

Contribution To Comprehensive Study Of Aluminium Alloy Aa 5083 Corrosion Induced By Elemental Mercury In LNG Industries.

D.Zerouali*, Z. Derriche And M.Y.Azri

Department of Chemistry, Faculty of Sciences, Laboratory of materials,
University of Sciences & Technology of Oran
U.S.T.O. BP -1505 el M'naouer Oran 31000 –Algeria
djizeroual@yahoo.fr – Phone (213)41582268

ABSTRACT

Corrosion induced by elemental mercury in aqueous media of industrial Aluminium alloys AA5083 used in heat exchanger industries of natural gas liquefaction has been studied by linear sweep voltammetry on rotating amalgamated disk electrode. Corrosion process depends on:

- *Chemical processes of amalgamation of aluminium with mercury.*
- *Diffusion process of aluminium in amalgam.*
- *Electrochemical oxidation of aluminium on amalgamated Interface/water.*

The diffusion step appears different from that usually found in studies of aqueous corrosion and was not dependent on rotation of electrode but on diffusion of dissolved aluminium in the amalgam before the electrochemical oxidation of amalgamated metal. This is the limiting step of the process at stationary phase of the chemical amalgamation. This occurs at contact time mercury-aluminium longer than 36 min .For shorter times less than 30 min, chemical amalgamation controlled the process. Characteristic parameters of electrochemical behaviour of amalgamated electrodes were investigated: time of cathodic deposit of mercury, time of immersion of electrode in electrolyte before polarisation as well as potential scanning rate.

INTRODUCTION

Aluminium alloys are successfully used in industries because they have a good corrosion resistance, good thermal and electrical conductivity and low density, which make them very competitive material for the heat exchangers in liquefaction of natural gas industry.

However, impurities like moisture and mercury¹ which meet in different layers of natural gas and interact with the metal equipments and sometimes cause a significant corrosion².

Aluminium alloys weakly resist corrosion in aqueous medium in the presence of mercuric compounds because aluminium

and its alloys are very reactive when they are not protected by their oxide film³.

The mechanism of reactivity is due to the adsorption of mercury, formation of amalgam film and activation of aluminium surface⁴.

Many interesting studies of mercury elimination are in progress. These results are not satisfactory because they do not allow a complete elimination of mercury. Concentrations of about 10 nanograms of mercury per normal cubic meter of gas and more are frequently encountered⁵ and corrosion appears after physical adsorption and local concentration of residual mercury in the equipments.

Mechanism of corrosion depends on many factors like adsorption of mercury on aluminium surface, electrochemical oxidation and intergranular diffusion⁶ of mercury in aluminium bulk. However, it appears that diffusion of aluminium in amalgam can be the limiting step of corrosion process.

Electrochemical behaviour of amalgamated industrial aluminium alloy type AA 5083 in aqueous medium containing chloride ions was investigated. Single voltammograms were plotted to identify the determinant stage of the process of corrosion.

EXPERIMENTAL

The samples were supplied by the Algerian natural gas industry and have a chemical composition data given in Table 1.

Samples were mechanically formed with a cylindrical form of 3mm diameter. These samples were inserted under press in Teflon ends adapted to an EDX type rotating disk electrode.

Electrolytes were prepared from doubly distilled water by the addition of KCl crystals to 1M concentration for all experiments. pH was adjusted to approximately 7 by the addition of HCl or KOH. All reagents were PROLABO products of analytical grade.

Amalgamated electrodes were prepared separately by cathodic deposition of mercury on mechanically and chemically cleaned surfaces of the samples at a constant potential $E = -0,15$ volt/ECS using 10^{-4} M HgCl₂ solution. Time of mercury deposition was 6-48 min according to experiments. Temperatures, measured before and after each experiment, were approximately $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

Voltammograms were plotted using a Tacussel 40 -1X type potentiostat driven with pilot type Servovit and registred on XY table model Leybold. Saturated calomel reference electrode (SCE) and counter-electrode of 2 cm² area of platinum plate were used.

Scans started from cathodic potential $E_i = -1.8$ volt /SCE to an anodic potential

$E_f = -0.8$ volt /SCE. Rotations of electrode were 5000 rpm for all experiments.

Table 1. Chemical composition of aluminium alloy type AA5083

Element	%mass
Mg	4 – 5
Zn	0.25
Si	0.4
Fe	0.4
Cu	0.1
Mn	0.4 – 1
Ti	0.25
Cr	0.05 – 0.25
Other	0.15
Al	Remainder

RESULTS AND DISCUSSION

Figure 1 curve a shows an electrochemical behaviour of non amalgamated electrode in 1M KCl at pH=7 and temperature $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Potential window was limiting to $E = -1$ volt/SCE in the anodic side by

aluminium pitting corrosion and $E = -1.8$ volt/SCE in the cathodic side by hydrogen reduction. This result showed a classical electrochemical behaviour of aluminium and its alloys in aqueous solutions containing chloride ions.

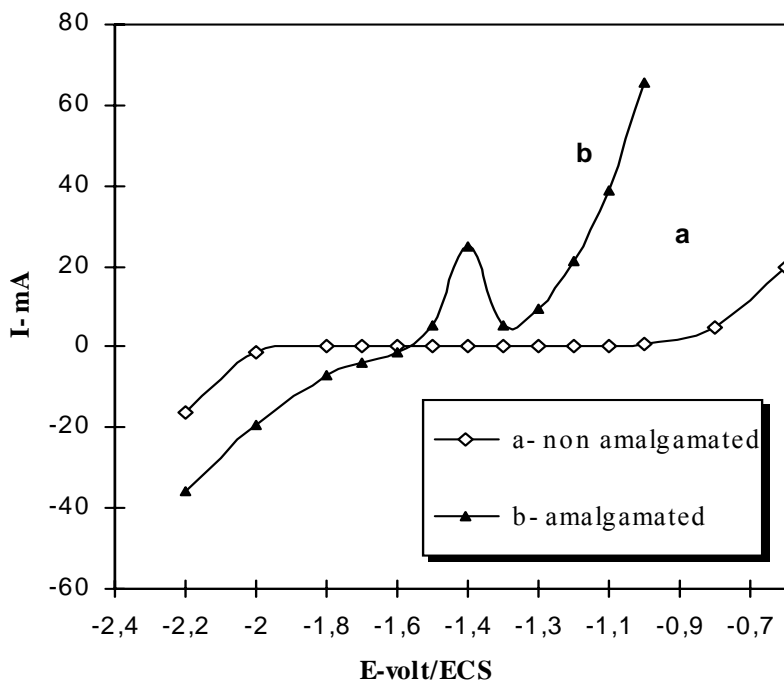


Figure 1: Voltamograms for amalgamated and non amalgamated alloy AA5083 in 1M KCl

Electrochemical behaviour of amalgamated alloy

Figure 1, curve b represents the electrochemical behaviour of alloy AA5083 after 10min of preamalgamation in a separated cell at constant potential of -0.15 volt/SCE, and after 6 min of immersion in the experimental electrolyte (1M KCl) before starting scanning. Results show an anodic oxidation peak at potential $E_p = -1.4$ volt/SCE, current peak was $I_p = 25$ mA and gave a value of corrosion potential of $E_{cor} = -1.6$ volt/ECS, the cathodic area shows the reduction of hydrogen.

Evolution of oxidation peak current in different experimental conditions

Three conditions were investigated: the time of immersion of amalgamated electrode, the time of mercury deposition and the scanning rate potential.

All specimens were amalgamated in 10^{-4} M HgCl_2 solution and immersed for definite time in the experimental solution (1M KCl). Rotation of electrode was at 5000 rpm for all experiments.

a. Time of immersion

Specimens were amalgamated for a period of 10min and then immersed in experimental solution for: 6, 18, 24, 30, 42, 48 and 120 minutes respectively. Scanning at 300 mv/min (5mv/s) was started immediately after these preliminaries.

The voltammograms (*Figure 2*) shows an increase in peak current I_p with time of immersion.

A plot of the peak current I_p with immersion time shows two zones (*Figure 3*): the first zone at a time less than 36 min, the curve was nonlinear and it increased rapidly at 233 $\mu\text{A}/\text{min}$; the second zone at a time beyond 36 min, variation of I_p becomes linear and stabilised at a low increment of 21 $\mu\text{A}/\text{min}$.

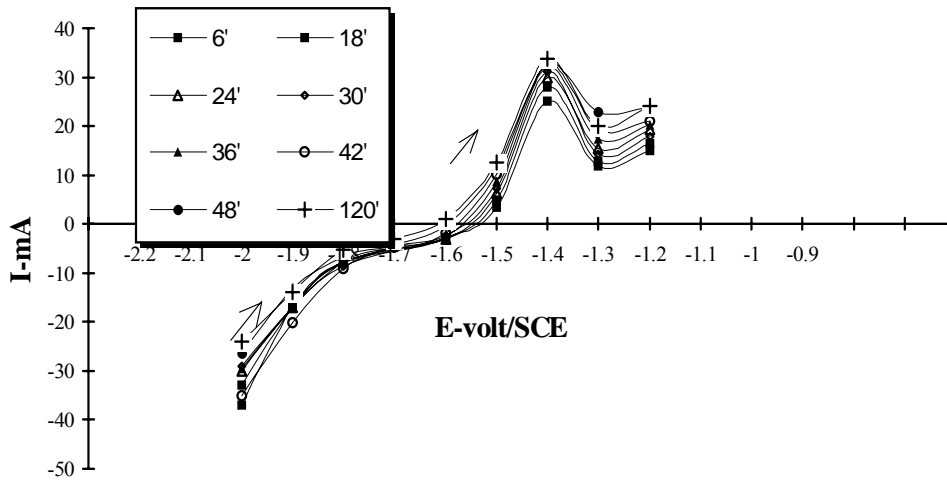


Figure 2: Voltammogram for amalgamated alloy AA5083 in KCl 1M for different times for immersion

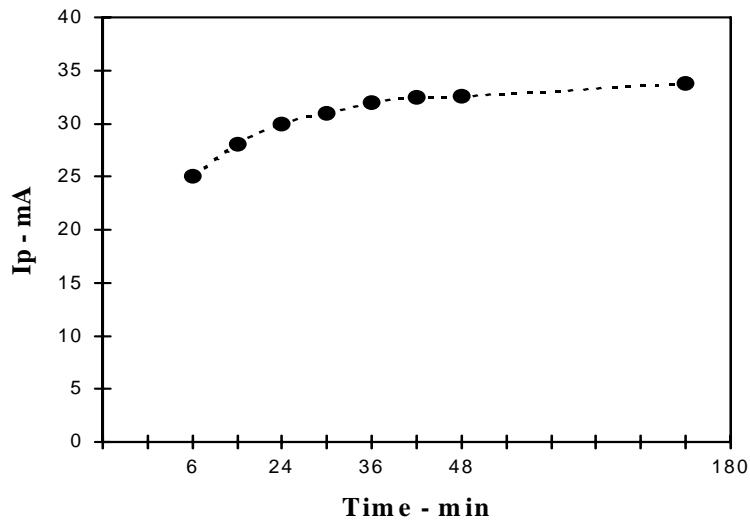


Figure 3: Peak current vs Immersion time

b. Time of amalgamation

Electrodes were amalgamated in 10^{-4}M HgCl_2 solutions at different times, $t = 6, 18, 24, 30, 36, 42$ and 48 min respectively; then they were immersed in an experimental solution of KCl (1M) for 30 min at a potential scan rate of 300 mv/min (5 mv/s) and electrode rotation rate of 5000 rpm .

Results in Figure 4 show an increase in amplitude of peak current with amalgamation time.

The dependence of peak current on time in Figure 5 exhibited two parts: the first one is at a time less than 30 min, the peak current increases linearly with rate of mercury deposition; the second part of the curve corresponding to time longer than 30 min, peak current tends to stabilise indicating a complete electrolysis of mercury.

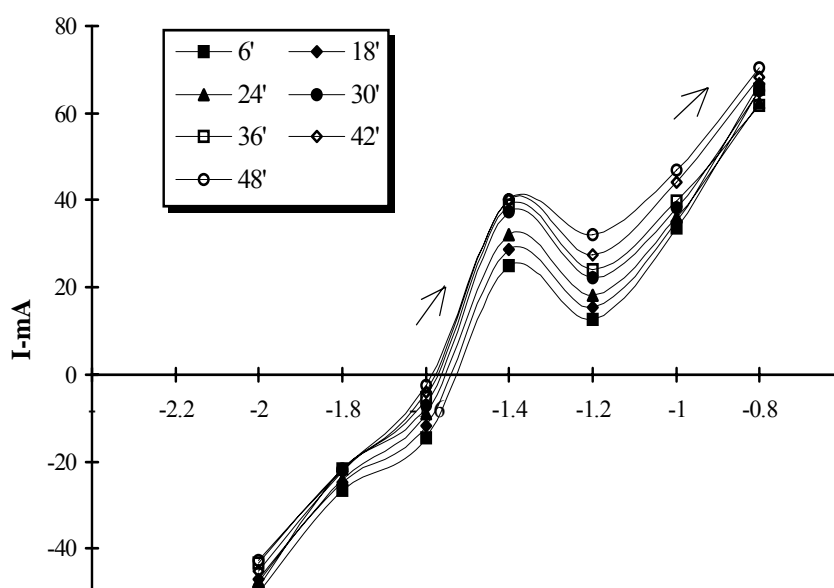


Figure 4 : voltamogram of alloy AA5083 for different amalgamation times

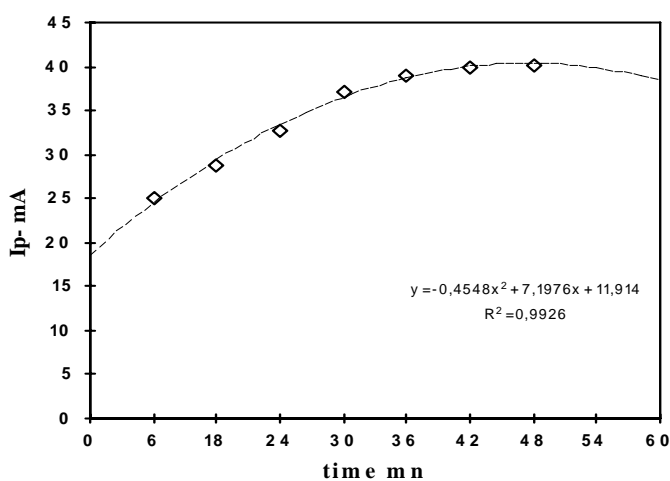


Figure 5 : current peak evolution vs time amalgamation

c. Scanning rate potential

Electrodes were amalgamated in 10^{-4} M HgCl_2 solution for 30 min and then immersed in experimental electrolyte for 36 min. Times adopted corresponded to the second part of the curves of Figures 3 and 5. Scanning rates were $v = 50, 100, 200, 300, 500, 800, 1000$ mv/min.

Results in Figure 6 show a decay of peak with increase in scan rate.

For scanning rates $v < 100$ mv/min, the slope was $\frac{dI_p}{dv} = -0.27$ mA/mv - mn

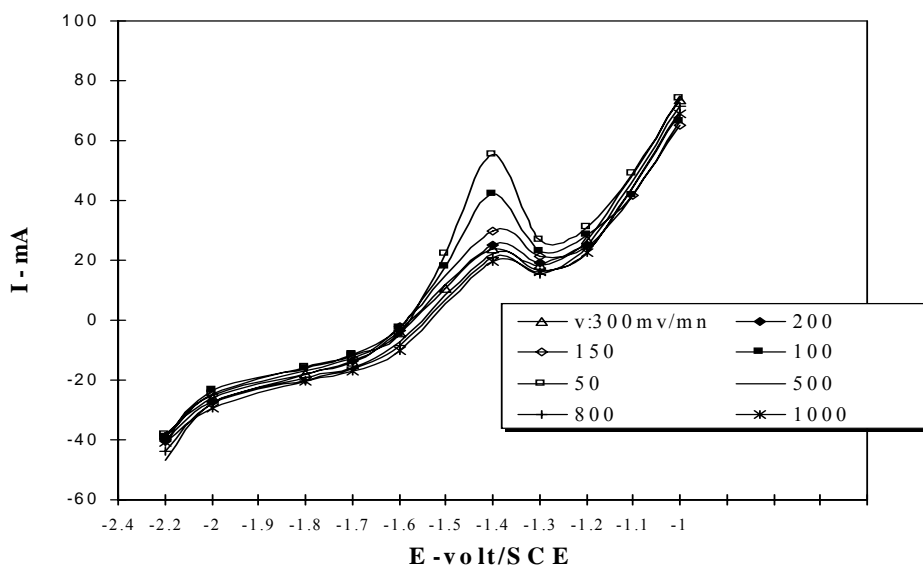


Figure 6: voltamograms for different scanning potentials

Variation of I_p with potential scan rate is represented in Figure 7 which shows two linear different dependences: For relatively low scanning rates, $v < 100$ mv/min, the decay was $\frac{dI_p}{dv} = -0.27$ mA/mv - mn

For the rates higher than 300 mv/min, the variation was much slower with a decay of $\frac{dI_p}{dv} = -0,013$ mA/mv - mn

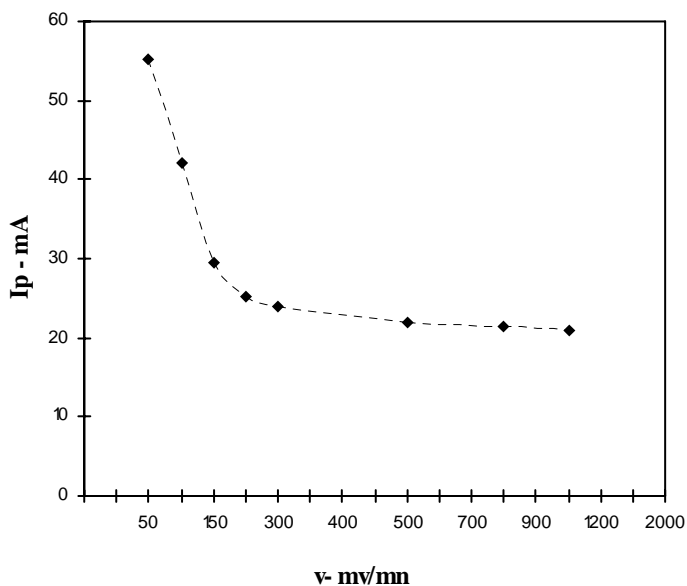


Figure 7: Peak current vs. potential scanning rates

Corrosion potential

Corrosion potential showed a negative value -1.52 volt to -1.60 volt /SCE and depended on experimental conditions.

Corrosion potential was shifted towards more negative values for longer time of immersion (Figure 8).

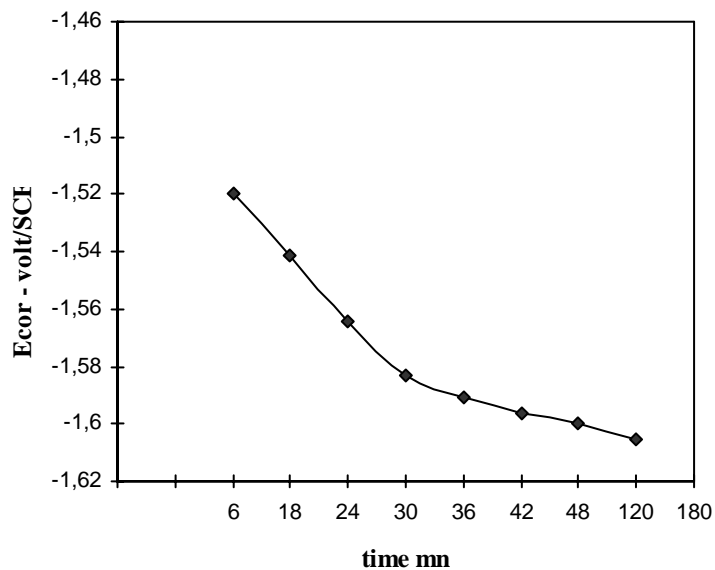


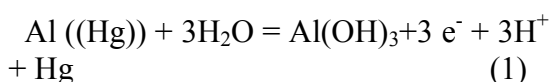
Figure 8: E_{cor} vs. time immersion

DISCUSSION

Corrosion of industrial aluminium alloy AA5083 in neutral aqueous medium

a spontaneous passivity and then deactivation (Figure 1a).

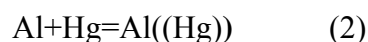
A different behaviour was unregistered when electrode was amalgamated, voltammograms showed, in their anodic area, an oxidation peak at a potential $E_p = -1.4$ volt /ECS, attributed to the reaction ⁷



Reaction (1) is well known and showed a catalytic reaction in which mercury is regenerated from the amalgam and will continue the process of amalgamation. This reaction occurs at the amalgam /water interface as indicated in Figure 9 and is electrochemically dependent.

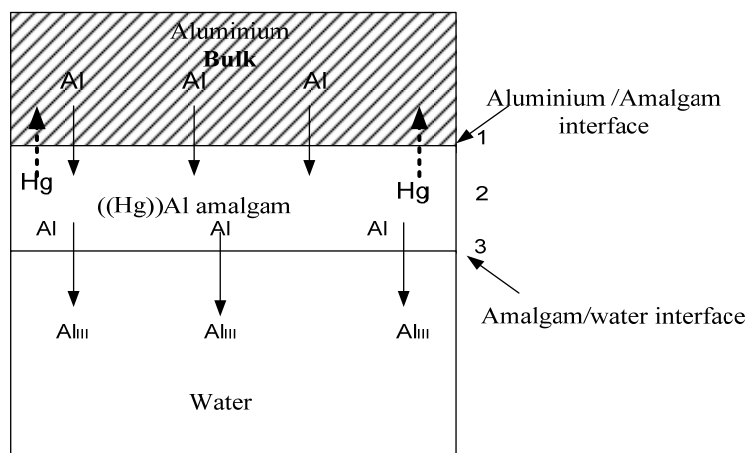
containing chloride showed a complex process on amalgamation.

The non amalgamated alloy exhibited a classical electrochemical behaviour with Amalgamation of aluminium (reaction2) is a chemical process which obeys a chemical kinetic with a rate constant, k_c , occurring at the interface amalgam /bulk aluminium interface.



Reaction 2 reached a stationary level when the amalgam becomes aluminium saturated. However, reaction 1 is an aluminium consumer and a gradient of aluminium concentration occurs and a diffusion process takes place.

The scheme of the general process is represented in Figure 9.



- 1 - Chemical reaction : $\text{Al} + \text{Hg} = ((\text{Hg}))\text{Al}$
- 2- Diffusion of Al in Mercury
- 3- Electrochemical oxydation of Aluminium : $\text{Al} = \text{Al}_{\text{III}} + 3\text{e}$

Figure 9: process of aluminium corrosion induced by Mercury

The two parts unregistered on curves in Figures 3, 5 and 6 showed 2 determinant steps in the process.

At short immersion times of direct contact of mercury with the active surface of aluminium, amalgamation (Reaction 2)

is a controlled process while, at a longer period of direct contact, the amalgam tends to be saturated according to solubility of aluminium in mercury and then diffusion of aluminium which controls the general process sets in.

During the amalgamation period, chemical process controls the general kinetics, because the rate of mercury deposition on electrode increases and the saturation cannot occur before the total electrolysis of mercury ions. However, for a determined concentration of mercury solution, total electrolysis occurs at a limited period and then diffusion control takes over.

Variation of I_p with potential scan rates showed the impact of chemical and diffusion steps on electrochemical corrosion.

At low scan rate diffusion controlled the process (first part of figure 7) but at

higher values, the process becomes chemically dependent. Peak current in similar cases (thin film of mercury) is given by the relation⁸

$$I_p = n^2 F^2 / v / 1 A C_{Al((Hg))} / 2.7 R T \quad (3)$$

For a total electrolysis of 50 ml of Hg^{++} solution, the calculated thickness of the amalgam, l , was $10.05 \mu m$ for a surface of electrode of $7.06 mm^2$. Slope of the function I_p vs has a value of $-0.27 mA / millivolt/min$ or $0.00021 A.s / volt$ (figure7). The deduced concentration $C_{Al((Hg))}$ at the amalgam /water interface was approximately $1 mg/100g$ of mercury.

The literature⁸ saturation concentration of aluminium in mercury at $20^\circ C$, is $2 mg / 100 g$ of mercury.

The aluminium concentration profile in the amalgam⁽⁸⁾ is presented in Figure 10.

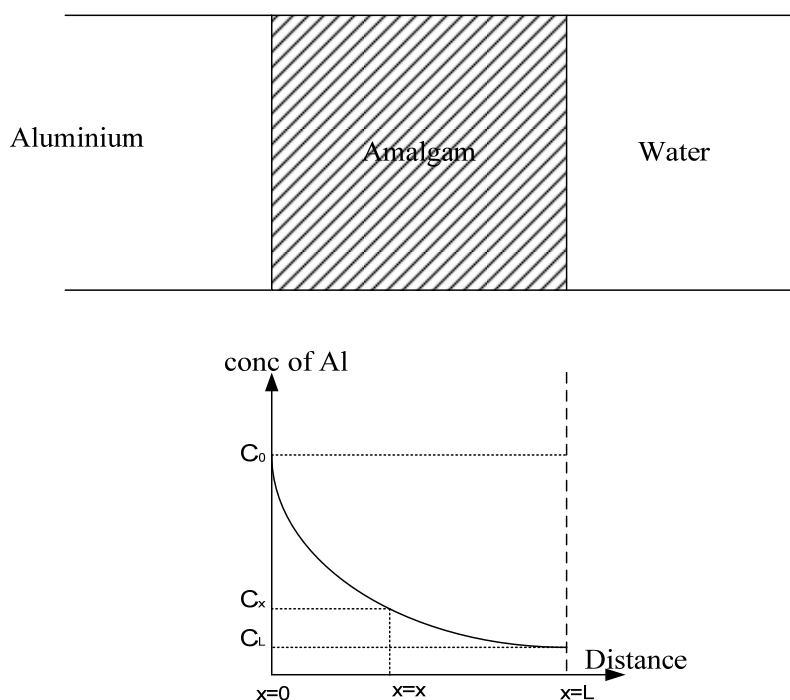


Figure 10: Profile of concentration of aluminium in amalgam

CONCLUSION

Electrochemical corrosion studies of industrial aluminium alloy AA 5083 in natural gas containing mercury metal and water as

impurities showed to be a complex process. Single scan voltamograms of amalgamated electrode showed electrochemical oxidation peaks around $E = -1.4$ volt /SCE and a

corrosion potential $E_{\text{cor}} = -1.6$ volt/SCE showing an active amalgamated surface.

Oxidation peak, I_p , relating rate of electrochemical oxidation of aluminium was dependent on three factors including thickness of amalgam, diffusivity of aluminium in amalgam and rate of chemical dissolution of aluminium in mercury which is the limiting step at high scanning rate potential and low immersion time. Diffusion step which controls kinetics at highest immersion time and lowest scanning rate and an intermediate step which controlled the two kinetics.

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