



REFLECTIONS CONCERNING THE COPPER CORROSION IN LIQUID ENVIRONMENTS

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ABSTRACT: *This paper presents the experimental results of copper corrosion in different liquid environments. The researchers Ives and Rawson managed to display what causes the copper to deteriorate in water. Thus, they believe that the dissolution rate increases as the oxydic film's thickness increases. In this way, the copper oxide produced in this way, gains properties similar to the property of the copper oxide formed directly by the oxygen, which is following a logarithmic law. The copper dissolving is based on the thermodynamics of the (anaerobic) chemical reaction. In this way, the accumulation of copper oxide decreases the corrosion rate. It is considered that the penetration of chlorides among the oxide layers occurs through cracks and crystalline defects; hence appear points of corrosion (pitting) which connects one another in the course of time, transforming themselves into stains or even plagues, putting in danger the copper's crystalline structure.*

Key-words: *corrosion, copper, acid.*

1. INTRODUCTION

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From the chemical point of view, it follows that, gradually, chloride ions replace the ions of the abstract acid in the melting process.

In the case of magnesium chloride which contains water (seawater), the copper corrosion is less dependent on the carbon dioxide, as the dissociation $MgCl_2$ produces acidity.

The researchers Heitz and Meysenbug have shown that the mixtures of mineral acids and organic solvents copper modifies the intensity of the copper atom relative to the solutions of mineral acids in water environment. They showed that the hydrochloric acid forms along with copper some solutions that destroy passive layers. Ethanol solutions are more corrosive because of the oxygen's absorption (approximately seven times higher than the water's).

The hydrogen chloride solution in ethanol corrodes less than hydrochloric oxide in water, as a result of a brown layer.

In solutions of sulfuric acid in ethanol is produced precipitate loose brown-green, and the corrosion is more advanced

2. THE CHEMICAL CONNECTION BETWEEN COPPER'S CORROSION AND DISSOLVING

The scientists Ives and Rawson have analyzed 7 ways of reaction (Table 1) by which copper is oxidized, if enters in contact with pure water. In Table 1, one can notice that the reactions 1 and 2 take place with a considerable loss of free energy, showing thus both the copper's melting and copper's oxide.

Table 1: COPPER'S CORROSION IN WATER - CHEMICAL EQUATIONS

Nr. Crt.	Chemical reaction	G^0 Kcal.	$\log K'$
1	$Cu + H_2O + 2CO_2 + \frac{1}{2}O_2 = Cu(HCO_3)_2$	- 19,88	$14,57 + 2 \log P_{CO_2} + \frac{1}{2} \log P_{O_2}$
2	$\frac{1}{2} Cu_2O + H_2O + 2CO_2 + \frac{1}{4}O_2 = Cu(HCO_3)_2$	-2,39	$1,75 + 2 \log P_{CO_2} + \frac{1}{4} \log P_{O_2}$
3	$Cu(OH)_2 + 2CO_2 = Cu(HCO_3)_2$	8,73	$-6,40 + 2 \log P_{CO_2}$
4	$CuO + H_2O + 2CO_2 = Cu(HCO_3)_2$	10,52	$-7,71 + 2 \log P_{CO_2}$
5	$\frac{1}{2}[CuCO_3 * Cu(OH)_2] + \frac{1}{2}H_2O + \frac{1}{2}CO_2 = Cu(HCO_3)_2$	11,90	$-8,69 + \frac{1}{2} \log P_{CO_2}$
6	$[2CuCO_3 * Cu(OH)_2] + H_2O + CO_2 = Cu(HCO_3)_2$	12,10	$-8,84 + \log P_{CO_2}$
7	$Cu_2O - Cu + H_2O + 2CO_2 = Cu(HCO_3)_2$	15,10	$-11,07 + 2 \log P_{CO_2}$

One can notice from Table 1 that oxygen and carbon dioxide is displayed in the following manner: in water, their content is determined by the speed of corrosion, the reaction no. 7 being the exception, which is anaerobic. The copper and copper oxide's melting and is reduced to some extent, because by means of reactions 3, 4, 5, 6, are formed compounds hardly soluble.

Their precipitation would hinder the reaction 1 and 2, with protective role.

Also to be noticed in the Table 1 that, while the presence in water of the gaseous oxygen causes the melting of the copper oxide, the presence of the metallic copper alone, in anaerobic conditions (reaction 7 of the Table 1), induces the melting of the copper oxide as well.

Cu_2O is unstable in a solid state excepting the fact when there is only small quantities of carbon dioxide (Table 1). So, carbon dioxide is indispensable for a strong copper corrosion and, in reduced aired conditions, it is partially responsible for the structure of copper's corrosion accumulations.

Moreover, the oxygen has an important influence on the copper melting. When the oxygen is present in the gaseous mix, in concentration of more than 20 %, the copper's pink color changes into black. The Cu^{++} ions slightly soluble, comparative with Cu^+ ions, become in this manner available for removing in the shape of Carbonic acid copper ($HCO_3)_2$.

The electrochemical importance of the junction between copper and a mix of oxygen-carbon dioxide is elucidated as follows:

It has been supposed that in a dry atmosphere, the epitaxial – i.e. protective – character of the copper oxide film-tape (sheet) could not surpass the thickness of 100Å. In watery mediums, this thickness is reduced to approx. 20Å and the subsequent increase of the film is significantly deformed, which fact leads to the apparition of a loose (fluffy) mass of Cu_2O . While this development allows the thin film to adhere to metal, the 20Å thickness is inadequate for impeding the transfer of metallic atoms on the interface on which the compact and loose sections of the film are meeting (Figure 1)

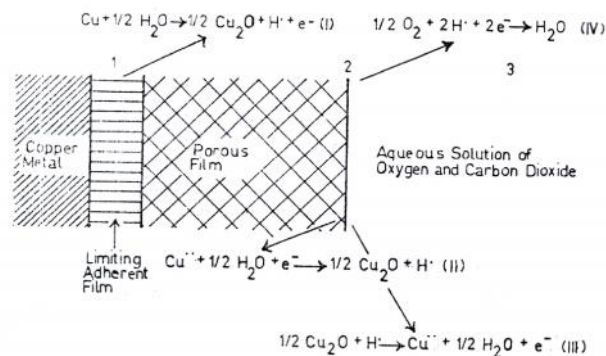


Figure 1. Double hypothetical cell, contributing to the copper corrosion

In acid fluid mediums, that is in significant concentrations of melted carbon dioxide, the copper oxide shall pass in solution, according to the following reaction:



While the gaseous oxygen melted in the same acid conditions will behave as oxidant agent:



But the concentration of Cu^{2+} ions in liquid environments, which surpass the balanced ionic product K' established by reaction 2 (Table 1), will generate the latter one in the opposite, subsiding thus a loose (fluffy) deposit of copper oxide, until the equilibrium is established.

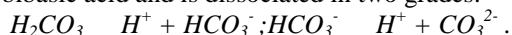


This reaction is made on the account of copper metal, which yields electrons and becomes an oxidizing agent, producing a compact, thin, adherent layer of copper oxide.



The role of carbon dioxide is not yet fully explained. The fact that it creates acid conditions does not seem to be the single factor. Moreover, carbon dioxide strongly interferes with the physical and chemical absorption of the oxygen. Regarding this phenomenon, a significant observation is that the oxygen absorption is an essential condition for the subsequent absorption of carbon dioxide. For such a situation to take place, the condition would be that the carbon dioxide to be easily absorbed through combination with "mobile" oxygen ions. Perhaps then are formed compounds loaded negatively of CO_3^{2-} formula. The access of carbon dioxide on the surface already covered with absorbed oxygen leads to rapid absorption of the carbon dioxide (until 70 % of the volume of oxygen absorbed initially). Ives and Rawson investigated also, the probabilities that lead to the deterioration of copper in water. A copper oxide film, produced by the interaction between metallic with gaseous oxygen, is dissolved according to reaction 2 of Table 1, but the melting speed increases as the oxide film becomes thick, suggesting thus the presence of a catalytic support to this melting.

The carbon dioxide is melted in water is partially present in the shape of carbonic acid H_2CO_3 . This latter one is a weak, dibasic acid and is dissociated in two grades:



In proportion to the grade in which these salts are formed, they are called primary carbonates (acids) and normal secondary carbonates.

On the outer side, the oxide film increased through the consummation of metal, showing in this way an autocatalytic capacity to advance towards the inner side. So, the corrosion is significant, though the oxide film thickness remains unchanged. Nevertheless, the presence of copper ions in water starts the settling down of copper, according to reaction 7 of Table 1, on the unoxidized copper layers, as for instance faults, corrosion spots and so on. The copper oxide produced in this manner contains those properties that are opposed to those related to the oxide formed directly by oxygen. Its increasing follows a logarithmic law, and its melting becomes significant only after a long term, bearing in mind the reaction's thermodynamics (Table 1). Thus the anaerobic accumulation of copper oxide reduces the corrosion speed.

The adding of salts in water changes the balance of the reactions mentioned in Figure 1, but this situation is not always unfavorable to the metal. Figure 2 shows that in water, neither the chlorides, nor the melted oxygen are not responsible for the corrosion, but what determines most the corrosion speed is the quantity of carbon dioxide. This state of facts is not difficult to understand, having in mind that the action of the hydrogen ions over the copper ions (Table 1, reaction 3), in neutral or alkaline environment, would immobilize them in the shape of insoluble copper oxide, and thus would impede the harmful function of chloride ions.

It is true that, in small concentration of melted carbon dioxide and big concentration of oxygen, the chlorides slow down corrosion and thus serve as inhibitors.

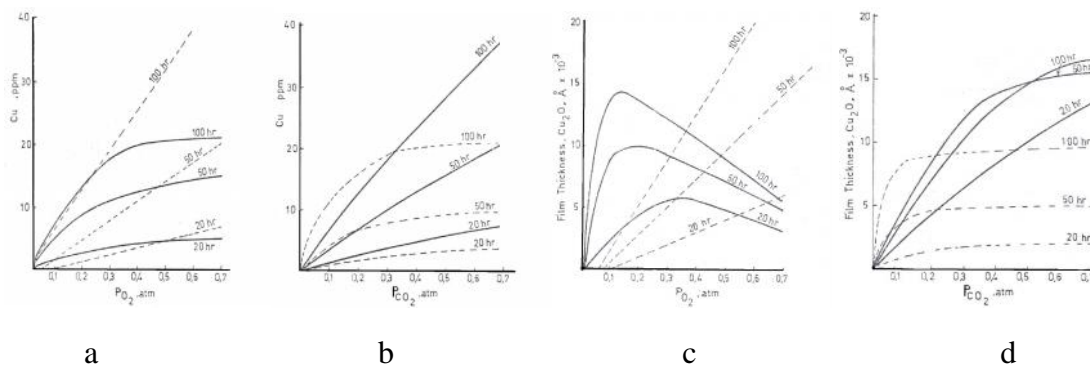


Figure 2. The Results of Corrosion Experiments involving the presence of approximately 110ppm Cl(NaCl): (a) and (b) dissolution and film growth, respectively. For $P_{CO_2} = 0,30$ atm (const); (c) and (d) the same for $P_{O_2} = 0,30$ atm (const).

It is believed that the penetration of chloride through the oxide layers takes place through faults and greater crystalline deficiencies, so that their presence is most probably stopped on the compact layer of bellow. In proportion to the chloride concentration, in the corrosion spot it is settling down either basic copper carbonate, or basic copper chloride. A long-term action of the local cell fills the corrosion spot with reaction products which can extend radially on the surface. "The small islands" that come out in this way can unite in a layer above the existing oxide layer. In the meantime, the loose cut of the oxide layer enters gradually in the solution; hence chloride ions replace equivalently the acid carbonate ions in the melting process.

3. THE COPPER CORROSION IN HCL SOLUTIONS

In the case of magnesium chloride, which contains water (sea water) the copper corrosion will be less dependent on the melted carbon dioxide, because the $MgCl_2$ dissociation creates a supplementary acidity.

Scholars as Heitz i Meysenbug have brought proofs according to which the mixes consisting of mineral acids organic solvents modifies the intensity of copper's attack, as compared with the solutions of the same mineral acids in water. Hydrochloric acid together with copper forms soluble compounds which destroy the pasivant layers. The sulfuric acid tends to produce compounds poorly soluble, that causes passivity. The only exception is acetic acid, which is strongly dissociating itself.

Solutions based on ethanol are corrosive, due to the big gaseous oxygen absorption (approx. 7 times greater than the water's), but a solution of hydrochloric acid in ethanol corrodes copper less than a solution of hydrochloric acid in water. This fact is determined by the deposit of a brown, compact layer, formed by a complex copper compound. In solutions based on hydrochloric acid in ethanol are, are produced loose precipitates (sediments) brown-greenish, instead of the compact ones and, of course, the corrosion is more advanced that in the case of sulfuric (dipping) solutions.

The solutions based on hydrochloric acid in dimethyl ketone attacks copper substantially. But a solution based on sulfuric acid in dimethyl ketone covers the metal with a light blue film of copper sulfate which serves as a good pasivant.

The pure acetic acid (methane carboxylic acid) corrodes copper but the adding of mineral acids reduces this tendency. At temperatures around the steam (boiling) point, the anticorrosive qualities of the copper sulfate are eliminated

4. THE DIAGRAMS DISPLAY THE CORROSION VARIATION IN PROPORTION TO THE TIME OF DIFFERENT CHEMICAL SUBSTANCE

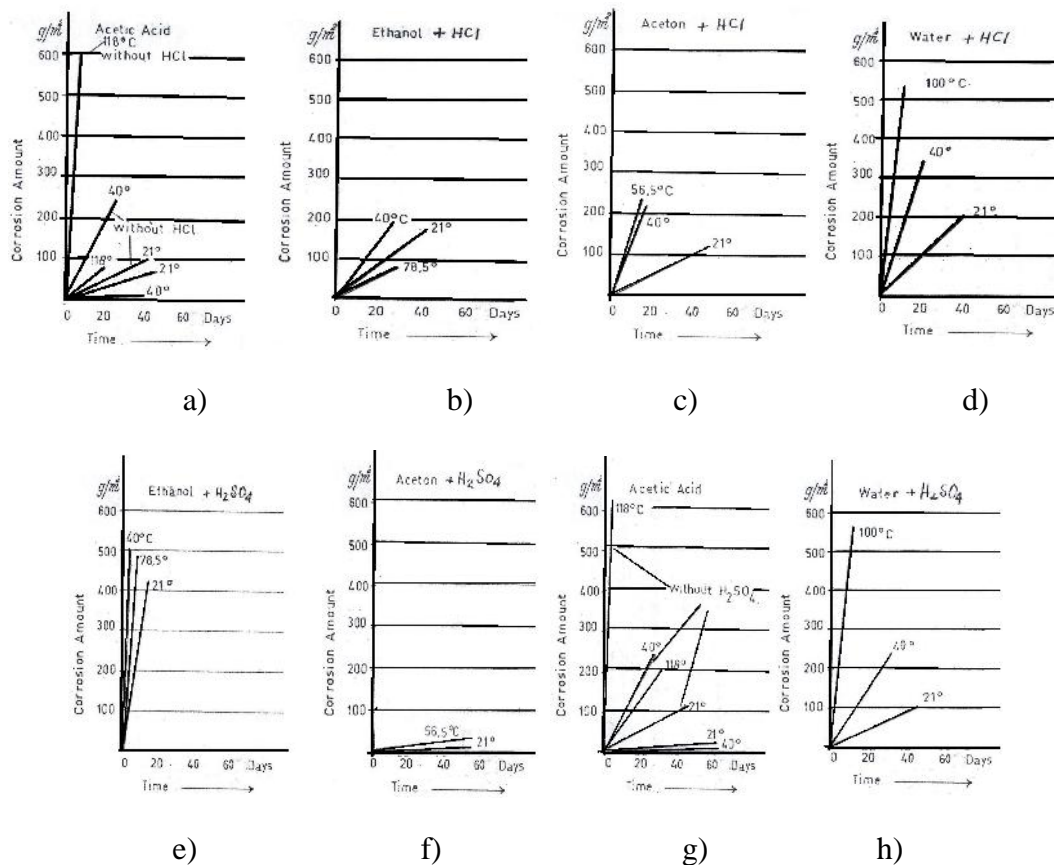


Figure 4. Corrosion of copper in 0,037% HCl solution

5. CONCLUSIONS

The work describes aspects of copper corrosion in water. The research that has been made displays clearly the copper oxidation in drinking water and especially in sea water, in consequence of the considerable NaCl content.

Rezultatele prezentate in acest articol au fost obtinute cu sprijinul Ministerului Fondurilor Europene prin Programul Operational Sectorial Dezvoltarea Resurselor Umane 2007-2013, Contract nr. POSDRU 187/1.5/S/155420.

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU 187/1.5/S/155420.

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