm, NaCl concentration=3.5%

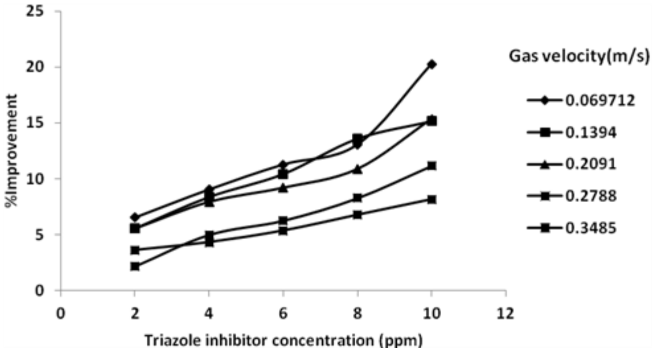

Figure 8. % improvement vs triazole inhibitor concentration at different gas velocity. Anode diameter=6cm, NaCl concentration=3.5%, S^{-2} concentration=10 ppm.

$$2Cu - 2e = 2Cu^{+} \tag{4}$$

$$2Cu^{+} + S^{-2} = Cu_2S \tag{5}$$

It is believed that a thin films of cuprous oxide and cuprous sulfide could be formed on the surface in some way. Both compounds are cation deficient and that enhance the Cu^{-2} diffusion to the film/solution interface. The buildup of these films is rather complex. The formation rate of both compounds Cu_2O and Cu_2S is different as the deviation from stoichiometry of Cu_2O is different from that Cu_2S and consequently rate of thickening of them on the surface will be different. Besides the cuprous oxide is a nonporous film while the cuprous sulfide is porous film. As mentioned above, the porous structure of the sulfide film allows the solution to come in direct contact with the copper surface and Cu_2O is obtained at the metal/electrolyte interface at the bottom of Cu_2S film.

3.3. Effect of Triazole inhibitor (AHT) concentration

Figures 7 and 8 show that the increasing the inhibitor (AHT) concentration has positive effect on the corrosion resistance of copper under the operating conditions. This could be interpreted to adsorption effect of the AHT inhibitors molecules to the copper surface, in this case the available surface area will be reduced or at least the adsorbed inhibitor molecules will hinder the Cu^{+2} diffusion from the copper surface to the solution bulk. and/or preventing hindering the oxygen reduction reaction at the cathode equation (3)[25]. In other words, available surface area for copper corrosion in contact to the corrosive medium has been decreased by the adsorbed molecules of the AHT inhibitor [26,27]. As per the previous investigations [28-30] particularly at high inhibitor concentrations a change in the rate of copper electrodissolution was found which was ascribed to the change that in the presence of AHT, copper dissolution as, in spite of dissolution via two electron reactions as represented by Equation (2), copper undergoes one-electron oxidation primarily to Cu+ as in equation (1), and forms an insoluble complex with AHT on the surface consequently reduces the corrosion rate. Figure 6 also show that the %improvement in corrosion resistance depends on two main parameters gas flow rate and amount of AHT inhibitor. For lower gas velocities the %improvement ranges from 6 to 22%, while for higher gas rate it ranges from 2 to 7% depending on the amount of inhibitor added.

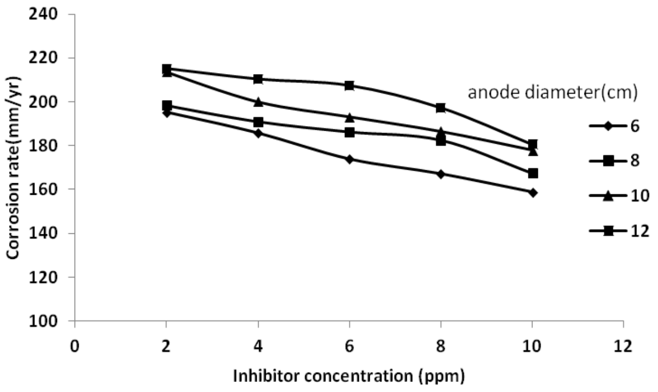

Figure 9. Effect of inhibitor concentration on the corrosion rate different anode diameter. 3.5% NaCl + 10 ppm S^{-2}, gas flow rate=0.35 cm/s.

3.4. Effect of anode diameter

Figure 9 shows a results which contradict with expected results as it was found that increasing the anode diameter has increased the corrosion rate. As increasing the anode diameter will certainly increase the thickness of the diffusion layer which reduce the diffusion rate of dissolved Cu^{+2} from the anode surface to the solution bulk and thus decrease the corrosion rate. The obtained results contradict these expectations as for this system there are two opposite effects, one due hydrodynamic conditions and the other is due to geometrical one. As for hydrodynamic conditions, gas sparging and small anode diameter (surface area) will reduce the diffusion layer thickness while increasing anode diameter will increase it. And for geometrical conditions we have to mention that increasing surface area will certainly increase the exposed surface area of the anode consequently the attack of cupper surface by either S^{-2} and/or Cl^{-} will be very easy which increase the rate of corrosion. The obtained results indicate that gas sparging reduced the diffusion layer thickness to the limit that geometrical conditions became more predominant and thus the copper dissolution rate was found to increased by increasing the anode diameter. For all cases the AHT inhibitor was efficient to reduce the corrosion rate by approximately 15-18%.

3.5.Effect of solution temperature

The solution temperature was changed within the range from 298 to 353K, as shown in figure 10, increasing the solution temperature affected the corrosion rate positively for both solutions with and without inhibitor. However presence of the inhibitor seems to reduce the corrosion rate by approximately 20% for the temperature range studied.

In addition as shown in figure 11, the activation energy of the process was calculated to be 1221 and 1603.8 Cal/mole for solution without and with the inhibitor respectively. The increase in the activation energy due to presence of AHT inhibitor confirms the action of the inhibitor for reducing the rate of corrosion.

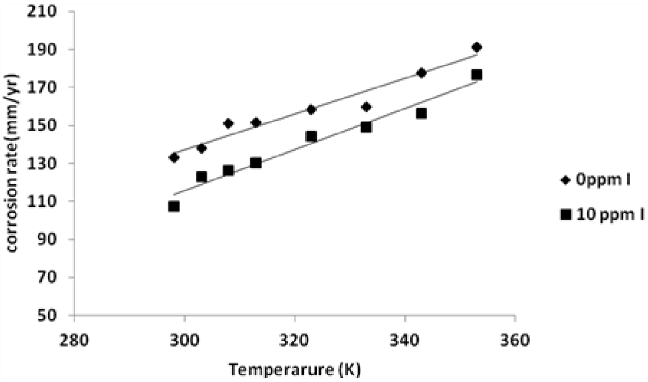

Figure 10. Corrosion rate vs Temperature for solutions with and without AHT inhibitor

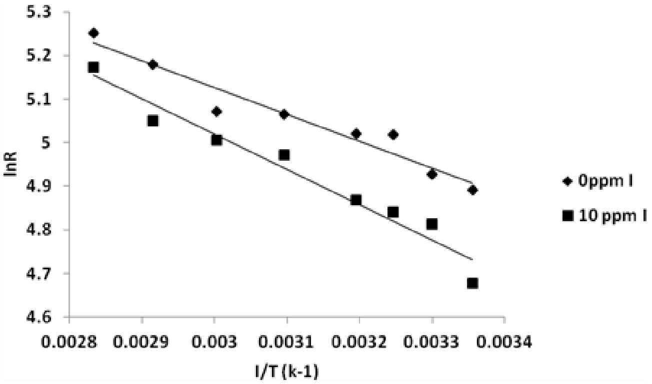

Figure 11. lnR vs 1/T for solution with and without AHT inhibitor

4. CONCLUSIONS

One of the triazole derivatives namely; 4-Amino-4H-1,2,4-triazole (AHT) was used for investigating effect on reducing the corrosion rate of copper in aggressive solution composed of Na_2S, NaCl under gas sparged flow conditions. The results show that gas sparging affect the corrosion rate of copper to a higher extent in NaCl and Na_2S polluted solutions, and that AHT inhibitor has good capability for reducing its effect and improving corrosion resistance and it was found that the %improvement in corrosion resistance depends mainly on two main parameters, gas flow rate and amount of AHT inhibitor added. For lower gas velocities 0.07 cm/s the %improvement ranges from 6 to 22%, while for higher gas rate 0.35 cm/s it ranges from 2 to 7% depending on the amount of inhibitor added.

5. ACKNOWLEDGEMENT

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