UNIVERSITY OF NAPLES "FEDERICO II"

ENVIRONMENTAL ENGINEERING
MASTER DEGREE

Department of Hydraulic, Geotechnical & Environmental Engineering

ABSTRACT

Localization of Corrosion Potential and Metal Release in Galvanically Affected Zone in Drinking Water

SUPERVISORS:
Prof. Eng. Massimiliano Fabbricino
Prof. Eng. Gregory V. Korshin

CANDIDATE:
Mariano Crimaldi
Matr. 324/000231

Academic Year 2011-12

ABSTRACT

In water distribution systems, different kind of metals are used. The most common ones are Lead, Lead-Tin solder, Cast Iron, Copper and Copper alloys.

When two or more dissimilar metals with different electrode potentials come into contact in an electrolyte (i.e. water) a galvanic couple is set up, one metal acting as anode and the other as cathode. The electrolyte provides a means for ion migration whereby metallic ions can move from the anode to the cathode generating cathodic corrosion (or galvanic corrosion). Issues due to galvanic corrosion are common in parts made of different metals. Recent concerns have also been highlighted regarding effects of galvanic couples on water quality. For instance, Nyungen et al noticed that if Pb/Sn solder and Copper are coupled, there is an increase of Pb release in water with concentration of Chloride between 27 and $129^{mg}/_{L}$ and Sulfate concentration between 3 and $121^{mg}/_{L}$. Waters with high concentration of Chloride (as $NaHClO_4$) tend to sustain high galvanic currents because of the increasing conductivity of water, preventing passivation of the solder surface, and contributing to lead contamination of potable water supplies. Moreover, if the concentration of Carbonate (as $NaHCO_3$) is high, passivation of Lead is accelerated until a certain concentration of $NaHCO_3$. The total mass of lead corroded and released in water is consistent with predictions based on the galvanic current as shown in this work. Small changes in water chemistry can sometimes dramatically increase the likelihood of lead contamination from lead pipes, soldered joints, and lead-bearing brass. The properties and dimensions of galvanic affected zone are critically important for determining the magnitude and persistence of corrosion and metal release effects associated with galvanic coupling.

The length and distribution of corrosion potential (E_{corr}) can be potentially modified by changing some water properties like conductivity, pH, Carbonate concentration, Chloride concentration, Sulfate concentration, Phosphate concentration and others. Also, the effect of time has been studied showing that, on newly exposed lead surfaces coupled with copper piping, the effect of direct galvanic coupling can be substantial instead of aged and passivated surfaces of lead coupled with new copper surfaces. This study focuses on the localization of corrosion potential and metal release in galvanically affected zone in drinking water.

The data shown in this work proves that, in the case of $Pb/Sn - Cu$ coupling, the length of galvanic affected zone does not exceed a few centimeters on either sides of juncture.

The experimental work that follows attempts to verify the expectations of changing water salts concentration ($NaHCLO_4$; $NaHCO_3$; Na_2HPO_4), of changing water conductivity *per se*, the effect of time on passivation process and the concentration of metal released in drinkable water due to galvanic corrosion.

Thus, the main objectives of this study are:

- to establish the position and length of the galvanically affected zone and distribution of the corrosion potential;
- to study the effect of time on passivation process;
- to study the effects of water quality and conductivity on the galvanic affected zone;
- to study the concentration of metals released in drinkable water due to galvanic corrosion.

Corrosion occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte (i.e. water). Corrosion can also change chemistry of water, consuming oxidants and disinfectants in the water, producing suspensions of metal particles. Corrosion mechanism can be schematized very easily: The anode and cathode, as two different metals, have a potential difference that drives the reaction.

Metal ions formation can be described, for a generic metal (Me) with valency equal to n, by the reaction (1):

$$Me \rightarrow Me^{+n} + ne^- \tag{1}$$

Electron acceptors such as oxygen, chlorine, hydrogen ion in aqueous solution or the more noble metal serve to complete the reaction.

The generic global reaction, for generic metal (Me), is:

$$Me + \frac{n}{4}O_2 + nH_2O \rightarrow Me(OH)_n \tag{2}$$

For example, in presence of Iron, the metal hydroxide produced by reaction (3) is:

$$Fe \rightarrow Fe^{++} + 2e^- \tag{3}$$

$$2(OH)^- + Fe^{++} \rightarrow Fe(OH)_2 \tag{4}$$

The Iron hydroxide $Fe(OH)_2$ dissolves in water contributing to the amount of metal release and metal concentration in water.

Salts and other dissolved compounds can change the situation because the hydroxide generated by reaction (3) could be not soluble in water forming particles in suspension or deposit as scale on the corroding metal surface creating a protective film (i.e. passivation) that prevents the metal ions flux.

The harmful health effects from Lead exposure through drinking water have been historically recognized since the 1850s. Several studies (see Subramanian and Connor, 1991, for example) have noticed that the corrosion or dissolution of Pb-based solder joints associated with copper plumbing could be a significant source of Pb in water supplies. This study reports the results of an experimental study of water contamination by Pb and Cu release due to galvanic corrosion of Copper coupons coupled with Pb/Sn solder coupons.

EXPERIMENTAL SETUP

In order to study the effects of time and galvanic coupling on metal release in drinking water, two experimental setups have been set.

Sliding Electrochemical Cell

An electrochemical cell is a device used for generating an electromotive force (voltage) and current from chemical reactions, or the reverse, inducing a chemical reaction by a flow of current. The current is caused by the reactions releasing and accepting electrons at the different ends of a conductor. An electrochemical cell consists of two half-cells. The two half-cells may use the same electrolyte, or they may use different electrolytes. Each half-cell consists of an electrode and an electrolyte. Each half-cell has a characteristic voltage. Different choices of substances for each half-cell give different potential differences. In this case, due to two different metal connected, a particular type of electrochemical cell has been set: a Galvanic Cell.

In this study an unique Galvanic Cell has been developed. This cell has been made by a sliding basin as half-cell in order to measure the potential over the plates surface. The other half-cell is the reference electrode.

A reference electrode is an electrode which has a stable and well-known electrode potential, this allows the potential of the other half-cell to be determined. One problem with reference electrodes is that, in order to ensure a stable voltage, it is necessary to maintain a steady flow of electrolyte through the porous frit. Thus there is a gradual contamination of the test solution with electrolyte ions. This problem is solved by adding a second salt bridge, or junction to the reference electrode to insulate the inner $Ag/AgCl$ reference element from the sample. This secondary salt bridge can then be filled with a reference electrolyte solution which does not contain a contaminant to the sample. In this study, a saturated KNO_3 filling solution has been used.

In particular, a *Pine Instruments© RREF0024 Double Junction Ag/AgCl Reference Electrode* has been used. In conjunction with the reference electrode a working electrode has been used. The working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring. In this study, the copper plate has been set as working electrode.

The Sliding Electrochemical Cell scheme is shown in Figure 1

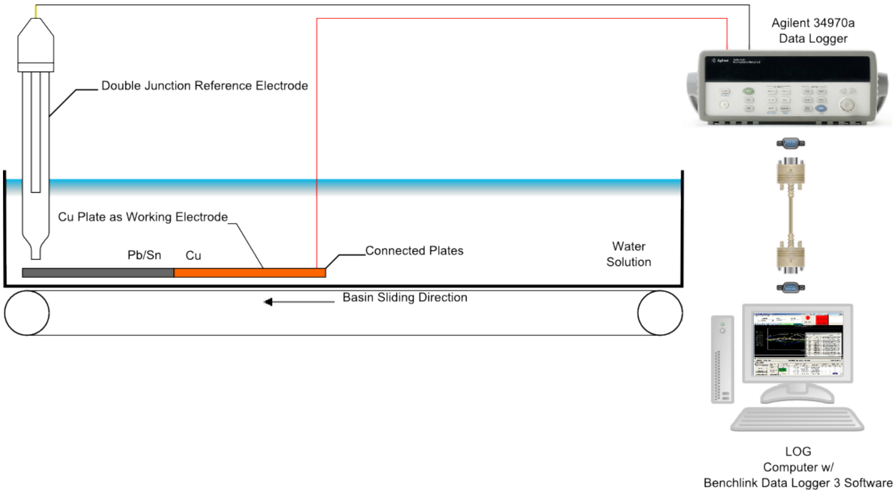

Figure 1: Scheme of Sliding Electrochemical Cell

The basin is filled with $1L$ of Seattle tap water, with different salt concentrations. The basin itself is connected to a sliding engine in order to provide the movement. The reference electrode is fixed in position by an holding arm. The reference electrode tip is about $1mm$ from the plates surface. The plates are connected each others by rubber bands in order to provide a stiff connection between the interface. This particular setup has been chosen because of its relatively easiness and flexibility of configuration. Different kind and geometries of metals can be used in the basin, also the open basin is indicated for easy sampling operations and water chemistry changes.

The reference and working electrodes are connected electrically to a data logger - multimeter (*AGILENT© 34970a*). The data logger is connected itself to a computer provided with *AGILENT © Benchlink Data Logger 3* software in order to log the potential measurements.

Jars

In order to study the effect of time on galvanic affected zone, a simple "jar" test has been set.

Two $1L$ jars have been fulfilled with Seattle Tap Water and hermetically closed to reduce the variation of oxygen concentration in the water. In every jar, two kind of metal coupons have been immersed, in particular, a half-divided $Pb - Cu$ plate in Jar 1 and two half-divided $Pb - Cu$ rods in Jar 2.

This kind of experiment has been made to understand the effect of time on galvanic coupling corrosive effect also with different kind of metal geometry (plates v. rods).

Water Chemestry

Water chemistry is one of the most important factor regulating the corrosion process in galvanic coupling.

Different water chemistry has been set in experiment 1 and experiment 2.

In experiment 1, the sliding basin has been filled with $1L$ Seattle tap water at room temperature (approx. $23^{\circ}C$) with different salt concentrations.

In experiment 2, jars has been filled with just $1L$ of Seattle tap water at room temperature.

In particular, in experiment 1, the scans have been made with different concentration of $NaHClO_4$and $NaHCO_3$ as in table below.

$NaHCO_3$	# scans	Salt Concentration	Conductivity
	1	$0.001M$	$271.5\frac{\mu S}{cm}$
	2	$0.0025M$	$573\frac{\mu S}{cm}$
	3	$0.005M$	$1052\frac{\mu S}{cm}$
	4	$0.01M$	$2038\frac{\mu S}{cm}$
	5	$0.025M$	$4580\frac{\mu S}{cm}$
	6	$0.05M$	$8540\frac{\mu S}{cm}$
	7	$0.1M$	$14100\frac{\mu S}{cm}$
$NaClO_4$	1	$0M$	$64.8\frac{\mu S}{cm}$
	2	$0.0001M$	$77.2\frac{\mu S}{cm}$
	3	$0.0003M$	$100\frac{\mu S}{cm}$
	4	$0.001M$	$183.4\frac{\mu S}{cm}$
	5	$0.003M$	$408\frac{\mu S}{cm}$
	6	$0.01M$	$1215\frac{\mu S}{cm}$

Table 1: Water chemistry in experiment 1

EXPERIMENTAL PROTOCOL

Experiment 1

Before setting the sliding machine, the metal coupons have been cleaned up with a metal brush and washed with a Methanol solution, then rinsed with microfiltrated water in order to remove any organic residual on the surface.

Then, the metal coupons have been connected with rubber bands and placed into the sliding basin.

The basin itself has been filled up with $1L$ Seattle Tap Water with different water chemistry.

The conductivity has been measured with *Orion Star A112 Conductivity Benchtop Meter* in standard conditions (22°C water temperature).

Afterwards, the reference electrode has been fixed on a holding harm with the tip distant $1mm$ from the plates surface.

To start the scan, all the electric connections have been made and the sliding speed set to have a scan time equal to *10 min* each. All the data has been logged with *AGILENT© 34970a Data Acquisition Unit* and computer software *AGILENT © Benchlink Data Logger 3*. The data logged has been processed subsequently with *Microsoft© Excel 2010* software.

Experiment 2

The jars experiment has been set dipping a metal coupon in $1L$ Seattle tap water placed in a air-free glass jar hermetically closed in order to eliminate the oxygen exchange between the air and water. Two kind of coupons geometry has been used. In Jar 1 a $10cm$ plate ($3.5cm$ Pb - $6.5cm$ Cu) has been dipped while in Jar 2 a $6cm$ long rod ($2cm$ Pb - $4cm$ Cu).

To study the metal release over time, daily and weekly samples have been taken.

In particular, $10mL$ daily samples from both jars, $12 \times .5mL$ weekly samples from jar 1 and $7 \times .5mL$ weekly samples from jar 2.

The weekly samples have been taken using a 12 tips Corning® Multipette® over the coupons surface, tips 1 and 12 placed on the edges of coupons and tips 4 and 5 across the galvanic interface. Each week, the water from jars has been changed with fresh Seattle tap water in order to have new independent weekly scans from the previous week and to assure that the water does not saturate by metal released from plates.

Every week, a slide scan has been made, then the coupons have been placed back in the jars with fresh Seattle tap water.

At the end of every month, all the samples collected have been used in a *Perkin-Elmer ELAN-DRCe inductively coupled plasma/mass spectroscopic* (ICP/MS) instrument in order to know the concentration of metal in water.

Goals

The main goal of this study is to understand how the distribution of galvanic corrosion changes with different conditions. Knowing the shape and distribution of galvanic corrosion and current could be very effective to choose an effective protection strategy. In theory, the degree and the distribution of galvanic corrosion damage can be expressed as an overall galvanic current and a distribution of the galvanic current density. Therefore, reliably estimating the galvanic current density or its distribution of a practical galvanic system is of great significance. Unfortunately, due to the complexity in geometric shape of some mixed-metal components, predicting the galvanic current and its distribution over a complicated component is actually difficult. In fact, apart from some very simple linear systems, no theoretical potential or current expression has been deduced so far for a complicated galvanic system. That is why a simple plates system has been used.

Modeling

If there are two pieces of metals (a) and (c) joined up (Figure 2),

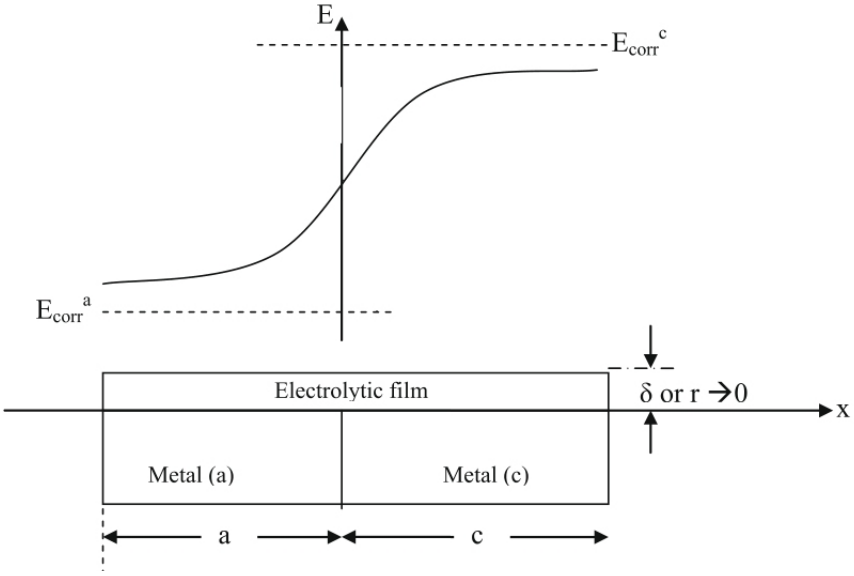

Figure 2: Schematic illustration of two coupled systems (a) and (b) and corresponding potential distribution.

each metal will be equivalent to a "dead end" single piece metal and the potential and current of the system can be obtained as:

$$E^a = E^a_{corr} + \frac{(E^c_{corr} - E^a_{corr})\sqrt{\rho^a_p}\,\tanh(\frac{c}{L^c})}{\left[\sqrt{\rho^a_p}\,\tanh(\frac{a}{L^a}) + \sqrt{\rho^a_p}\,\tanh(\frac{c}{L^c})\right]}\left[\frac{\cosh(\frac{x}{L^a})}{\cosh(\frac{a}{L^a})}\right] \tag{5}$$

with $0 \leq x \leq a$, and:

$$E^c = E^c_{corr} + \frac{(E^a_{corr} - E^c_{corr})\sqrt{\rho^c_p}\,\tanh(\frac{a}{L^a})}{\left[\sqrt{\rho^a_p}\,\tanh(\frac{c}{L^c}) + \sqrt{\rho^c_p}\,\tanh(\frac{a}{L^a})\right]}\left[\frac{\cosh(\frac{x-a-c}{L^c})}{\cosh(\frac{c}{L^c})}\right] \tag{6}$$

with $a \leq x \leq a + c$, and where:

- E_{corr}= corrosion potential relative to the reference electrode;
- E^a_{corr}= corrosion potential of material a relative to the reference electrode;

- E^c_{corr}= corrosion potential of material c relative to the reference electrode;
- a, c = length of material a and c;
- L^a= characteristic distance of material a;
- L^c= characteristic distance of material c;
- ρ^a_p= polarization resistivity of material a;
- ρ^c_p= polarization resistivity of material c.

RESULTS AND DISCUSSION

Experiment 1

According to experimental protocol the results of the scans made with different concentration of $NaHCO_3$ are the following.

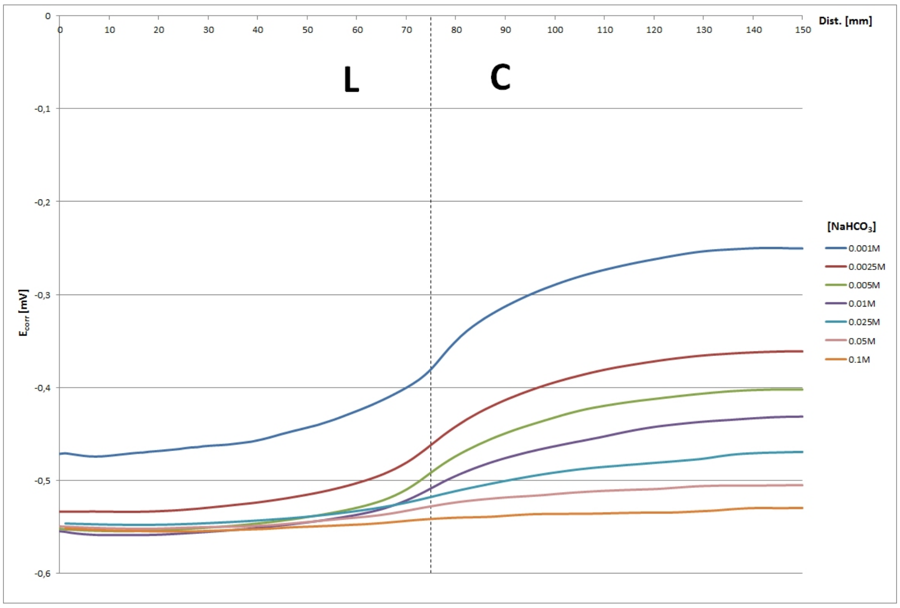

Figure 3: Experiment 1 results for different $NaHCO_3$ concentrations

While the scans with only Cu and Pb plates, in order to calculate the E^a_{corr} and E^c_{corr} are the following.

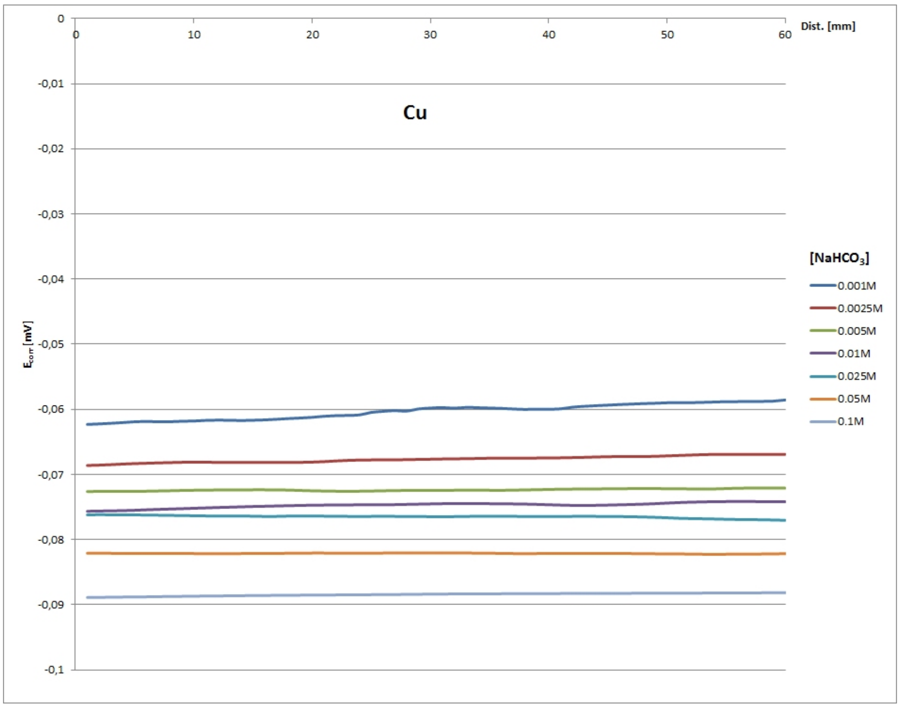

Figure 4: Experiment 1 results - Cu plate scanned with different $NaHCO_3$ concentrations

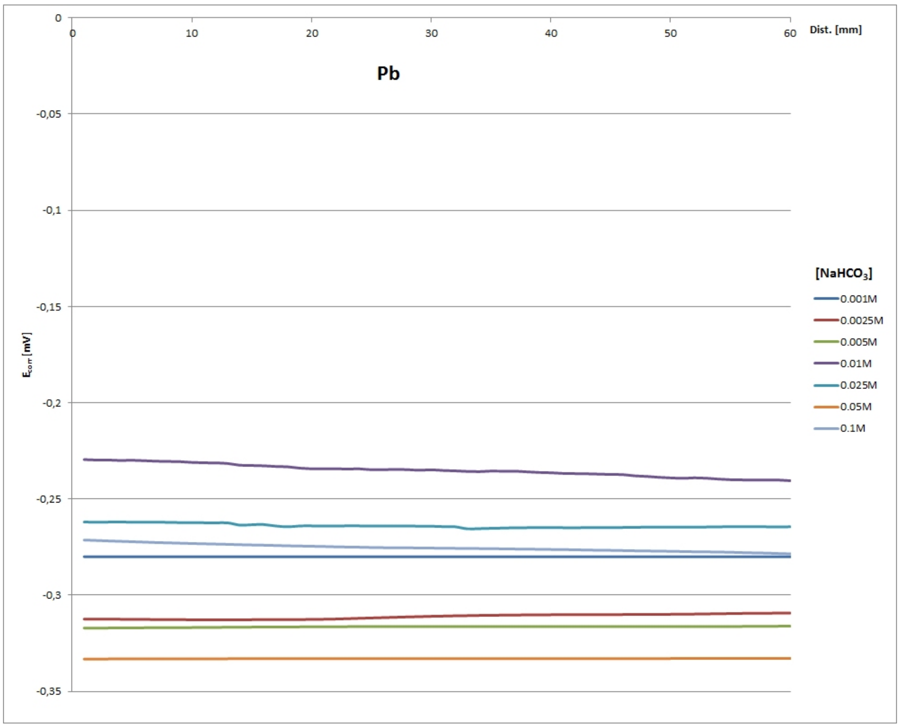

Figure 5: Experiment 1 results - Pb plate scanned with different $NaHCO_3$ concentrations

In Figure 3 is possible to see the typical shape of $E_{corr} - x$ model.

With different $NaHCO_3$ concentration, the shape of model is different. Rising the $NaHCO_3$ concentration is possible to see how E_{corr} drops substantially while the length of galvanically affected zone gets wider from the connection. (Figure 3)

As example, in Figure 6 is shown the calculation of E^a_{corr}, E^c_{corr}, L^a and L^c for $NaHCO_3 = 0.001M$. The calculation is the same for the other concentrations.

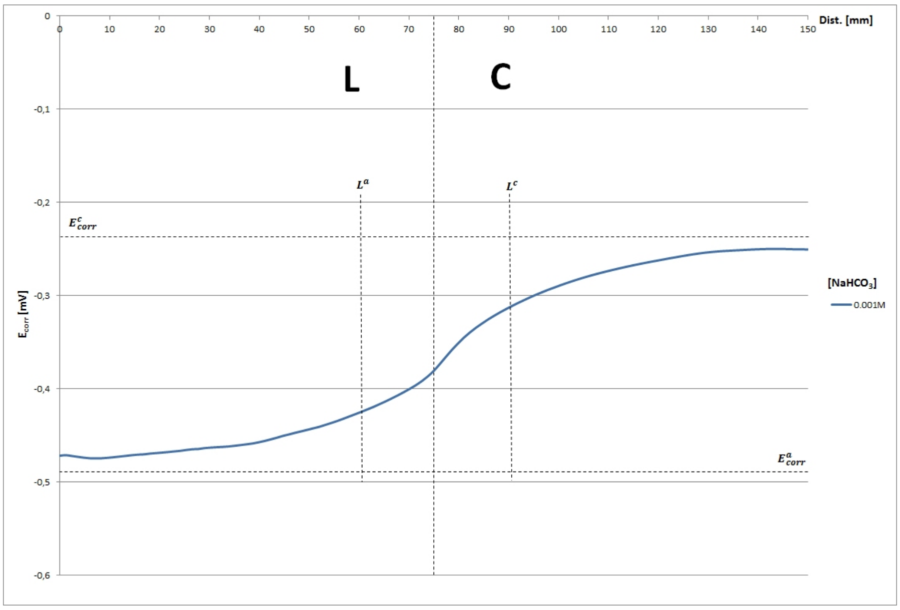

Figure 6: Calculation of E^a_{corr}, E^c_{corr}, L^a and L^c for $NaHCO_3 = 0.001M$

The results of the scans made with different concentration of $NaClO_4$ are the following.

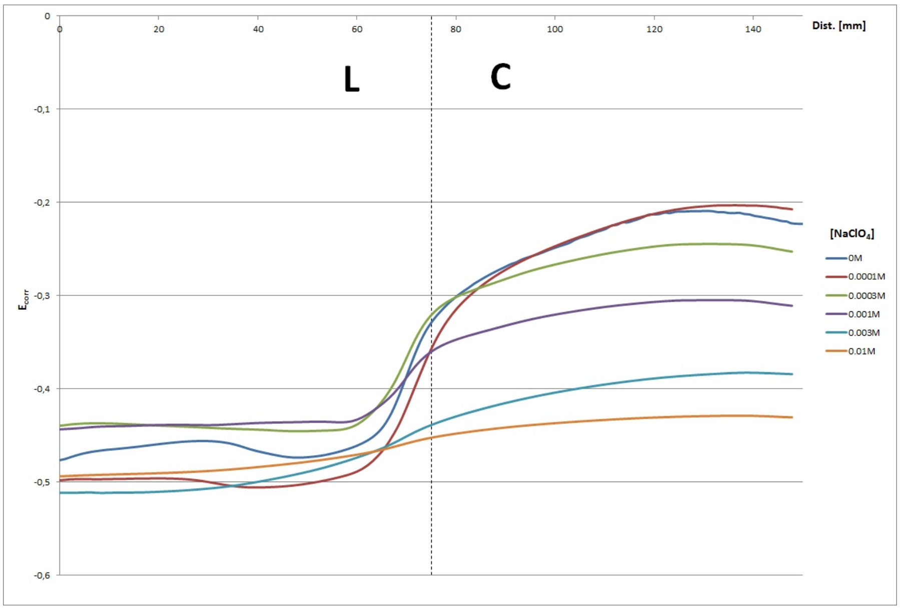

Figure 7: Experiment 1 results for different $NaClO_4$ concentrations

As in Figure 3 is possible to see how the shape of $E_{corr} - x$ model changes with different concentrations of $NaClO_4$.

E_{corr} drops substantially while the length of galvanically affected zone gets wider from the connection (Figure 7) as with changing concentration oh $NaHCO_3$.

Also in this case, as example, in Figure 8 is shown the calculation of E^a_{corr}, E^c_{corr}, L^a and L^c for $NaClO_4 = 0.001M$. The calculation is the same for the other concentrations.

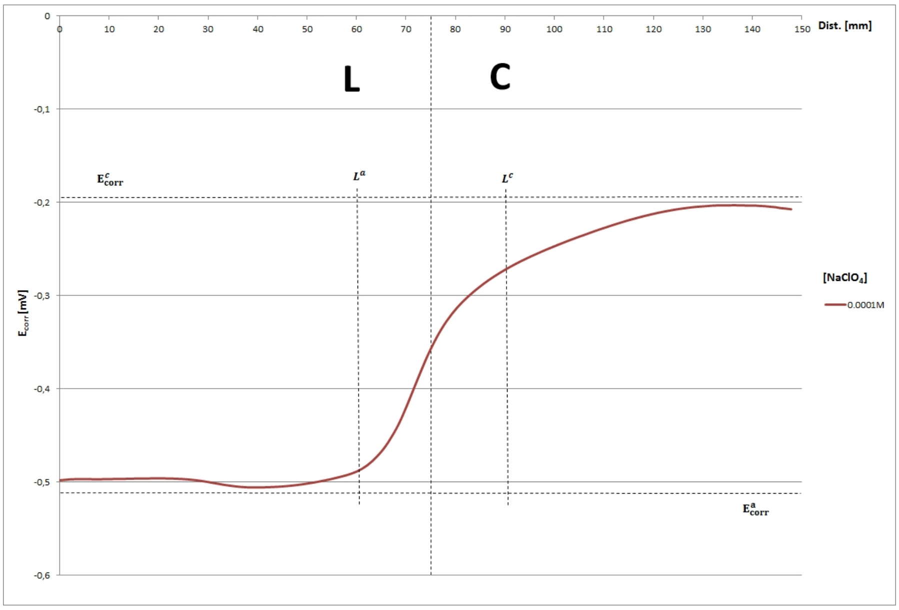

Figure 8: Calculation of E^a_{corr}, E^c_{corr}, L^a and L^c for $NaClO_4 = 0.001M$

Profiles Fitting

Using the numerical model described above is possible to produce several charts showing how the length of galvanically affected zone changes with different $NaHCO_3$ and $NaClO_4$ concentrations and how is related to the conductivity of water solution.

For $NaHCO_3$ concentration, different profiles fitting have been modeled. In Figure 9 is possible to see the model relating the length of galvanically affected zone vs. $\sqrt{\rho}$ square root of conductivity regarding the copper side of plate.

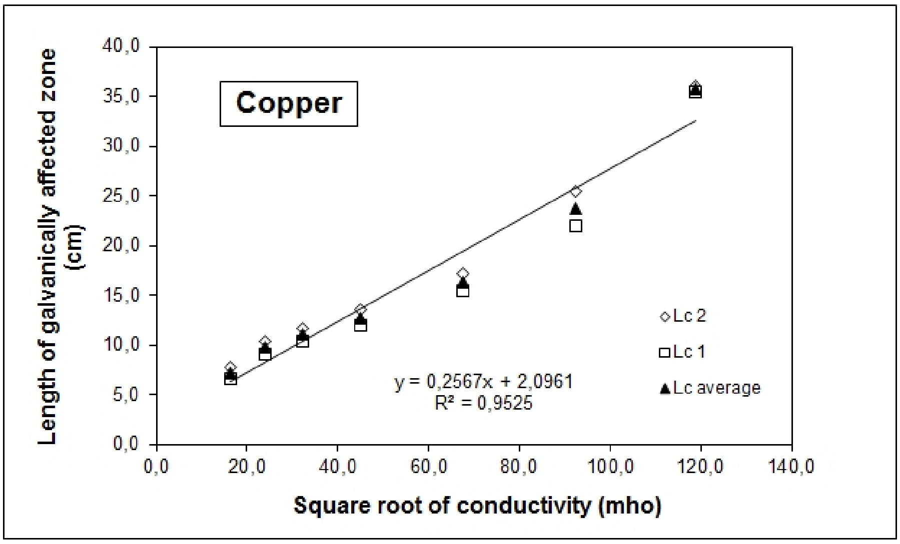

Figure 9: Length of galvanically affected zone vs. $\sqrt{\rho}$ - Copper side

While in Figure 10 is shown the relationship between the length of galvanically affected zone and $\sqrt{\rho}$ for the Lead side of plate.

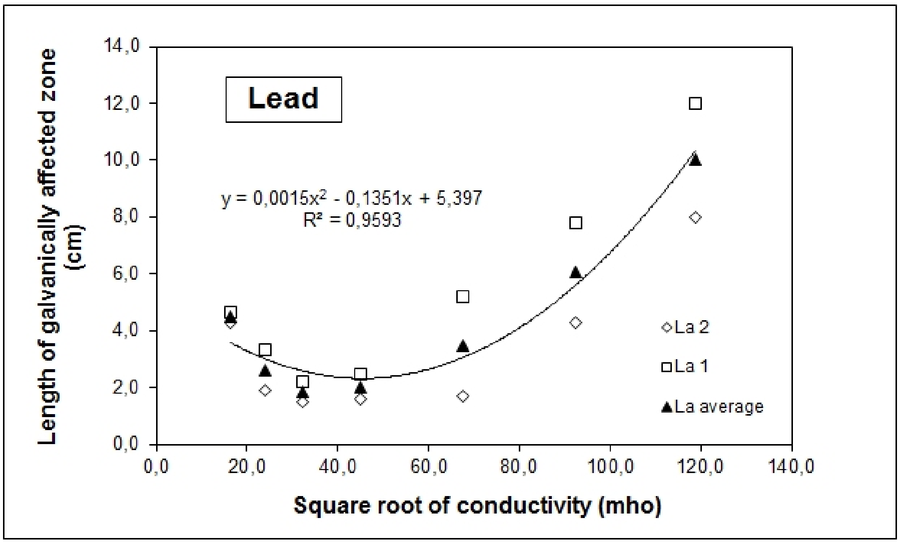

Figure 10: Length of galvanically affected zone vs. $\sqrt{\rho}$ - Lead side

In Figure 11 and Figure 12 is possible to see the relation between the length of galvanically affected zone and the concentration of $NaHCO_3$.

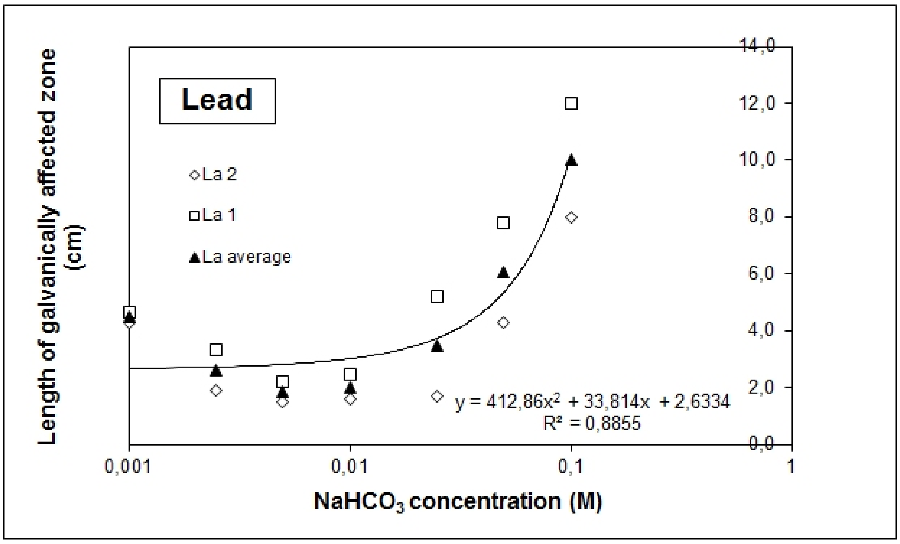

Figure 12: Length of galvanically affected zone vs. $NaHCO_3$ - Lead side

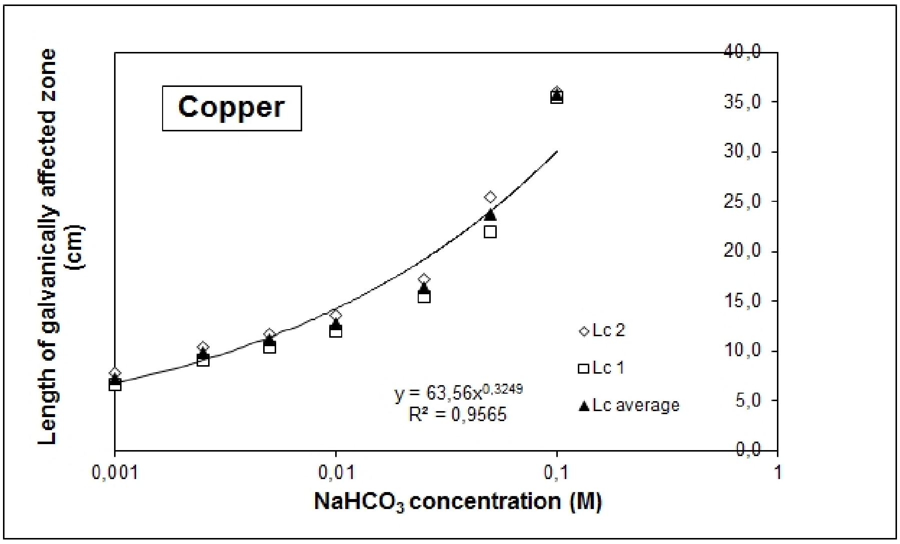

Figure 11: Length of galvanically affected zone vs. $NaHCO_3$ concentration - Copper side

The concentration of $NaHCO_3$ has been related also to $\frac{\rho_a}{\rho_c}$ ratio in order to understand the relation between the conductivity and salt concentration as shown in Figure 13.

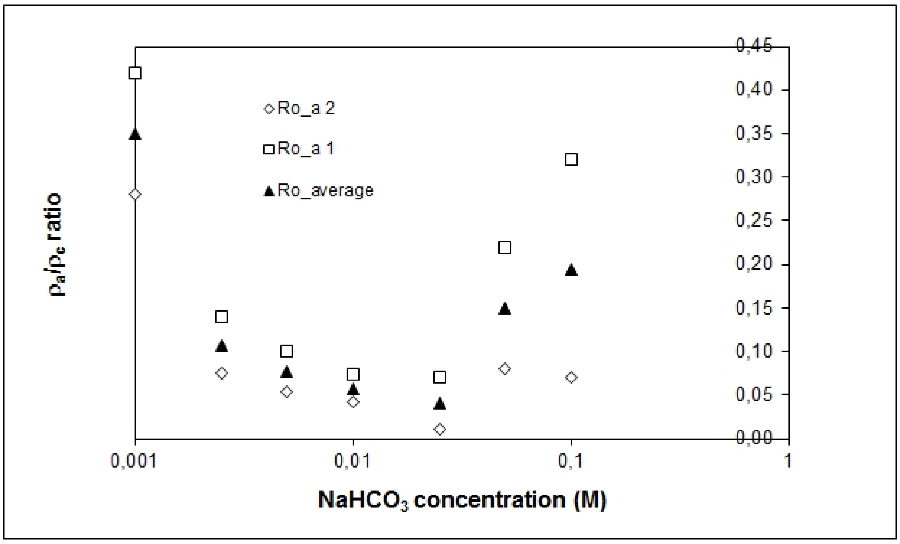

Figure 13: $\frac{\rho_a}{\rho_c}$ ratio vs. $NaHCO_3$ concentration

Moreover the $\frac{\rho_a}{\rho_c}$ ratio and $\frac{R_a}{R_c}$ ratio have been related to the square root of conductivity $\sqrt{\rho}$ as in Figure 14 and Figure 15.

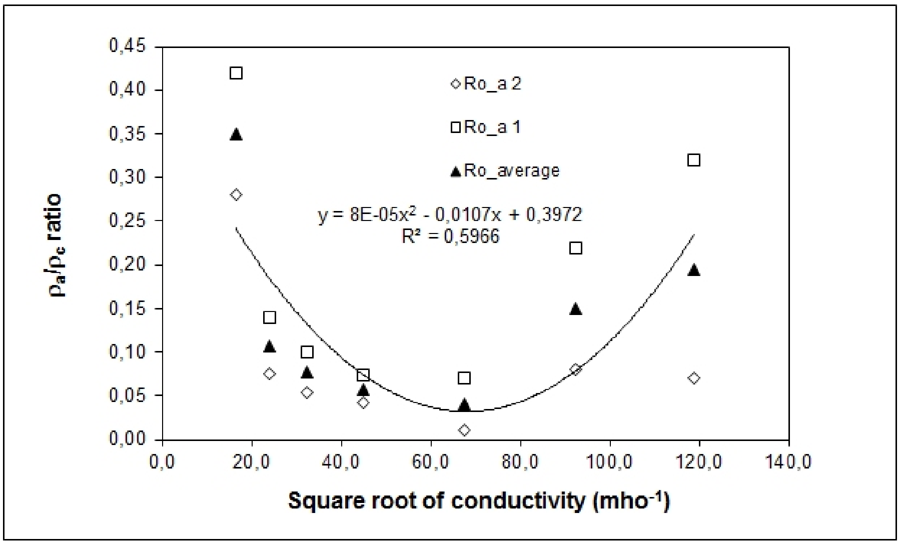

Figure 14: $\frac{\rho_a}{\rho_c}$ ratio vs. $\sqrt{\rho}$ - $NaHCO_3$

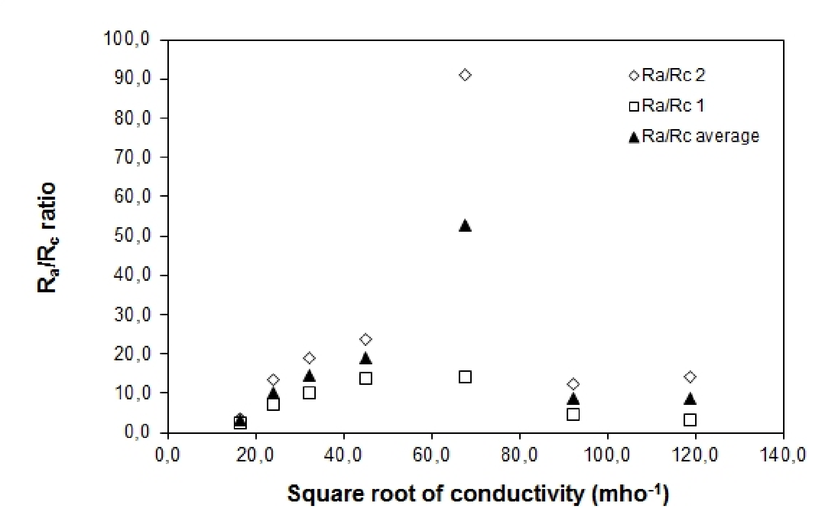

Figure 15: $\frac{R_a}{R_c}$ ratio vs. $\sqrt{\rho}$ - $NaHCO_3$

Regarding $NaClO_4$, as above, different profiles fitting have been modeled. In Figure 16 and Figure 17 is possible to see the relationship between the length of galvanically affected zone vs. the square root of conductivity.

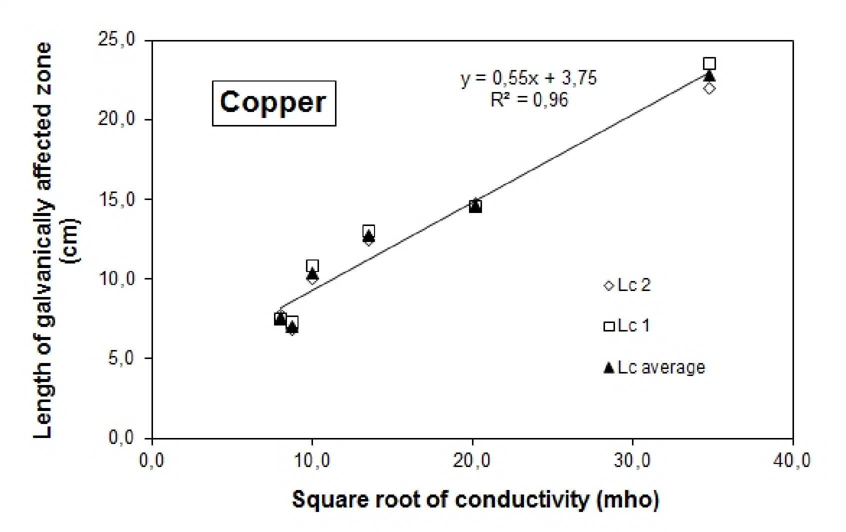

Figure 16: Length of galvanically affected zone vs. the square root of conductivity - Copper side

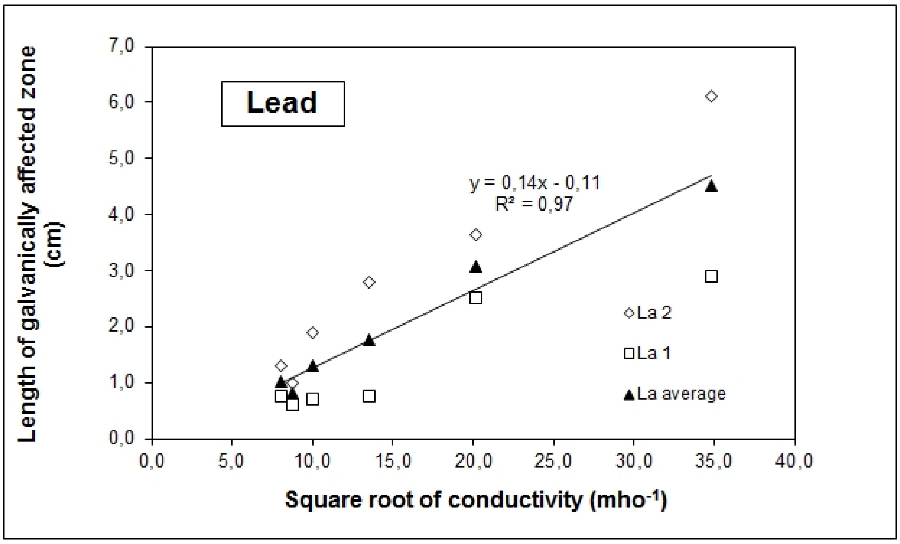

Figure 17: Length of galvanically affected zone vs. the square root of conductivity - Lead side

As above, also the $\frac{\rho_a}{\rho_c}$ ratio and $\frac{R_a}{R_c}$ ratio have been related to the square root of conductivity $\sqrt{\rho}$ as shown in Figure 18 and Figure 19.

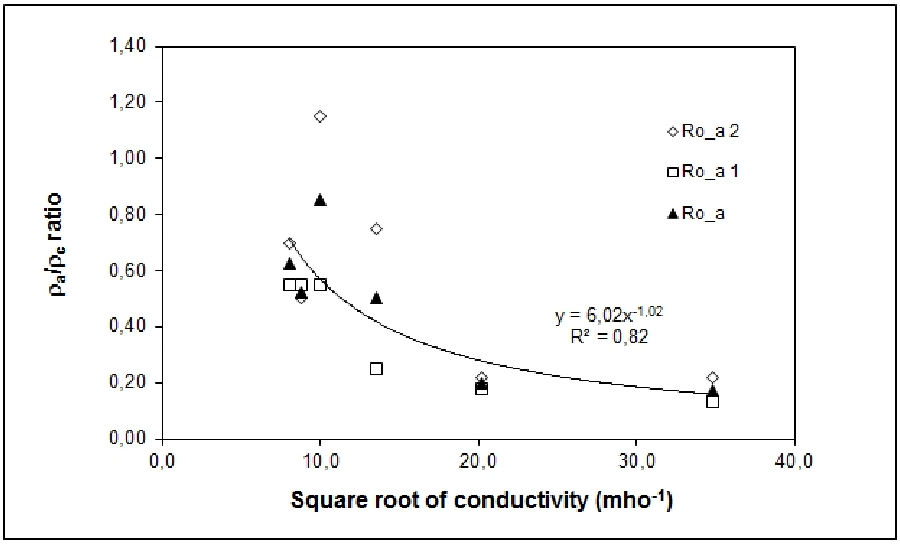

Figure 18: $\frac{\rho_a}{\rho_c}$ ratio vs. $\sqrt{\rho}$ - $NaClO_4$

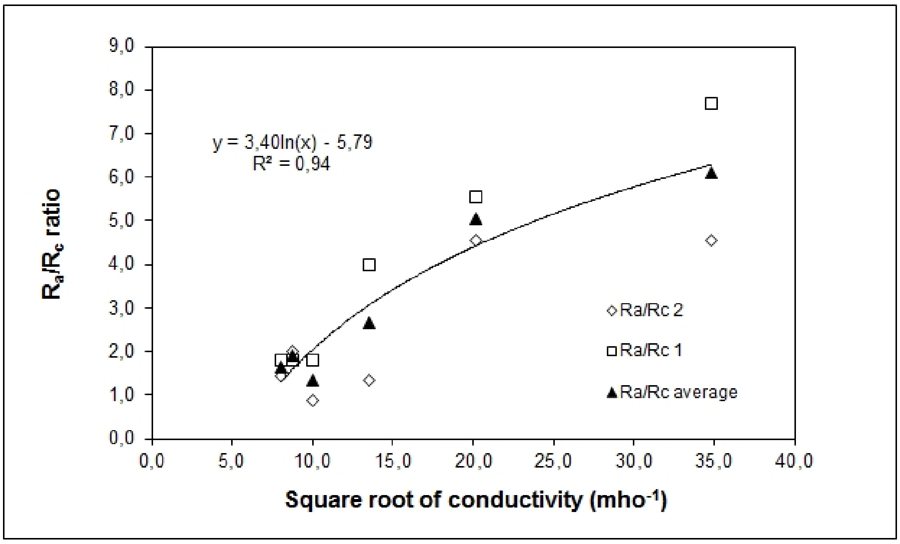

Figure 19: $\frac{R_a}{R_c}$ ratio vs. $\sqrt{\rho}$ - $NaClO_4$

The models above show how raising the conductivity as concentration of $NaHCO_3$ there is the formation of a protective film on the plate, faster on Lead side than on Copper side. If the concentration of $NaHCO_3$ raises over a certain value, there is the formation of carbonate compounds that break the protective film so the Lead is not protected anymore from corrosion.

Otherwise, raising the concentration of $NaClO_4$ as electrolyte, there is more galvanic current flowing, so the corrosion of Lead is faster than Copper. It is possible to see this effect in Figure 13, Figure 14, Figure 15, Figure 18 and Figure 19.

While in Figure 9, Figure 10, Figure 11, Figure 12, Figure 16 and Figure 17 is possible to see how the length of galvanically affected zone gets wider with different concentration of $NaHCO_3$ and $NaClO_4$ and with different values of conductivity as $\sqrt{\rho}$, as expected and shown in Figure 3 and Figure 7.

Experiment 2

According to experimental protocol, daily samples over a month have been taken from both Jar 1 and Jar 2 and analyzed with an ICP/MS system to know the concentration of metal released.

In Figure 20 is possible to see the concentration of Lead in Jar 1 over a month.

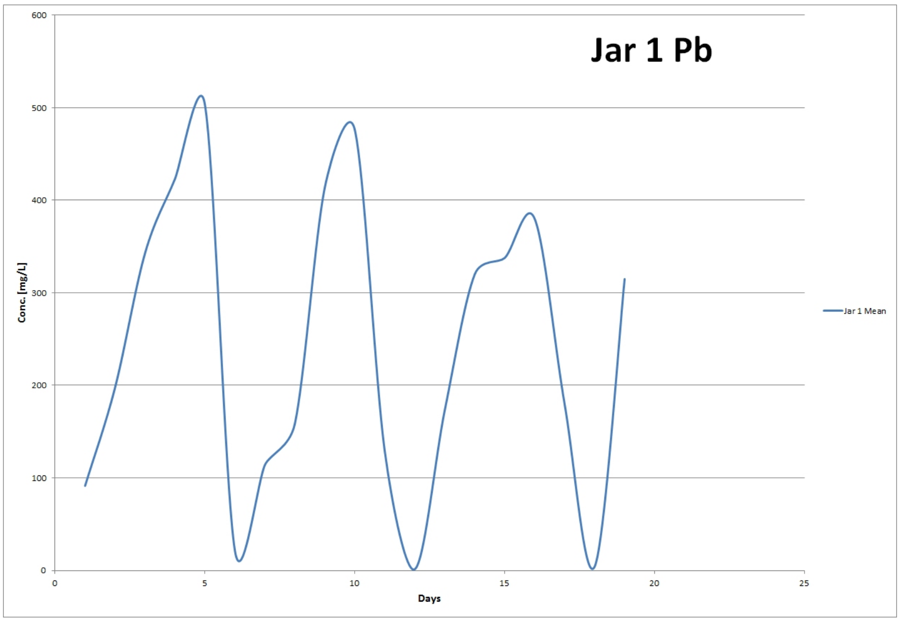

Figure 20: Daily samples results for Jar 1 - Pb

The concentration of Pb decreases over a month due to passivation of the surface.

The concentration of Cu in Jar 1 over a month is reported in Figure 21.

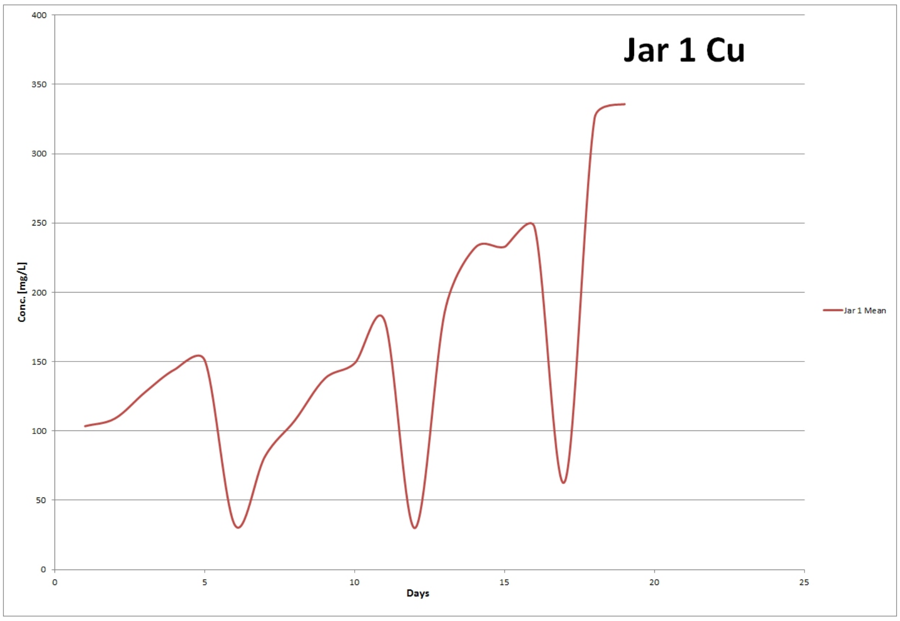

Figure 21: Daily samples results for Jar 1 - Pb

Despite the Pb concentration, in this case Cu concentration is raising over a month because there is probably no passivation on Copper.

The concentration of Lead in Jar 2 over a month is reported in Figure 22.

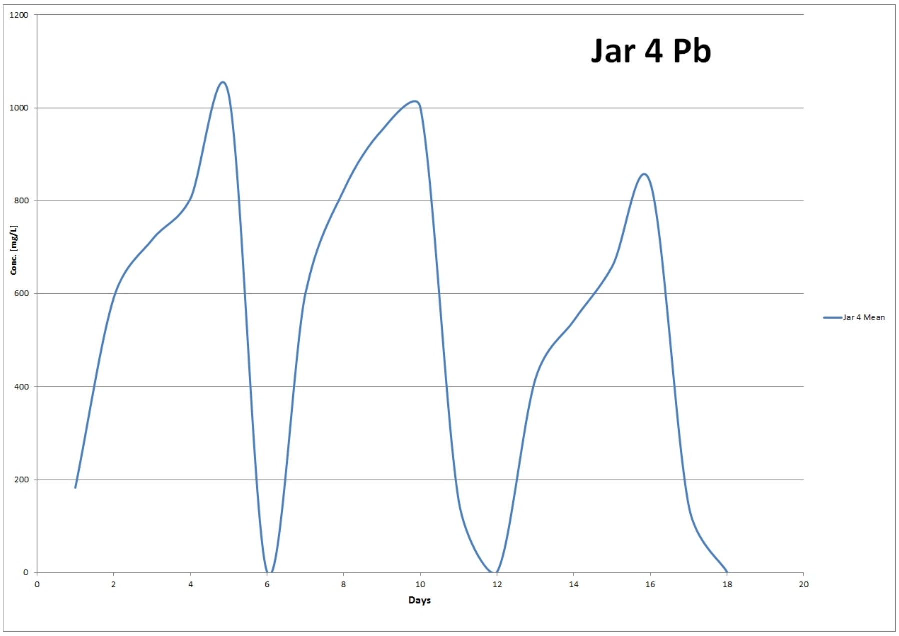

Figure 22: Daily samples results for Jar 2 - Pb

While the concentration of Copper in Jar 2 over a month is reported in Figure 23.

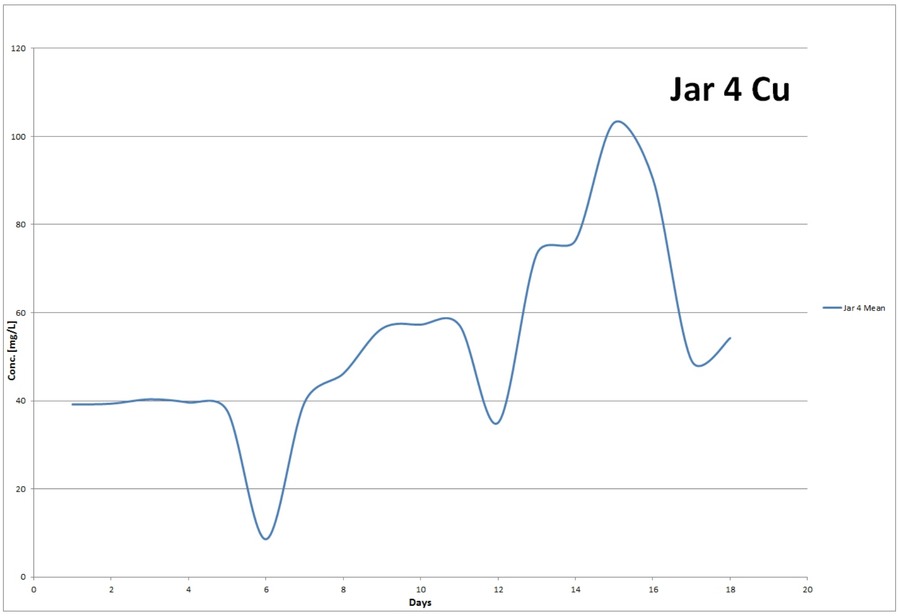

Figure 23: Daily samples results for Jar 2 - Cu

As in Jar 1, the concentration of Pb decreases due to passivation while the concentration of Cu raises.

Comparing the daily samples of Jar 1 and Jar 2 is possible to assume that the geometry of coupons used in Jar experiment (**??**) does not affect the mechanism of galvanic corrosion and metal release.

The weekly scans using the sliding machine (**??**) for Jar 1 are reported in Figure 24.

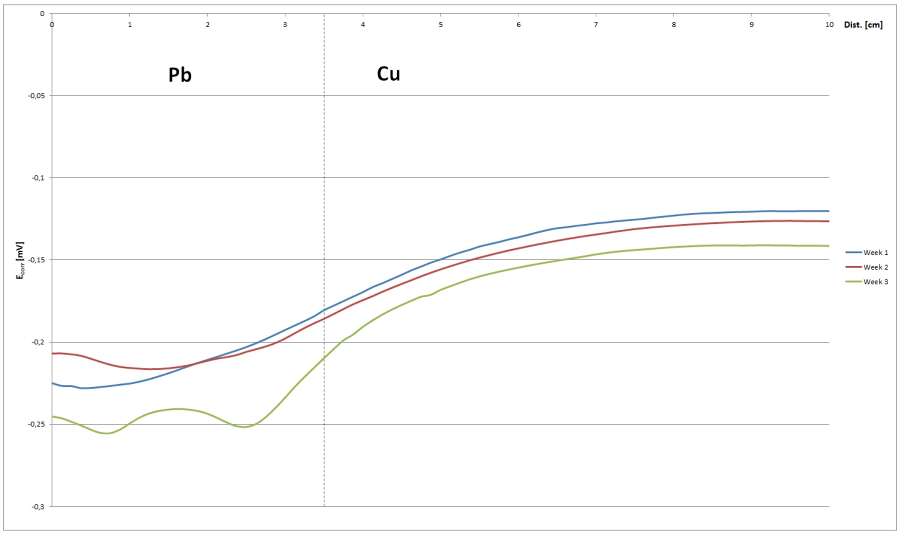

Figure 24: Weekly scans - Jar 1

While the weekly scans for Jar 2 are reported in Figure 25.

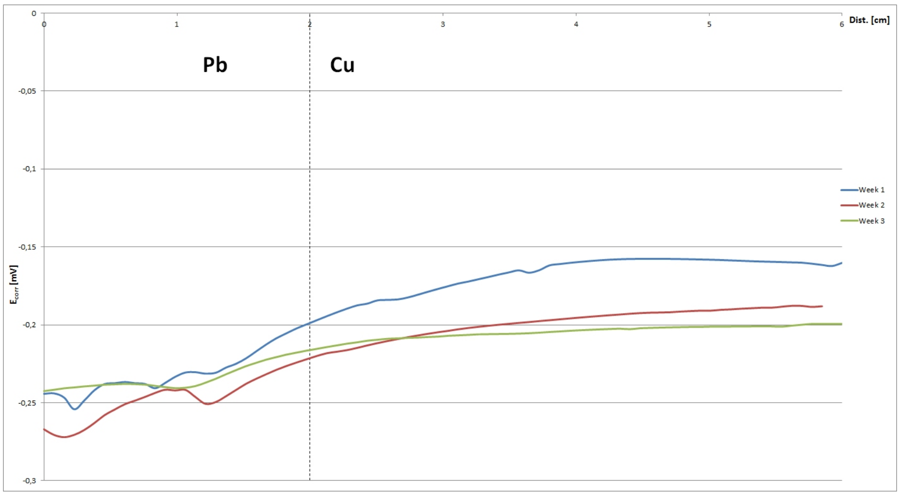

Figure 25: Weekly scans - Jar 2

These results show how also time can change the shape of model. In Figure 24 and Figure 25 is possible to see how the E^a_{corr}, E^c_{corr} and the length of galvanic affected zone changes over time as with changing salt concentration. This is possibly due to the formation of a protective film over the surface during time known as "passivation".

CONCLUSIONS

The results of experiment 1 show how the conductivity of water as concentration of $NaHCO_3$ can change the length of galvanic affected zone and the difference of E_{corr} potential. Raising the concentration of $NaHCO_3$, the length of galvanic affected zone gets wider on the Copper side of plates than the Lead side until a certain value of $NaHCO_3$ concentration. Over this value, there is the formation of carbonate compounds that break the protective film on Lead surface letting the Lead corrode quickly while L^a becomes wider.

Rising the concentration of $NaClO_4$ as electrolyte, there is an increase of galvanic current letting the Lead corrode quickly as Copper. Also the length of galvanic affected zone gets wider on both sides of plate.

The results of experiment 2 show how also time can affect the E_{corr} value, the length of galvanic affected zone and the amount of metal released in water.

The concentration of Lead decreases over time due the passivation regardless of the shape of coupons used on the contrary for the concentration of Copper that rises over time because there is no passivation over Copper surface.

The weekly scans done in experiment 2 also demonstrate that time can change the value of E_{corr} and $L^{a/c}$. Due to formation of a protective film over Lead surface, the length of galvanic affected zone gets wider while the difference between the corrosion potential of Lead and the corrosion potential of Copper ($E^c_{corr} - E^a_{corr}$), decreases over time.

Further Studies

The methodology used in this work and the kind of machine created are suitable for almost infinite possibilities of studies about the galvanic corrosion. It is possible to have different metals connected, different shapes of coupons and different water chemistry.

According to the results of experiments in this work, the Author proposes to continue the studies also with changing Na_2HPO_4 concentration and continue wit the Jar experiment over a longer time.

Also, the Author proposes to continue the study with flowing water electrochemical cells instead of the one with static water used in this work.