# 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 electrochemical 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.*

**Key words:** Corrosion; pollution water; sulphides.
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## 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.

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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].

The sulfidation of metals is a process of practical importance as well as of theoretical interest as oxidation. From the theoretical point of view, sulfidation reactions afford important parallels and contrasts with the corresponding oxidation reactions. Stoichiometric and non-stoichiometric copper sulfide films have been widely used in dielectric metallization [16] and as ion specific electrode [17], when soluble sulfides are present in potable water or seawater, a thick black, poorly adherent scale forms on copper or brass surface [18].

In a previous study [19], we showed that the corrosion product formed on a copper surface in anaerobic $5 \times 10^{-4}$ mol dm$^{-3}$ Na$_2$S + 0.1 mol dm$^{-3}$ NaCl solution was a single-layered compact Cu$_2$S film, whose growth kinetics appeared to obey a parabolic law over an exposure period up to ~ 1700 h. However, the results of Smith et al. [20-21] showed that the properties of the sulfide film formed on copper depend on the solution concentrations of both sulfide and chloride. In solutions with a high chloride to sulfide concentration ratio, the sulfide film possessed a cellular structure.

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.

## MATERIALS AND METHODS

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 cm². 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°C 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$_2$S 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.

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## RESULTS AND DISCUSSION

### 3.1. Analysis of irrigation water
### 3.1.1. Chemical analysis

Table 1 gathers the chemical analyses of two samples of irrigation water : The first is from the perimeter of Souss where the problem of MMI corrosion exists and the second samples is from the perimeter of Massa 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.

**Table.1 Results of chemical analyses of irrigation water**

| Concentration (°F) | Perimeter of Souss | Perimeter of Massa |
|---|---|---|
| $Cl^-$ | 4.52 | 4.30 |
| $SO_4^{2-}$ | 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 | - |

*Complet alcalimetric titre ; ** Total hardness*

### 3.1.2. 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 [22]. After 48 hours, we have 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:

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

$$S^{2-} + Fe^{2+} \rightarrow FeS$$
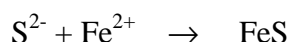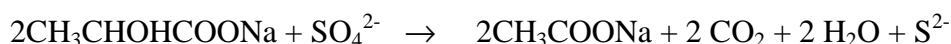
### 3.2. Results of electrochemical tests
### 3.2.1. Variation of corrosion potential in function of time

Fig. 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

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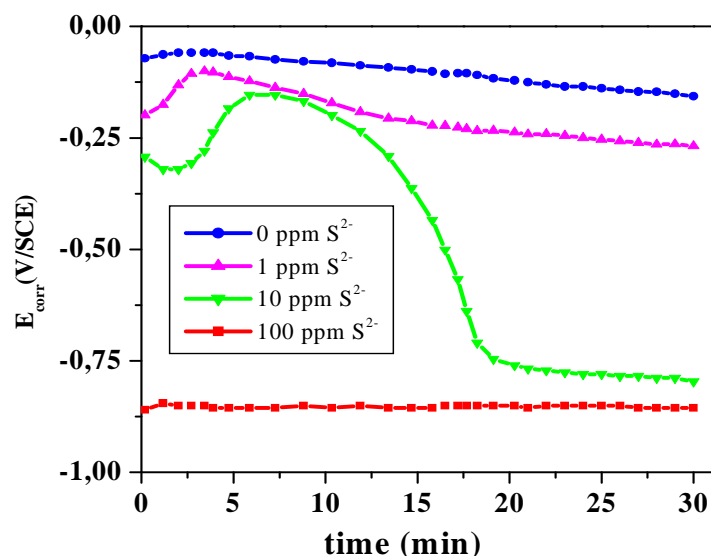accompanied with the formation of non adhesive black sheet based on the sulphides of copper [23].



**Fig. 1. Variation of the corrosion potential E$_{corr}$ of copper in function of the time in water irrigation at different sulphide concentrations**

### 3.2.2. Studies of cyclic voltmeter
### 3.2.2.1. Non-polluted Souss water
The recorded successive voltamogrammes of copper in non-polluted water between –1.2 and 0 V/SCE are represented in Fig. 2.
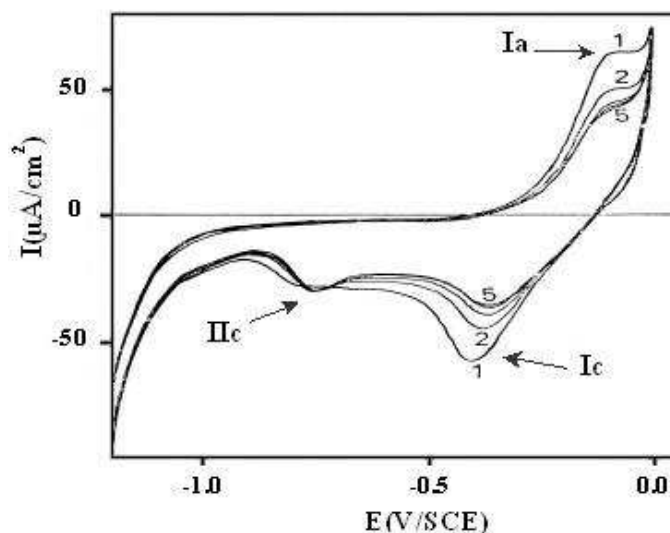


**Fig. 2. Voltamperometric curves of copper in non-polluted overall irrigation water**

Fig. 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) [24]. 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 [25]. We have to notice that the intensity of the peaks *Ia* and *Ic* decreases when the number of the cycle increases. This result

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may be interpreted by the decrease of the quantity of the $Cu^{2+}$ in solution during the time of maintenance in $E_{corr}$.

### 3.2.2.2. 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 Fig. 3.
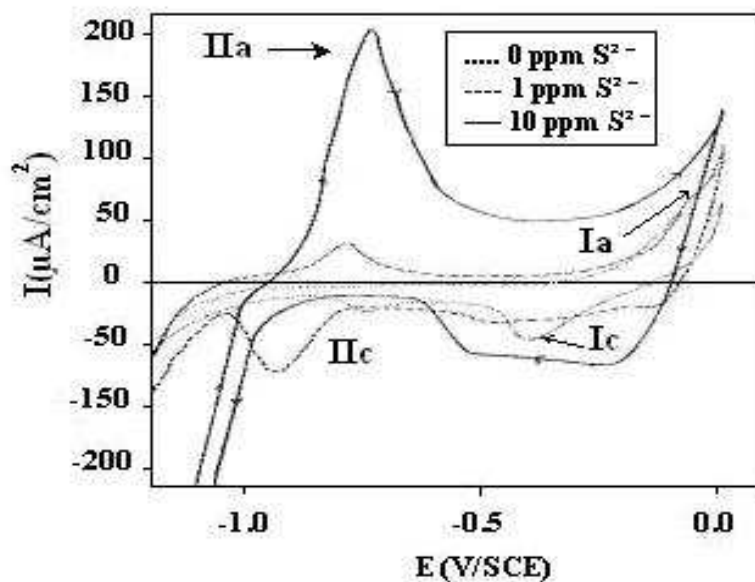


**Fig. 3. voltamperometric curves of copper in synthetic water of irrigation at different sulphide concentrations**

From Fig. 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 sulphide according to the following reactions [23]:

$$Cu \longrightarrow Cu^+ + 1\,e^-$$
$$2Cu^+ + S^{2-} \longrightarrow Cu_2S$$

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 favours 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).

**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*) ($\mu A/cm^2$) | *Ip* ($\mu A/cm^2$) |
|---|---|---|---|
| 0 | -85 | - | - |
| 1 | -170 | 44 | 07 |
| 10 | -840 | 260 | 62 |
| 100 | -880 | 490 | 200 |

The electrochemical parameters values related to the behaviour of copper in polluted and in non-polluted environment by sulphides ions are gathered in table 2. Fig. 4. illustrate also the

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evolution of the densities of the current *Ia* (peak *IIa*) and the landing *Ip* in function of sulphide concentration.
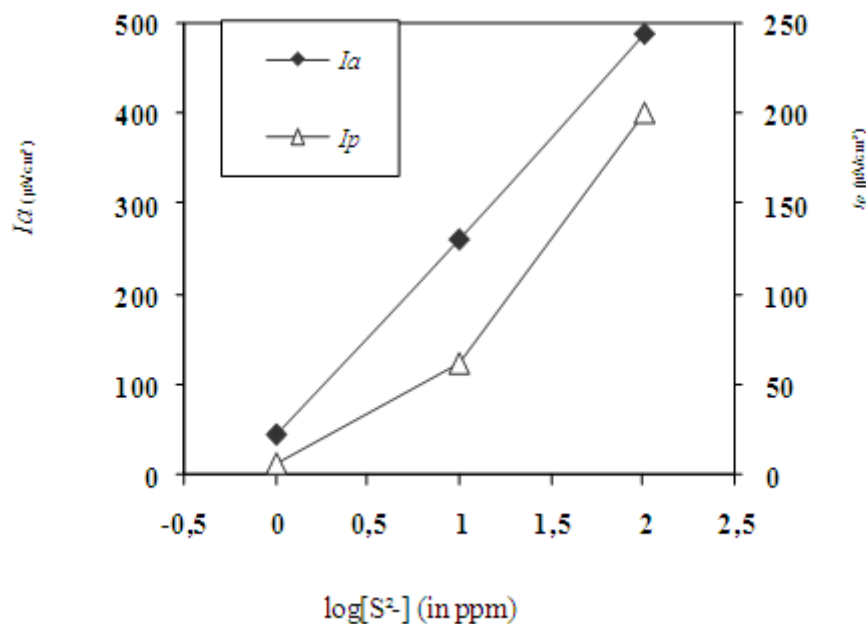


**Fig. 4. Evolution of the current density of peak activity *Ia* (peak *IIa*) and the landing *Ip* in function of sulphide concentration**

## CONCLUSION

In this work, we have studied the behaviour 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 hydrogenocarbonates which favour a chemical dissolution of passive film according to the following report [26].

$$2HCO_3^- + Cu_2O \longrightarrow CuCO_3 + 2OH^-$$
$$CuCO_3 + HCO_3^- \longrightarrow [Cu(CO_3)_2]^{2-} + H^+$$
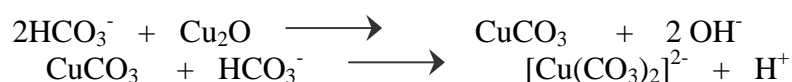
In a polluted environment by sulphides ions, there is a formation of non adhesive black sheet based on the sulphide of copper. This porous sheet catalyses the crossing of copper in solution and prevents the natural growth of protector oxide film. These results show the importance of the location of different 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, in : Corrosion 98 Conference, NACE, **1998**, 147.

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

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

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

[5]   T. S. Rao, K. V. K. Nair, *Corr. Sci*., **1998**,40, 1821.

[6]   J. Chen, Z. Qin, D.W. Shoesmith, *Electrochimica Acta*., **2011**, 56, 7854.

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

[8]   L. Bazzi, S. Kertit, M. Hamdani, *Revue de Métallurgie CIT/Sciences et Génie des Matériaux.*, 1994, 91,1835.

[9]   I. Zaafarany, H. Boller, *Journal of Saudi Chemical Society*., **2010**, 14, 183

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

[11]  L. Bazzi, S. Kertit, M. Hamdani, *Revue de Métallurgie CIT/Sciences et Génie des Matériaux*., **1995**, 92, 690.

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

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

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

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

[16]  L.I. Stepanova, T.V. Mazolevskaya, O.G. Purovskaya, *Met. Finish,*. **2003**,101, 18.

[17]  A. Zirino, R. De Marco, I. Rivera, B. Pejcic, *Electroanalysis., **2002**, 14, 493.

[18]  S. Jacobs, M. Edwards, *Water Res*., **2000**, 34, 2798.

[19]  J. Chen, Z. Qin, D.W. Shoesmith, *J. Electrochem. Soc*., 2010, 157, C338.

[20]  J.M. Smith, Z. Qin, D.W. Shoesmith, Electrochemical impedance studies of the growth of sulfide films on copper, in: 17th International Corrosion Congress, , Las Vegas, NV, **2008**, 3111.

[21] J.M. Smith, Ph.D. Thesis, The University of Western Ontario, **2007**.

[22]  P. A. I. A. Dégradation Microbienne des Matériaux, Eds. Technic., **1974**, 17

[23]  A. Vogel, A Text Book of Quantitative Inorganic Analysis, 3$^{eme}$ edition, Longman London, **1961**.

[24]  M. Drogowska, L. Brossard, H. Menard, *Corrosion*., **1987**,43, 549.

[25]  P. S. Sanchez, M. Barrera, S. Gonzaley, R. M. Souto, *Electro. Acta*., **1990**,35, 1337.

[26]  M. Drogowska, L. Brossard, H. Menard, *J. Electrochem. Soc*., **1993**, 140, 1247.