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Abstract

CYCLIC VOLTAMMETRIC STUDY OF EFFECTS OF CARBONATE, PHOSPHATE AND HYDROXYL ION ON THE ELECTROCHEMICAL PROPERTIES OF COPPER AND LEAD/TIN SOLDER ALLOY

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ABSTRACT

Iron, steel, lead, lead/tin alloy but especially copper and copper alloys are materials broadly used in drinking distribution systems.

Copper pipe is widely used in water supply systems because of its relatively high resistance to corrosion, which relies on the ability of the metal to form protective films under favourable condition. A protective oxide layer grows naturally on their surface, which prevents further corrosion from the base metal.

In some environments, however, the metal may corrode to form products which are non-protective and which may subsequently lead to failure of the pipes. Therefore, the corrosion resistance of the copper pipes used in such reticulation systems strongly depends on the performance of their protective passive film. On copper-based substrates, the film is primarily composed of Cu_2O. Malachite $Cu_2(OH)_2CO_3$ and in some cases tenorite CuO are also formed on corroding copper surfaces.

The stability of the passive film and its ability to prevent damage depend on film composition, thickness, and ultimately on the nature of the products formed at the surface of the metal and hence on the environment (composition and temperature of the water) in which they are used.

Many investigations published in leading journals over the last years have addressed the various issues that govern the corrosion of metal and in particular copper corrosion in drinking waters.

Some have studied the effect of diverse alloying elements, for example the influence of Zn as alloying element on the improvement of the corrosion resistance. Others have investigated the use of corrosion inhibitors to prevent the dissolution of metals. These inhibitors should be fit for use in drinking water applications, and ultimately for human consumption and they should not have a negative impact on the environment. One compound that meets these requirements and one that has been widely studied and used is orthophosphate (e.g., Na_3PO_4).

The use of these corrosion inhibitors can favour the development of a more resistant superficial layer that minimizes metal dissolution. It was shown that the presence of a protective passive film on the metals surface is necessary to have for the inhibitive

effect of these compounds to become prominent enough. However, this layer can suffer localized rupture or pitting that can lead to pipe perforation.

Given the complexities of corrosion processes, one general question related to their understanding can be formulated as: "what are the exact conditions when the electrolyte composition and pH allow the development of a superficial protective layer on the metal?"

For several decades the corrosion behaviour of copper in acidic, neutral and alkaline solutions has been explored. In all cases the rate of oxidation of this and other metals is counter-balanced by the electrochemical oxygen reduction. In general, the corrosion rate is influenced by the pH, composition and temperature of the water; it is also infuenced by the the presence of microrganisms and bacterial adhesion in this same system or by presence of *NOM* and has its lowest value in slightly alkaline solutions.

This study focuses on the influence of pH and water chemistry on the corrosion rate of two representative metals (copper and lead/tin solder alloy) through a Voltammetric Analysis. Voltammetric experiments carried in this study were designed to understand the relationship between variations of corrosion rates of the metals exposed to waters having varying pH and total concentration of PO_4 and CO_3 . For the reasons described above we have chosen a pH range 7.3–9.0; metals that have been examined are copper and Pb/Sn alloy (50% Tin – 50% Lead).

Thus, the main objectives of the study are:

- Voltammetric examination of effects of pH on the electrochemical properties of copper and lead/tin solder alloys;
- Voltammetric examination of effects of carbonate and phosphate on the electrochemical properties of copper and lead/tin solder alloys;
- Incorporation of the data into a quantitative model describing the equilibrium speciation of solution components.

Voltammetry is an analytical technique based on the measure of the current flowing through an electrode placed in a solution containing electro-active compounds, while a potential scanning is imposed upon it. This electrode is called **working electrode** and could be made with a material of interest for any specific investigation. Usually, the working electrode has a relatively small surface; this is necessary to control quickly and accurately the potential imposed by an external electrical device (a potentiostat). Voltammetry is a versatile technique for research purposes, it allow to examine several aspects of the electrochemical reactions, namely those reactions in which electrons exchanges are involved between reagents and products. For those reactions it is possible to investigate on the laws governing the dependence of the current by the potential imposed on an electrode dipped into the reaction environment. The use of the voltammetric techniques is the basis of the comprehension of the laws concerning several electrochemical phenomena and has a great importance in several thecnological fields, like:

- Research of corrosion proof materials;
- Research of new electrodic processes for chemical industries (in fact, for example, million of tons of aluminium, chlorine, soda are produced by means of electrochemical reactions);
- Production of new type of batteries that can store rapidly a great quantities of energy.

One of the most important application of voltammetry is the *quantitative analysis of trace of metals* (or, anyway, of those reducible or oxidizable chemicals) at *μg/L* levels or less.

This study deals with the *quali-quantitative* aspects of the voltammetric analysis of metals, copper and alloy, subject to corrosion when immersed in an electrolyte as tap water.

Cyclic Voltammetry *(CV)* is the most often used electroanalytical technique. In this method, linear scan of the electrode potential is performed one or more time. In this way a redox couple in solution is exposed before to an oxidation and afterwards to a reduction (or vice and versa). A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, E^0, of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration. The equipment required to perform cyclic voltammetry consists of a conventional three-electrode potentiostat connected to three electrodes (working, reference, and auxiliary) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode (charge flows between the working electrode and the auxiliary electrode). A recording device (such as a computer or plotter) is used to record the resulting cyclic voltammogram as a graph of current versus potential. *Figure1* depicts a generic cyclic voltammogram. The potential (*E*) is graphed along the *x-axis*, the current (*i*) is plotted on the *y-axis* of the voltammogram, with anodic (*i.e.*, oxidizing) currents plotted *up* along the positive direction, and cathodic (*i.e.*, reducing) currents plotted *down* in the negative direction. A voltammogram is almost always plotted in this fashion by Europe electrochemists, but North American the axes are typically reversed.

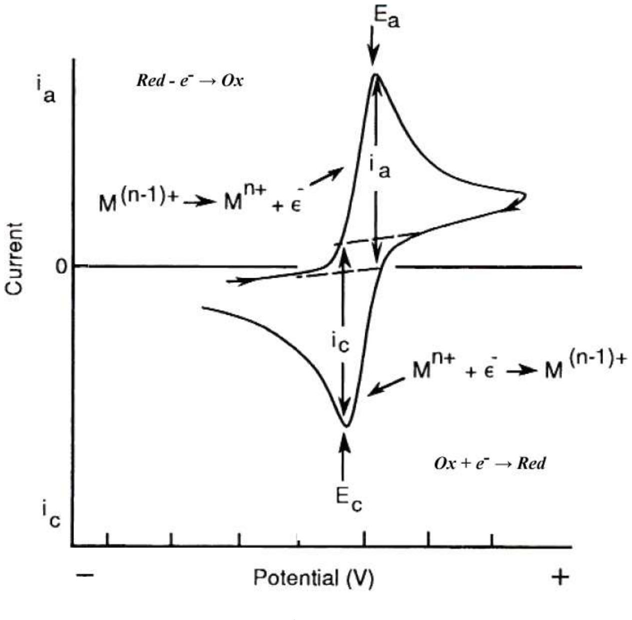

Figure 1

The peaks appearing in a voltammogram can be said to be similar, at least in some important cases, to those found in a spectrum or chromatogram. Each peak corresponds to a particular electroactive analyte in the test solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetric, with the leading side being very steep and the trailing side falling off gradually. The peaks observed during the reverse sweep have the same general shape as those seen in the forward sweep, but they are inverted because the direction of current flow is reversed. The first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) direction or in the negative (cathodic) direction. There is a great deal of quantitative information that can be gleaned from a high-quality cyclic voltammogram. First, it can be attest to see if a redox couple is indeed reversible.

The potential peak is the analytical parameter that allows to make a *qualitative* characterisation a redox couple in a solution. The formal potential, E^0, for a reversible redox couple is easily determined as the average of the two peak potentials as follows:

$$E^0 \cong E_{1/2} \cong \frac{E_a + E_c}{2}$$

The peak current height is proportional to the concentration of the electro-active compound in the solution:

$$i_p = K \cdot \left[Cu^{2+} \right]$$

and than correspond to the analytical parameter useful for a *quantitative analysis.*

Two kinds of working electrodes were used: a copper electrode of 1.0mm diameter and a lead/tin alloy electrode with a diameter of 1.58mm. The electrodes were constructed from spectroscopic grade copper (99.99%) and from 50%Sn-50%Pb alloy. The electrodes were 20cm long. Of those, 10cm were covered with fast curing liquid electrical tape to insulate them from ambient water (*Figure2*).

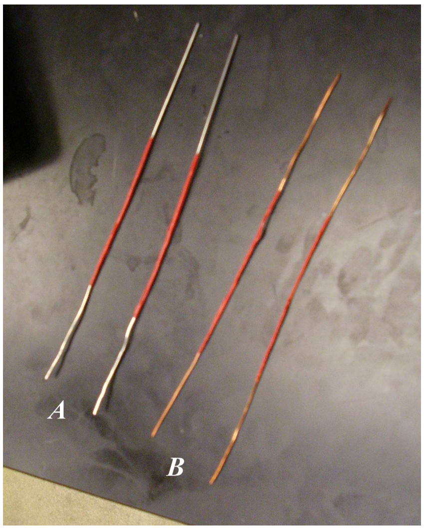

Figure 2 Working Electrodes: ***A***-Lead/Tin Electrodes - ***B***-Copper Electrodes

Each electrode had two exposed metal surfaces (5cm long), one was in contact with the solution and another on the back of each sample was an electrical contact. The geometrical area exposed to the solution was, for copper, 1.57cm^2, while for the alloy electrode it was 2.48cm^2. The experiments were carried out using three different solutions, with varying phosphate (PO_4), or carbonate concentration (CO_3) and also in the presence of both carbonate and phosphate. But for this three different solutions we had prepared several samples with a differents concentrations of phosphate and carbonate. The solution background composition was DI distilled water with a supporting electrolyte. In this study we used Sodium Perchlorate ($NaClO_4$= 0.05M) added to the test solution to ensure sufficient solution conductivity. For copper electrode, the cyclic scanning started in the anodic direction, starting with a potential of *-500mV* and ends with a potenzial of *300mV*; the sweep rate was *50mV/s*. For Pb/Sn electrode, the cyclic scanning starts in the anodic sense, starting with a potential of *-700mV* and ends with a potenzial of *0mV*; the sweep rate was *50mV/s*.

For copper we studied the effect in contact with three different solutions, DI distilled water with Phosphates, Carbonates and Phosphates plus Carbonates. The *pH* was not kept constant but we have chosen a *pH* range 7.3–9.0. For lead/tin solder alloys we studied the same effects as those examinec for copper, using the same solutions, *pH* range (7.3–9.0) and the same settings with which were conducted and described previous tests. The only change is the range of potential *E=[-700mV ; 0mV]*. This change is related to the different nature of material electrode in question.

The VA experiments described above clearly show that the oxidation and reduction currents indicative of corrosion processes at the surfaces of copper and lead/tin solder are influenced by the *pH* and concentrations of phosphate ion PO_4^{3-} and carbonate ion CO_3^{2-} (*Figures 3.A-B*).

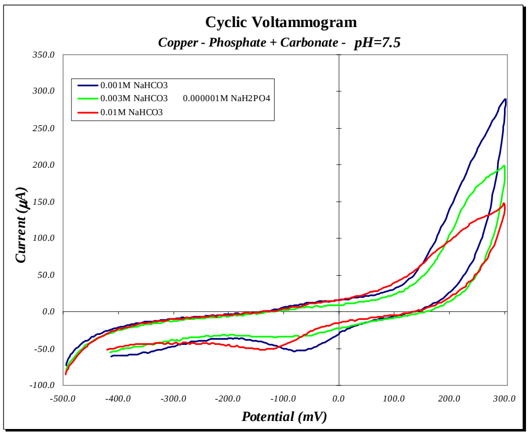

Figure 3.A – Cyclic Voltammogram: Copper Electrode, Phosphate + Carbonate, pH=7.5

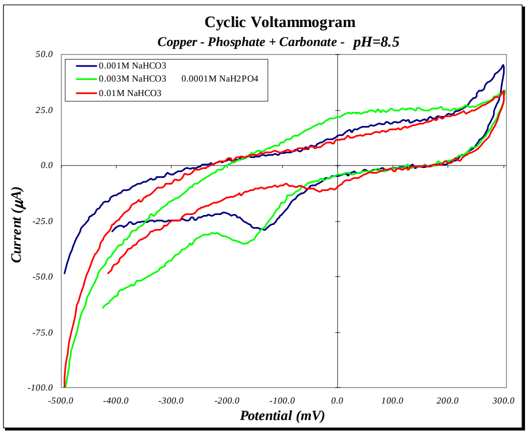

Figure 3.B – Cyclic Voltammogram: Copper Electrode, Phosphate + Carbonate, pH=8.5

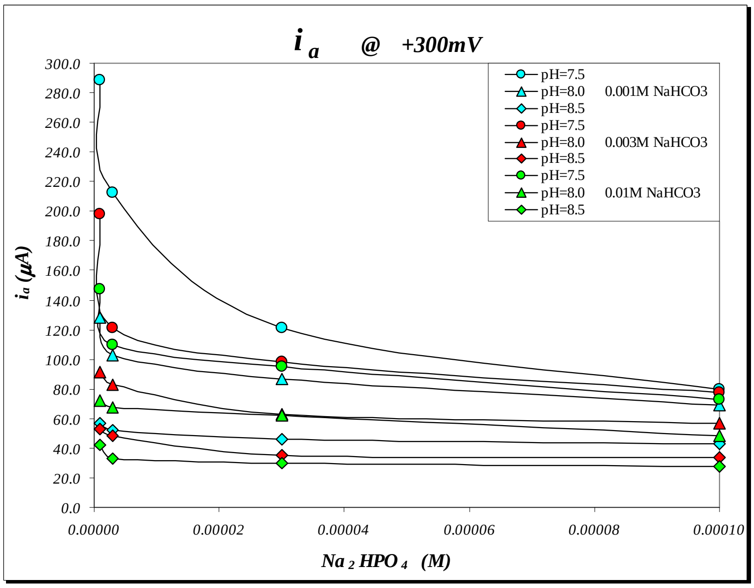

Figure 4 – Anodic Current: i_a different $[PO_4]$ and *pH*

To provide an explanation for these observations, we tried to use a mathematical expression that accounts for the process observed and studied in this work. For instance, the concentration of $\left[PO_4^{3-}\right]$, $\left[CO_3^{2-}\right]$ and $\left[HO^-\right]$ present in the solution at varying pHs can be determined as:

$$\left[PO_4^{3-}\right] = \frac{TotPO_4 \cdot k_1 \cdot k_2 \cdot k_3}{\left[H^+\right]^3 + k_1 \cdot \left[H^+\right]^2 + k_1 \cdot k_2 \cdot \left[H^+\right] + \left(k_1 \cdot k_2 \cdot k_3\right)}$$

$$\left[CO_3^{2-}\right] = \frac{TotCO_3 \cdot k_1 \cdot k_2}{\left[H^+\right]^2 + k_1 \cdot \left[H^+\right] + \left(k_1 \cdot k_2\right)}$$

$$\left[OH^-\right] = \frac{k_w}{\left[H^+\right]} = \frac{k_w}{10^{-pH}}$$

Where k_1, k_2 and k_3 are the deprotonation constants of phosphoric acid (the corresponding pK values are 2.2, 7.2 and 12.4). The data obtained in these calculations were incorporated into a model addressing the equilibrium speciation of solution components.

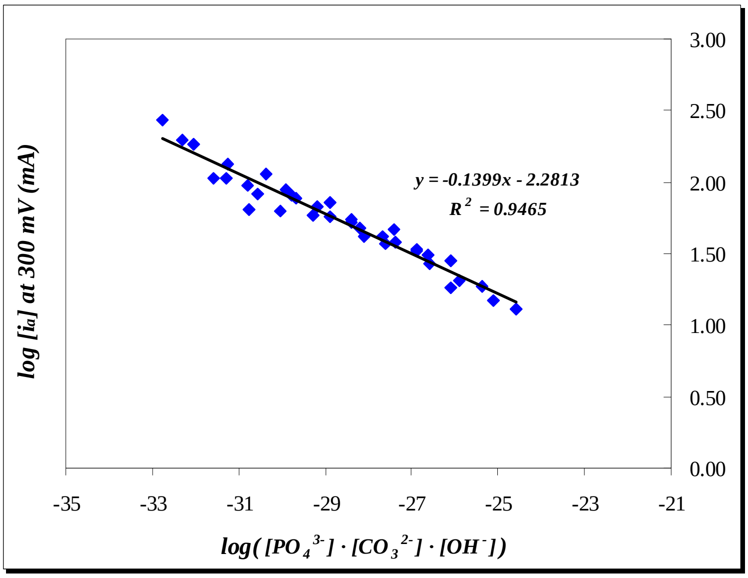

Figure 5 – Linear Trend: Log(i_a) *vs* Log($[PO_4^{3-}] \cdot [CO_3^{2-}] \cdot [OH^-]$)

Figure 5 shows an almost perfect linear relationship between the logarithm of VA anodic currents (at a given potential *E*) and the sum of logarithms concentrations of *ions* $\left[PO_4^{3-}\right]$, $\left[CO_3^{2-}\right]$ and $\left[HO^-\right]$. Based on the results of cyclic voltammetry it was examine the performance of a phenomenological equation describing the relationship between VA oxidation currents for copper with the concentration of PO_4 , CO_3 and the pH:

$$\log(i_E) = \log(i_0) + \alpha \log\left[PO_4^{3-}\right] + \beta \log\left[CO_3^{2-}\right] + \gamma \log\left[OH^-\right]$$

The VA experiments described above clearly show that the oxidation and reduction currents indicative of corrosion processes at the surfaces of copper and lead/tin solder are influenced by the *pH* and concentrations of phosphate ion PO_4^{3-} and carbonate ion CO_3^{2-} .

This inhibiting effect of these ions appears to be associated with their adsorption and their effects on the surface oxide films grown on copper and lead/tin solder. These effects can be summarized as :

- Examination of the VA data showed that increase of OH^- concentrations at higher *pHs* result in a positive effect on the electrochemical properties of copper and lead/tin solder alloys;

- VA data also show that a higher concentrations of phosphate and carbonates reduces the apparent corrosion rate of copper and lead/tin solder alloy;

- It should be noted that for copper, these inhibitors (*pH*, PO_4 and CO_3) act as anodic inhibitors and they do not seem to suppress cathodic currents, However, in the case of lead/tin solder alloy, these inhibitors do suppress the intensity of cathodic currents ;

- Of all species of phosphates and carbonates possibly present in the ambient water, only PO_4^{3-} and CO_3^{2-} ions affect the electrochemical properties of copper and Pb/Sn solder alloy. Calculations of concentrations of these ions at varying *pHs* and $TOTPO_4$ and $TOTCO_3$ levels allow developing strong phenomenological correlations between the equilibrium properties of drinking water (e.g., its *pH*, $TOTCO_3$, $TOTPO_4$) and, on the other hand, suppression of electrochemical oxidation and reduction current caused by these anions.

- More VA and other electrochemical experiments are needed to expand the approach developed in this study and incorporate effects of chloride, sulphate and natural organic matter into a phenomenological model relating levels and properties of these solution components and, on the other hand, electrochemical properties of copper, lead/tin solder and other metals exposed to drinking water.