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Effect Of The Presence Of Sulphides Ions In Irrigation Water On The Resistance Of Copper Corrosion

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ABSTRACT

The location of different materials in the network of irrigation has a great importance. In our previous works, we have illustrated the major role of water containing cuprous ions in local destruction of mobile material of irrigation(MMI). The origin of these ions comes from the attacked of irrigation network caused during stream water that's contain sulphides ions. Therefore, our study deals the effect of irrigation water polluted by these sulphides ions on the corrosion resistance of copper. In fact, the microbiological analyses that we have made show that this water is infected by sulfito-reductrice bacterium. These later are responsible of the reduction of the sulphates to sulphides. The results obtained by electro-chemical method show that a weak concentration of a sulphide as one ppm provokes a strong dissolution of copper in the studied environment. This active process is caused by the formation of a porous layer based on sulphides compounds and on copper oxide naturally formed in the non-polluted environment.

KEYWORDS

Corrosion;
Pollution water;
Sulphides.

INTRODUCTION

Before the use of water stream in the irrigation in the agriculture region of Agadir(south of morocco), it crosses a complicated network. In fact, once it's pumped to different drilling by a pumping system containing copper alloy, water is gathered in a great basin whose capacity is around 30 m^3. From this basin, water is pumped for a second time in buried canalisations in order to arrive to the boundary irrigation.

Those canalisations are related to a mobile material of irrigation(MMI) by connectors in aluminium alloys and copper which are related to the aspersers.

Generally, one of the most frequent problems that appear on copper and its alloys is microbiologically induced corrosion(MIC), which can be attributed to the presence of bacteria that changes the condition in the metal/electrolyte interface and promote localized corrosion. The mechanism typical of this kind of attack has been studied in carbon steels[1,2], where the phenomenon is well understood particularly for the case of sulphate-reducing bacteria. This interest has also expanded to other materials such as stainless steels[3,4] and copper-alloys[5-7], which are generally resistant to corrosion.

In our previous works, we have studied the behaviour of MMI in simulated irrigation water and we have exanimate the effect of certain chemical compounds either on the activation or on the inhibition of the corrosion of MMI[8-15]. We found that the pollution of irrigation water is caused by Cu^{2+} dissolved from copper alloys existing in MMI. Moreover, we suggest studying the behaviour of copper in irrigation water and examining in particular the effect of the contamination of water by the sulphides ions in the maintenance of material of irrigation.

EXPERIMENTAL

The potentiokenitique current-voltage characteristics are recorded with a potentiostat(Amel 550) using a linear sweep generator(Amel 567) and X-Y recorder(Amel 580) at scan rate of 10 mV/min. All measurements are carried out in a conventional three-electrode glass cell. The working electrode, in the form of a disc cut from copper sheet(99.8% of purity), has a geometric area of 0.5 cm^2. A saturated calomel electrode(SCE) and a platinum electrode are used as reference and auxiliary electrode. Before each experiment, the electrode surface was polished mechanically and rinsed with bidistilled water.

Bacteriological and chemical analyses that we have studied are described before[2]. The electrochemical investigation was carried out at 20^0C in synthetic irrigation water(see composition in TABLE 1). Each solution was prepared with merck analytical grade reagent and bidistilled water. The sulphide was added to the solution from Na_2S solution. The exact concentration of sulphide was determinated by iodometric methods[16] and the solution pH was adjusted at value 8. The test solution is de-aerated for with pure nitrogen. Gas pubbling is maintained prior and through the experiments.

RESULTS AND DISCUSSION

Analysis of irrigation water

1. Chemical analysis

TABLE 1 gathers the chemical analyses of two samples of irrigation water: The first is from the perimeter of souse where the problem of MMI corrosion exists and the second samples is from the perimeter of mass where we notice the absence of this problem. The water of this last perimeter has its source in Youssef Ibn Tachfine barrage. We observe that the main difference between the two samples is the presence of aggressive elements as sulphate and TAC which are present a highest concentration in the case of souss water. We note also the weak concentration of oxygen in souss water in the condition of stagnation and in the presence of cuprous ions.

2. Bacteriological analysis

In the present work, we are interested in underline anaerobic bacterium sulphito-reductrice. In fact, the composition of water of irrigation(see TABLE 1) gives good conditions to the development of such bacterium. The culture of this bacterium is done in their adequate conditions[17]. After 48 hours, we have

TABLE 1: Results of chemical analyses of irrigation water

Concentration (°F)	Perimeter of souse$^+$	Perimeter of mass^{++}
Cl^-	4.52	4.30
SO^{2-}_4	7.15	4.11
TAC*	31.6	8.83
TH**	33.1	9.33
Na^+	7.14	6.0
K^+	2.30	2.05
O_2 dissous(ppm)	2.4	7.7
Cu^{2+}(ppm)	2.08	-

N.B. *Complet alcalimetric titre
**Total hardness

noticed the appearance of a black precipitate characteristic of sulphides ions. So, the present sulphates in the environment are reduced to sulphide by the action of these bacterium according to the following reaction:

$$2CH_3CHOHCOONa + SO_4^{2-} \rightarrow 2CH_3COONa + 2\,CO_2 + 2\,H_2O + S^{2-}$$

$$S^{2-} + Fe^{2+} \rightarrow FeS$$

Results of electrochemical tests

Variation of corrosion potential in function of time

Figure 1 represents the evolution of the corrosion potential E_{corr} of copper in function of time in non-polluted and in polluted irrigation water at different concentration of S^{2-}.

In the non-polluted environment, we notice that E_{corr} moves slightly towards a cathodic values when the time immersion increases. This phenomenon is probably due to the lack of oxygen in the solution which contributes to the destabilization of the passive sheet in a well-ventilated environment. The same phenomenon is observed in polluted water by the sulphides ions at a weak concentration(1 ppm). However, at high concentration(10 and 100 ppm), it's remarkable that E_{corr} decreases towards a more active values after a certain immersion time. This time depends on the contents of sulphides ions in the solution. It decreases from 18 minutes at the concentration 10 ppm S^{2-} to a few seconds in the case of 100 ppm. This variation of E_{corr} is accompanied with the formation of non adhesive black sheet based on the sulphides of copper[16].

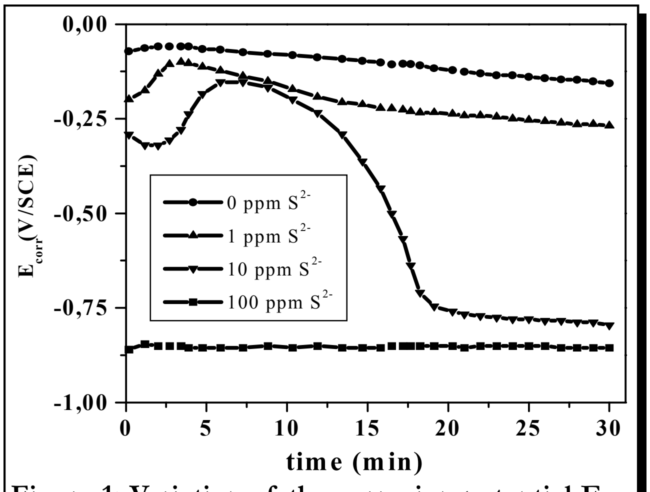

Figure 1: Variation of the corrosion potential E_{corr} of copper in function of the time in water irrigation at different sulphide concentrations

Studies of cyclic voltmeter

1. Non-polluted souss water

The recorded successive voltamogrammes of copper in non-polluted water between -1.2 and 0 V/SCE are represented in figure 2.

Figure 2 indicate that the course of the potential in the anodic sense shows a peak Ia followed by a continuous increase of the anodic current density. This peak Ia represents the reaction of oxidization of Cu/Cu(I)[18]. In the cathodic sense, the overvoltage involves the appearance of two peaks Ic and IIc. The peak Ic characterizes the reaction of reduction of Cu(II)/Cu(I) and the peak IIc corresponds to the reduction reaction of Cu(I)/Cu[19]. We have to notice that the intensity of the peaks Ia and Ic decreases when the number of the cycle increases. This result may be interpreted by the decrease of the quantity of the Cu^{2+} in solution during the time of maintenance in E_{corr}.

2. Polluted Souss water by the sulphides ions

The recorded voltamogrammes of copper between -1.2 and 0 V/SCE at different sulphide concentrations are represented in figure 3.

From figure 3, we note the appearance of an anodic peak IIa followed by a wide landing of current. The intensity of this peak becomes important when the sulphides concentration increases in the solution. It's referred to the formation of cuprous

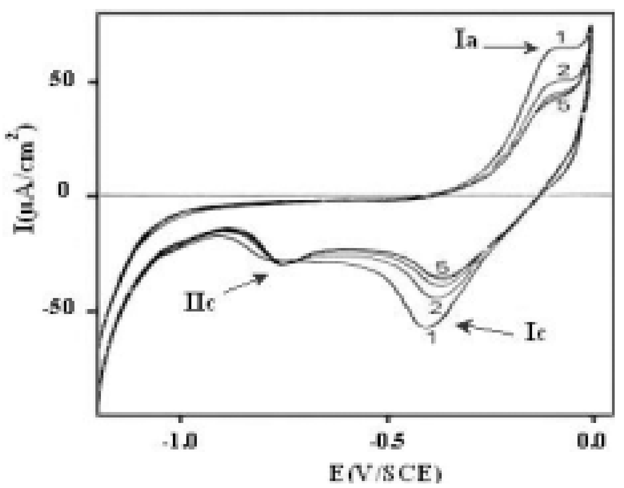

Figure 2: Voltamperometric curves of copper in non-polluted overall irrigation water

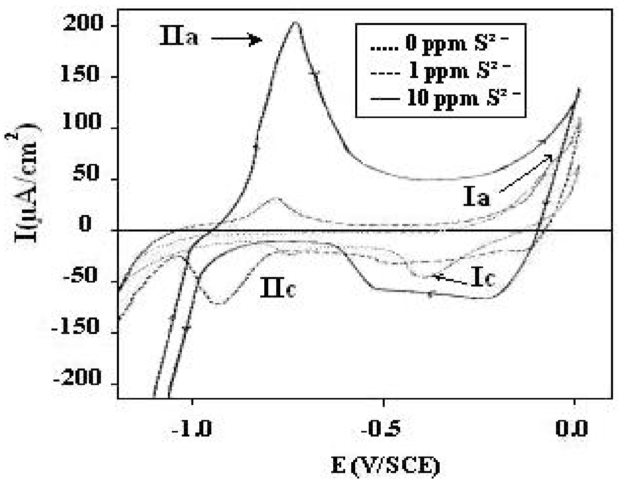

Figure 3: Voltamperometric curves of copper in synthetic water of irrigation at different sulphide concentrations

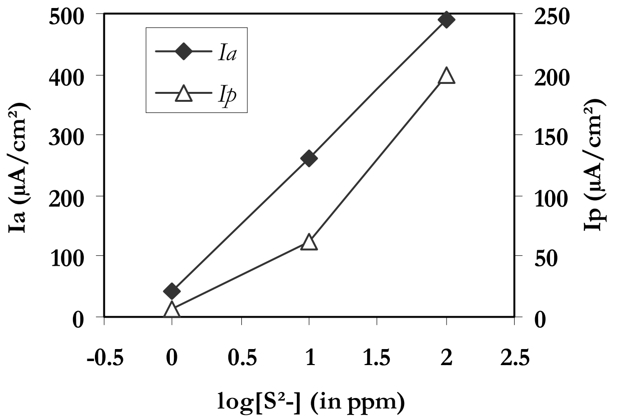

Figure 4: Evolution of the current density of peak activity Ia(peak IIa) and the landing Ip in function of sulphide concentration

sulphide according to the following reactions[16]:

$Cu \rightarrow Cu^+ + 1e^-$

$2Cu^+ + S^{2-} \rightarrow Cu_2S$

In the cathodic domain, it's appeared that there is a landing current peak Ic found in the case of non-polluted environment. This result shows that the pollution of water by sulphides ions favors the crossing of Cu^{2+} in solution and the formation of copper sulphide precipitate on the surface. The peak IIc which becomes more intense at a weak sulphides concentration(1 ppm) doesn't remain at high concentrations(10 ppm).

The electrochemical parameters values related to the behavior of copper in polluted and in non-polluted environment by sulphides ions are gathered in TABLE 2. figure 4. Illustrate also the evolution of the densities of the current Ia(peak IIa) and the landing Ip in function of sulphide concentration.

TABLE 2: Electrochemical parameters of copper in synthetic irrigation water in function of the sulphide concentration

$[S^{2-}]$(in ppm)	E_{corr} (mV/SCE)	Ia(peak IIa) (μA/cm²)	Ip (μA/cm²)
0	-85	-	-
1	-170	44	07
10	-840	260	62
100	-880	490	200

CONCLUSION

In this work, we have studied the behavior of copper in polluted and in non-polluted water of irrigation by sulphides ions. The results obtained show that the composition of this water affects the copper corrosion processes. Particularly, in the absence of sulphides ions, this process has no intense. The weak quantity of past copper in solution return to the presence of aggressive ions such as hydrogen-ocarbonates which favor a chemical dissolution of passive film according to the following report[20].

$2HCO_3^- + Cu_2O \rightarrow CuCO_3 + 2\,OH^-$

$CuCO_3 + HCO_3^- \rightarrow [Cu(CO_3)_2]^{2-} + H^+$

In a polluted environment by sulphides ions, there is a formation of non adhesive black sheet based on the sulphide of copper. This porous sheet catalyses the crossing of copper in solution and prevents the natural growth of protector oxide film. These results show the importance of the location of different materials in the network of irrigation. Thus, the contamination by the anaerobic bacterium sulfato-reductrice provokes the pollution of Souss water by the sulphides ions. Moreover, they stimulate the dissolution of copper in solution and they contribute to the pollution of water by cuprous ions which are responsible of the MMI destruction.

REFERENCES

[1] G.A.Cragnolino, D.S.Dunn, P.Angell, Y.M.Pan, N.Sridhar; Corrosion 98 Conference, paper No. 147, NACE, **(1998)**.

[2] W.A.Hamilton; Annu.Rev.Microbiol., **39**, 195 **(1985)**.

[3] J.E.G.Gonzalez, F.J.H.Santana, J.C.Mirza-Rosca; Corr. Sci., **40**, 2141 **(1998)**.

[4] S.E.Werner, C.A.Johnson, N.J.Laycock, P.T.Wilson, B.J.Webster; Corr.Sci., **40**, 465 **(1998)**.

[5] T.S.Rao, K.V.K.Nair; Corrosion, Sci., **40**, 1821 **(1998)**.

[6] D.Wagner, A.H.L.Chamberlain, W.R.Fischer, J.N. Wardell, C.A.C.Sequeira; Mater.Corr., **48**, 311 **(1997)**.

[7] J.T.Walker, K.Hanson, D.Caldwell, C.W. Keevil; Biofouling, **12**, 333 **(1998)**.

[8] L.Bazzi, S.Kertit, M.Hamdani; Revue de Metallurgie CIT/Sciences et Genie des Materiaux, **91**, 1835 **(1994)**.

[9] L.Bazzi; These d'Etat, Agadir, **(1995)**.

[10] R.Salghi, L.Bazzi, B.Hammouti, A.Bouchtart. Z.El Alami, S.Kertit; Ann.Chim.Sci.Mat., **25**, 593 **(2000)**.

[11] L.Bazzi, S.Kertit, M.Hamdani; Revue de Metallurgie CIT/Sciences et Genie des Materiaux, **92**, 690 **(1995)**.

[12] L.Bazzi, S.Kertit, M.Hamdani; Corrosion, **51**, 811 **(1995)**.

[13] L.Bazzi, S.Kertit, M.Hamdani; J.Chim.Phys., **92**, 1612 **(1995)**.

[14] L.Bazzi, S.Kertit, M.Hamdani; Bull. of. Electrochem., **14**, 34 **(1998)**.

[15] L.Bazzi, S.Kertit, M.Hamdani; J.Chim.Phys., **94**, 93 **(1997)**.

[16] A.Vogel; 'A Text Book of Quantitative Inorganic Analysis', 3rd Edn., Longman London, **(1961)**.

[17] P.A.I.A.Degradation Microbienne des Materiaux, Eds. Technic., **(1974)**.

[18] M.Drogowska, L.Brossard, H.Menard; Corrosion, **43**, 549 **(1987)**.

[19] P.S.Sanchez, M.Barrera, S.Gonzaley, R.M.Souto; Electro.Acta, **35**, 1337 **(1990)**.

[20] M.Drogowska, L.Brossard, H.Menard; J.Electrochem.Soc., **140**, 1247 **(1993)**.