AN ELECTROCHEMICAL BEHAVIOR OF CO2 CORROSION OF STATIC CARBON STEEL ELECTRODE IN PRESENCE OF ACETIC ACID, ACETATE AND METAL INHIBITOR (Zn^{+2}, Ca^{+2}) USING AC AND DC ELECTROCHEMICAL TECHNIQUES

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Abstract: AC and DC electrochemical techniques: electrochemical impedance spectroscopy (EIS), and (Potentio-dynamic), electrochemical corrosion measurements are conducted on static carbon steel electrode at room temperature in 3.5 % NaCl Solution, bubbled with 1 atm CO_2, or 1 atm. N_2 or air exposed test solution. Different chemicals; e.g. (acetate, sodium acetate, acetic acid, sodium sulphate, calcium chloride and zinc chloride) were added to test solution. The results of polarisation curves are compared with impedance measurements results to understand the mechanism of the corrosion process. And take the benefits of the comparison to understand more the physical meaning of AC corrosion data. The results of polarisation curves suggest that CO_2 makes a large contribution in the corrosively of all solutions. However, in the presence of acetic acid the solutions were found to be corrosive even in the absence of CO_2, and this can strongly attributed to the pH. The impedance results confirm the mentioned findings; also there was a good agreement between AC (Impedance) and DC (Polarisation curves) results. Zinc and Calcium considered as metal ions inhibitors, DC and AC results suggest that, Ca^{+2} in aerated solution may tends to forming ($CaOH_2$) that gives more isolation for cathodic species (i.e. hinders the diffusion links leads to fresh metal surface). Regarding zinc ions the polarisation curves indicate that electrochemical behaviour of zinc in terms passivity, depends strongly on the electrode potential.

Keywords: Electrochemistry, CO2 corrosion mechanism, and steel surface inhibition

INTRODUCTION

In CO_2 corrosion there are many studies on the effect of fluid characteristic (e.g pH, CO_2 pressure and temperature, (Nesic et al, 1996). This is based on the fact that CO_2 corrosion is by far the most common form of attack encountered in upstream operations (Kermani and Morshed, 2003). Basically, an empirical parameter models have been developed; these models have been used as major tool for prediction and selection of material performance in sweet environments. Unfortunately, these models are not accurate for many working conditions, as there are some factors that are not taken into account. Furthermore, relatively new factors, such as acetate, which are observed to affect on CO_2 corrosion rate, are not

fully understood (Crolet & Nicolas 1999, and Guo et al, 2005). Electrochemical techniques; polarisation curves and electrochemical impedance spectroscopy (EIS) shall be used to study CO_2 corrosion of steel. Some workers found that corrosion in the CO_2 environment was higher than in the aerated solutions (Aagotnes et al, 1999). Polarisation curves are used to study the electrochemical behaviour of carbon steel in CO_2 saturated solutions and compared with deaerated and aerated solutions. The investigation will drive us to understand the electrochemical behaviour of carbon steel in the presence metal ions (e.g.$Ca^{2\pm}$,Zn^{2+}) as well as acetic acid and acetate species. Previous work has been carried out about the effect of acetate in CO_2 saturated solution but most of them done only in static conditions. In the current research (Part. I, Part II will follow in the next issue of this Journal), all corrosion tests are conducted using static electrode and

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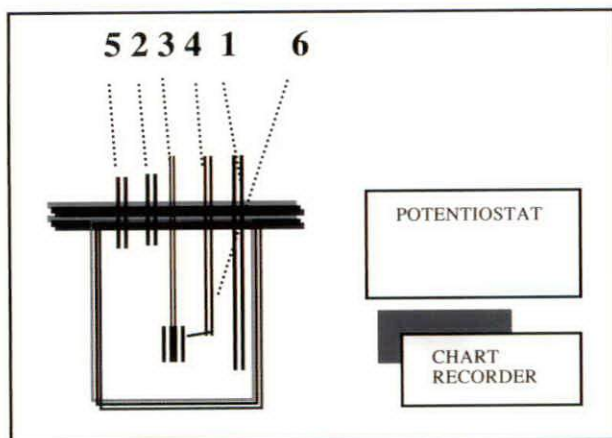
Sketch. 1 shows schematic drawing of corrosion cell utilized in corrosion measurements [Sketch. 1 shows schematic drawing of corrosion cell that was used to conduct lab corrosion measurements: (1) gas inlet; (2) gas outlet; (3) carbon steel working electrode; (4) Saturated calomel electrode with capillary salt bridge (SCE); (5) platinum auxiliary electrode; (6) salt bridge].

Picture 1 shows the iron oxide film formed as result of anodic polarization

Picture. 2 Nice view of zinc hydroxide on steel Surface.

future work (Part II) expected to be published in next Petroleum Research Journal versions. This future work (Part II) is aimed to focus on carbon steel electrochemical respond by AC and DC techniques in a dynamic CO_2 saturated medium and the emphasis will be on the flow effect in presence of Acetates and calcium chloride, using rotating electrode.

EXPERIMENTAL WORK

Equipment

All experimental work was done at atmospheric pressure and room temperature in enclosed cells similar to that shown in Sketch 1. In this experiment carbon dioxide [CO_2] and nitrogen [N_2] gases were bubbled inside the cell continuously before the experiment (to remove dissolved oxygen gas from the solution) and during the experiment (to exclude oxygen). The electrochemistry of the carbon steel for corrosion evaluation was studied using AC and DC electrochemical techniques. Three conditions were used for the static (unstirred) solution. They are; aerated, de-aerated using N_2 bubbling and CO_2 saturated solution. Solutions were bubbled for 10 minutes before starting the test. The three electrodes were placed in the cell, where a platinum electrode (used to collect the current) was used as a counter electrode (CE). A saturated calomel reference electrode (RE) was connected to the cell externally using a Luggin Capillary Salt Bridge. A digital pH-meter was used to measure the pH of the solution before and after the experiment finished.

The electrochemical polarization curves were developed using ACM potentiostat with sweep rate generator connected to an X-Y recorder, and the correction for IR-drop was made manually after the experiment. Impedance measurements were developed using a Solartron Frequency Response Analyser (FRA) and potentiostat connected with personal computer.

Material

A low carbon steel rod, of 1 cm diameter was used. Specimen of chemical composition is given in Table 1. The steel specimen was connected to a copper current lead wire using a spot welding machine and then some wax was used to isolate the upper and lower end of the cylindrical specimen, leaving an exposed area of 6.28 cm^2 (see Picture 1).

Table 1 A low carbon steel rod, of 1 cm diameter was used. Specimen chemical composition

Chemical Element	C	Si	Mn	P	S	Cr	Mo	Ni	Al
%Mass/Mass	0.18	0.16	0.8	0.005	0.034	<0.02	0.03	0.1	<0.005
Chemical Element	Co	Cu	Sn	Ti	V	W	-	-	-
%Mass/ Mass	0.007	0.18	0.02	<0.005	<0.02	<0.02	-	-	-

Solutions

All the solutions used in this experiment were in three conditions: aerated, de-aerated by N_2 gas and saturated by CO_2 gas at room temperature and atmospheric pressure.

The solutions used in the static electrode tests were:

1- 3.5% NaCl in distilled water (15Ω cm^2)

2- 3.5% NaCl + the following chemical additive is added individually,

- 0.1M acetic acid
- 0.1M sodium acetate
- 0.1M $CaCl_2$
- 0.1M $ZnCl_2$

Work Procedure

All the electrochemical measurements were applied with 1 litre of fresh solution for each experiment and all of them at room temperature. Solutions that were de-aerated were initially rapidly bubbled with nitrogen for 10-15 minutes then the gas flow reduced. For solution saturated in carbon dioxide, nitrogen bubbling was carried out first, then CO_2 bubbling was performed for 10 minutes. The pH of the solution was measured after the experiment to know the situation of solution species equilibrium. The steel-working electrode was prepared by grinding with 400 grit using SiC grinding papers and rinsed using distilled water and ethanol to remove any greases or wax. The clean specimen was fixed immediately in the glass cell electrolyte. The open circuit potential (Ecorr) was observed using a digital voltmeter. The experiments were starting after Ecorr had stabilised.

Potentiodynamic Measurements

Potentiodynamic polarization was applied to produce polarization curves of mild steel area of 6.28cm². The experimental work was carried out at room temperature in three different solution conditions (i.e aerated, N_2 and CO_2 bubbled) at one atmosphere pressure. The electrochemical experiment was carried out in a suitable cell with gas inlet and outlet gas connections. It is connected with a saturated calomel electrode

(SCE) as reference electrode by a using salt bridge to minimize IR-drop. The working electrode was cylindrical in shape. An ACM potentiostat with sweep rate generator controlled the scan rate potential at 30mV/min. The current was measured using the voltage drop across a resistor and recorded on an X-Y recorder; the potential was monitored via a sensitive voltmeter. The electrochemical test was undertaken by applying a full polarization on fresh/clean specimen in new solution. The potential was swept from-1200mV (SCE) up to 0 mV (SCE). Any IR-drop correction that was required was estimated from Ohmic behavior at high current and corrected manually.

Impedance measurements

AC Impedance measurement were carried out by applying a corresponding potential to of ± 10mV (SCE) around the open circuit potential to the working electrode. This is equivalent to a AC voltage of 7mV rms. The frequency range used in the measurements was (30000 Hz-0.03Hz). All impedance measurements were performed at open circuit potential using a Saturated Calomel Electrode (SCE) as reference electrode. The aeration conditions and test condition and sample geometry which were used in the impedance measurements are the same as those were used in the potentiodynamic technique. (Princeton Applied Research AC-1 note).

RESULTS AND DISCUSSION

Potentiodynamic polarization experiments were performed in order to understand the electrochemical behavior of steel in aerated, and nitrogen and carbon dioxide bubbled solution. Therefore, the curves obtained shall be compared in order to determine the electrochemical behavior of the salt solutions, containing acetic acid and acetate, in the presence and absence of CO_2, also to know how the degree of aggressiveness of acetic acid. More explanations and details discussion relates to the effect of metal ion inhibitors in the presence and absence of CO_2 are mentioned below. More explanations and details are discussed below.

Electrochemical test procedure

Full polarization was applied on freshly prepared and abraded specimens and for each new solution the potential was swept from-1200mV (SCE) up to near zero mV (SCE). Where it is necessary, IR-drop correction was estimated from the high-current portion of the polarization curve.
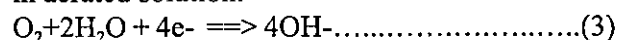
Basic Reactions in this Experiment
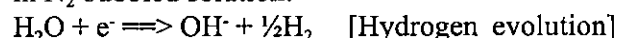
Anodic Reaction

Mainly iron dissolution:

$Fe ==> Fe^{2+} + 2e-$ ....(1)

SO_4^{2-} (aq) + Fe^{2+}(s) <==> $FeSO_4$ (aq) + 2e- ..... (2)
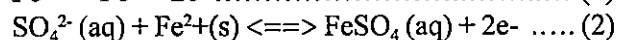
Cathodic Reaction

in aerated solution:

$O_2 + 2H_2O + 4e- ==> 4OH-$ ....(3)

or

$2H^+ + 2e- ==> H_2$ .... (4)

in N_2 bubbled solution:

$H_2O + e- ==> OH- + \frac{1}{2}H_2$ [Hydrogen evolution]

in CO_2 bubbled solution:

$CO_2 + H_2O$ <==> H_2CO_3 <==> $H^+ + HCO_3^-$ ....(5)

$2H^+ + 2e- ==> H_2$
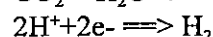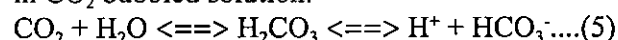
Effect of acetate (in acetic acid or as the acetate anion)

3.5% NaCl Solution and without acetate

In aerated solution the polarization curves revealed that hydrogen evolution and oxygen reduction were the cathodic reactions and iron dissolution was the anodic reaction. According to the polarization curves, the increases in dissolution rate is not strongly changed with increasing the potential this may be due to the known property of steel in aerated near natural solutions , which usually featured by greater stability of formed oxide layers over acid solutions (Newman, RA. 2002). but in N_2 bubbled solution the anodic kinetics depends on the potential changing since E_{corr} decreased to more a negative value (-880mV).

In CO_2 bubbled solution, the corrosion increased because the presence of carbonic acid lower the pH and makes the solution more corrosive. This is because it represents an additional source of H^+ and, hence, cathodic reactant. At room Temperature it is reported that the CO_2 corrosion rate is controlled by charge transfer processes (Tourgoose 2004). During corrosion, iron oxide forms on the metal surface (see picture 1). As well as due to the presence of carbonate (from the dissolved carbonic acid) in the solution, it is thermodynamically possible for a black/thin iron carbonate layer to form. A cathodic limiting current in CO_2 bubbled solution was found to start at a potential different from the aerated solution. The maximum limiting current was about 0.09mA/cm in CO_2 bubbled solution (Figs.1, 2 and 3).

3.5% NaCl + 0.1M Sodium Acetate solution

The results suggest that higher corrosion rate in CO_2 containing solution is controlled by carbonic acid diffusion but in N_2 bubbled and in aerated solution the corrosion rate is mass transport controlled as well. The polarization curves show that the corrosion rate is about 10 times lower in these solutions than that observed in CO_2 containing solution. This can be explained from fact that CO_2 makes the solution more aggressive and lowers the pH (Figs. 1 and 4). In addition, as for the polarization curves, iron oxide formation is more favoured by the higher pH value $\approx$ 10.5 (Fig. 5) and pH $\approx$11.5 (Fig. 6) and may be some passivation is occurring.

3.5% NaCl +0.1 Acetic Acid solution

In this solution all three polarization curves show the corrosion rate quite close to each other. In other words, because acetic acid is considered aggressive and keeps the pH values in range of (3-4) for all solutions, thus the resulting corrosion rate is approximately five times greater than for the other two solutions. In N_2 bubbled solution the corrosion process appeared mainly under activation control. This indicates that acetic acid is aggressive since formation of an oxide/corrosion product film is clearly hindered. Eventually, an un-filmed steel surface is exposed

Table. 2 show corrosion test condition

Material	Carbon steel & mild steel
Test solution	Mainly 3.5% NaCl + others additives
Temperature	RT
Pressure	1bar
pH	Dependence on the solution
Test duration	Dependence on the technique
Sweep rate	0.5mV/s
AC impedance	±10 mV .VS. Ecorr 30000Hz up to 0.3Hz
Potentiodynami sweep range	-1200 to 0 mV (SCE). VS.Ecorr

to the solution most of the time and this activates the electrochemical process and stimulates the iron dissolution reaction.

Effect of metal ion inhibitors
3.5%NaCl + 0.1M CaCl$_2$ solution

The presence of calcium chloride in the three solution conditions causes a reduction in the corrosion rate (Figs. 7, 8 and 9). The lowest corrosion rate was in aerated solution and this can be attributed to the formation of a calcareous protective layer (CaOH$_2$) that gives more isolation for cathodic species to reach the fresh iron surface (i.e. hinders the diffusion processes). Since the presence of the oxygen encourages the formation of Fe$_2$O$_3$, by shifting the Ecorr to more positive value, (E-pH diagram for iron water system; Module Notes - Aqueous Corrosion UMIST, 2003), the pH of solution (near neutral) will favour formation of Ca(OH)$_2$ and Fe$_2$O$_3$. However, in the absence of oxygen, i.e. with Picture 1 shows the iron oxide film N$_2$ bubbling, the current density (Icorr) increases about five times, formed as result of anodic polarization. Obviously, in CO$_2$ containing solution, the pH is further lowered to 5 or below and the current density might be higher. Also, the measured corrosion rate is still low since in this case formation of protective calcium carbonate occurs because of the dissolved CO$_2$.

3.5%NaCl+ 0.1ZnCl$_2$ solution

Zinc ions are considered as good cathodic inhibitors in solution and should work well to protect steel in near neutral solutions in a similar way (but more effective than) calcium ions. In this experiment zinc chloride was considered as a source of zinc metal ions that will suppress the cathodic reaction by precipitation of zinc hydroxide according to this reaction;

$$Zn^{2+}+2OH^- ==> Zn(OH)_2 \quad ....(6)$$
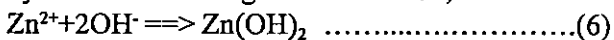
Eventually the iron surface will be covered with a layer of zinc hydroxide. The polarization curves in Fig.10, 11 and 12 show an active state at lower potential values -1000 to –900mV (SCE). In CO$_2$ containing solution, the passivity range is small but in aerated solution the passivity range was greater (-1000 to –580mV (SCE) but the CO$_2$ passivation current < N$_2$ passivation current< O$_2$ passivation current; i.e. the presence of oxygen has no synergetic effect with zinc in CO$_2$. On the other hand, in aerated solution (pH=6.2), it is

expected to find a beneficial affect of oxygen, since oxygen causes an extension of the passivity range (Newman, 2002a & b). This can be understood from the E-pH diagram of the iron/water system. In the presented polarization curves the observed active state may result from instability of the zinc hydroxide protective layers in this solution.

The electrochemical behaviour of mild steel in 3.5% NaCl + 0.1MNaSO$_4$ solution

In aerated solution, in presence of NaSO$_4$, oxygen reduction and hydrogen evolution happen at lower potential than in 3.5% NaCl solution alone. Some authors suggest that the most probable anodic reaction in such sulphate concentration in natural solution is iron sulphate formation. There is region of passivity and formation of iron sulphate layers that provide protection against further corrosion. At a potential of approximately 660mV SCE, the formed protective film is destroyed and the anodic dissolution re-activates again to higher values than before. In aerated solution the potential where the limiting current observed is lower than -880mV SCE (Fig .4).

In N$_2$ bubbled solution the E-logI curve shows a clear cathodic Tafel region and this implies that the corrosion process strongly dependent on the H$_2$ evolution as cathodic reaction. In CO$_2$ bubbled solution there is similarity with the NaCl solution in the shape of polarization curve and E$_{corr}$ values, but in NaCl solution the limiting current shall be less than that observed in Na$_2$SO$_4$ contained solution (Figs. 2 and 5). (Arzola, 2003).

Impedance (EIS) results

The impedance measurements have been performed in order to measure the electrolyte resistance , and the polarization resistance and if there is any change in corrosion mechanisms (Table 2). The results from all impedance plots have agreement that the worst corrosion resistance (i.e. faster corrosion) is in the presence of CO$_2$ (Kinsella et al 1998).

Effect of acetate
3.5% NaCl + 0.1M sodium acetate solution

Fig. 19 shows the impedance response in the presence of sodium acetate. This result suggests that there is a higher corrosion resistance in N$_2$ bubbled solution. Also, from the plot (Fig. 19), lower Rs values were observed. In the presence of CO$_2$, a
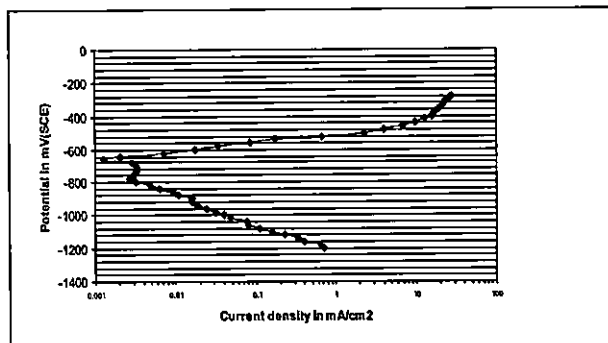
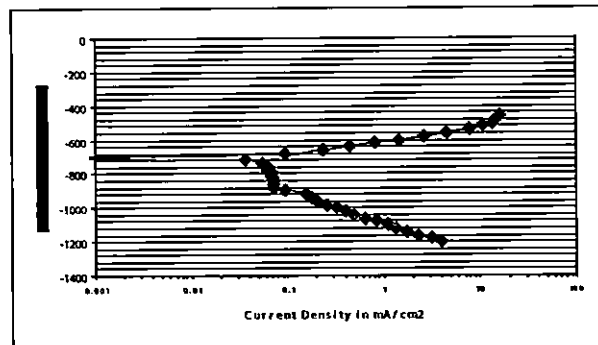Fig.1: Polarization curve of mild steel in 3.5% NaCl aerated solution.

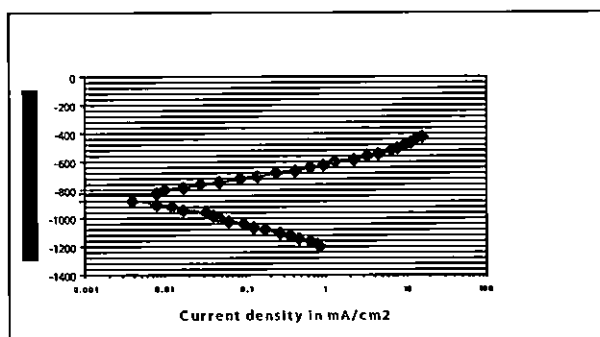Fig. 2: Polarization curve of mild steel in 3.5% NaCl CO2 bubbled solution.

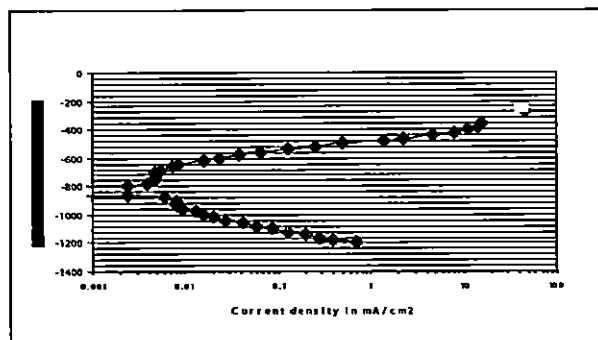Fig. 3: Polarization curve of mild steel in 3.5% NaCl N2 bubbled solution.

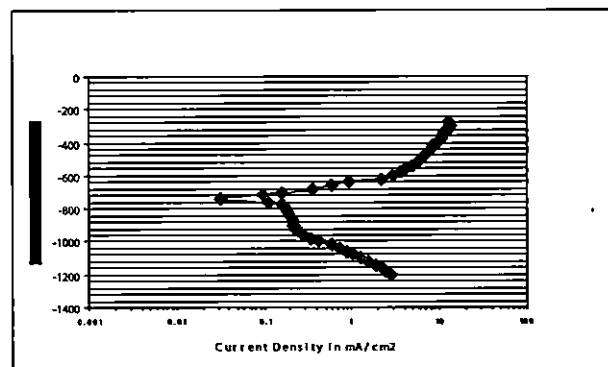Fig.4: Polarisation curve of mild steel in 3.5% Na2SO4 aerated solution.

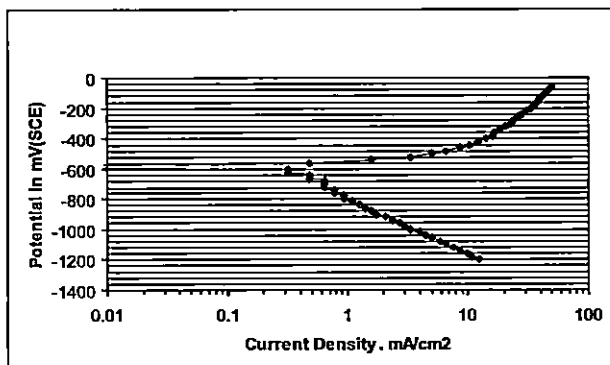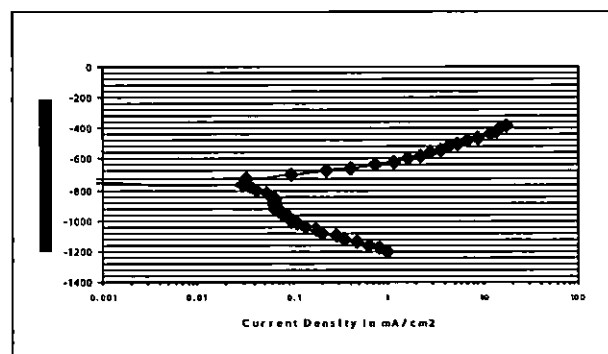Fig. 5: Polarisation curve of mild steel in 0.6M Na_2SO_4 CO2 bubbled solution.

Fig. 6: Polarisation curve of mild steel in 0.6M Na_2SO_4 N_2 bubbled solution.

Fig.7: Polarisation curve of mild steel in 3.5% NaCl +0.1M acetic acid aerated solution , pH=3.5.
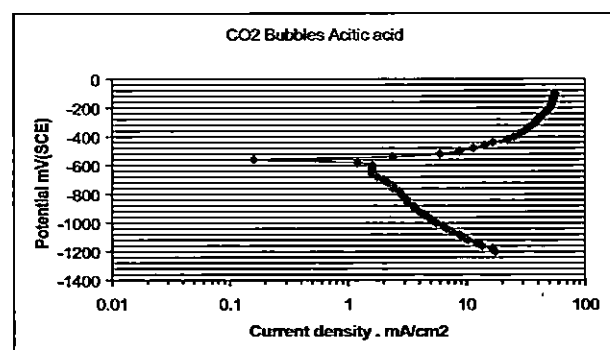
Fig.8: Polarisation curve of mild steel in 3.5% NaCl + 0.1M acetic acid, pH=3.75.
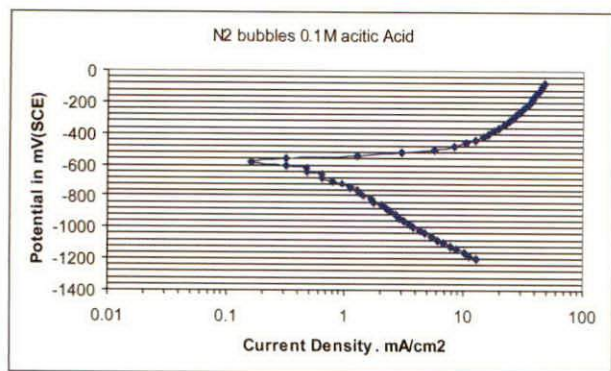
Fig.9: Polarisation curve of mild steel in 3.5% NaCl+ 0.1M acetic acid, pH=3.4.
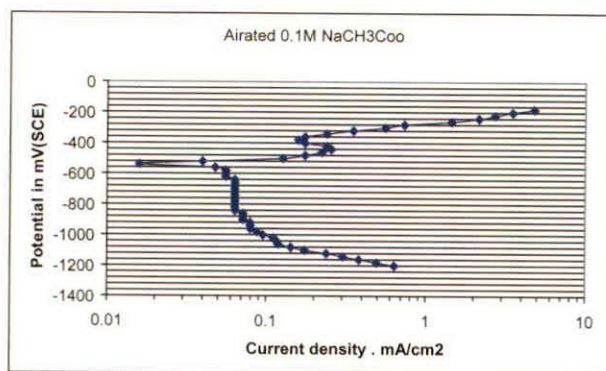
Fig.10: Polarization curve of mild steel in 3.5% NaCl + 0.1M sodium acetate, pH= 11.5.
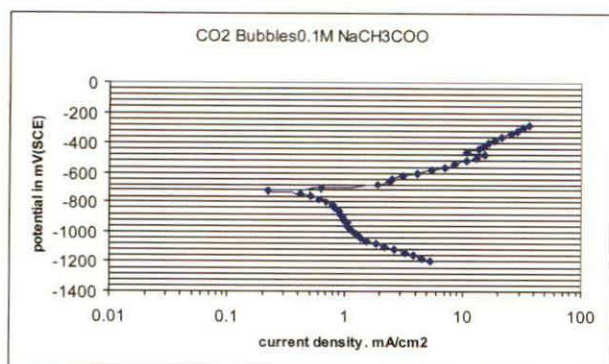
Fig.11: Polarisation curve of mild steel in 3.5% NaCl + 0.1M sodium acetate, pH=4.5.
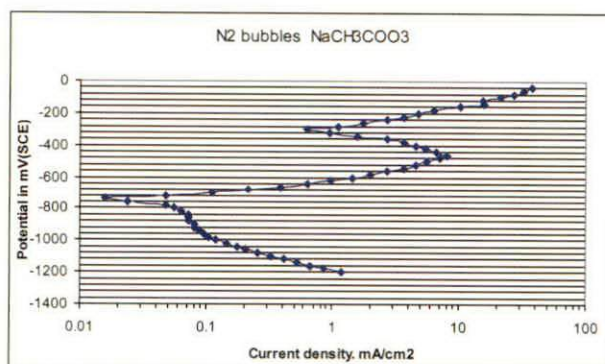

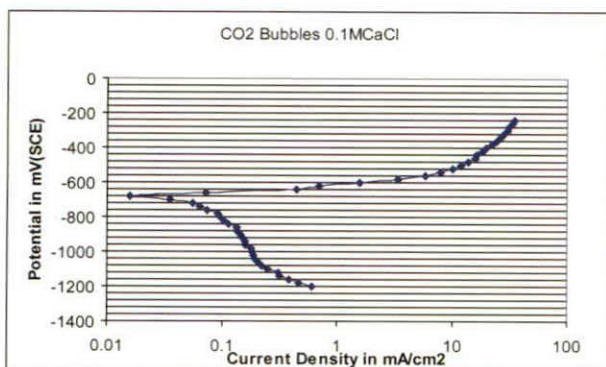Fig.12: Polarisation curve of mild steel in 3.5% NaCl + 0.1M sodium acetate, pH=10.5.

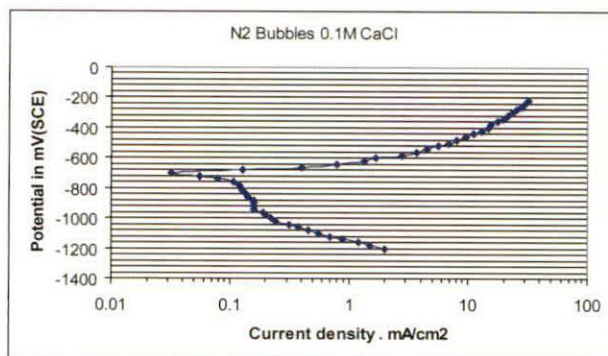Fig.13: Polarisation curve of mild steel in 3.5% NaCl + 0.1M calcium carbonate, pH= 5.7.

Fig.14: Polarisation curve of mild steel in 3.5% NaCl+0.1M calcium carbonate, pH= 8-9.
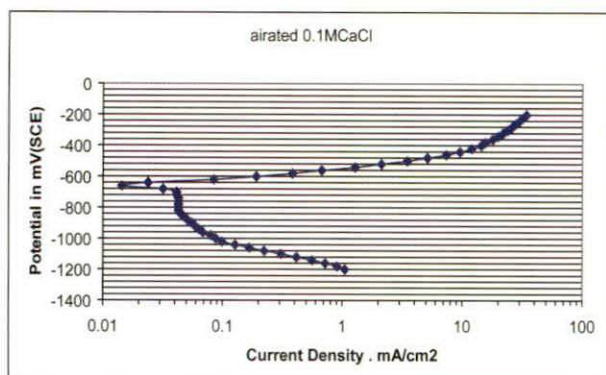

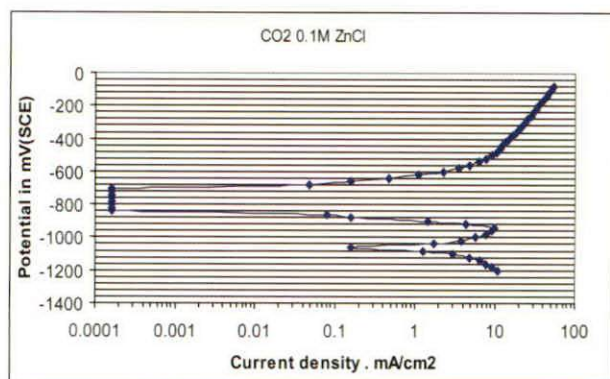Fig.15: Polarisation curve of mild steel in 3.5% NaCl + 0.1M calcium carbonate, pH= 7.

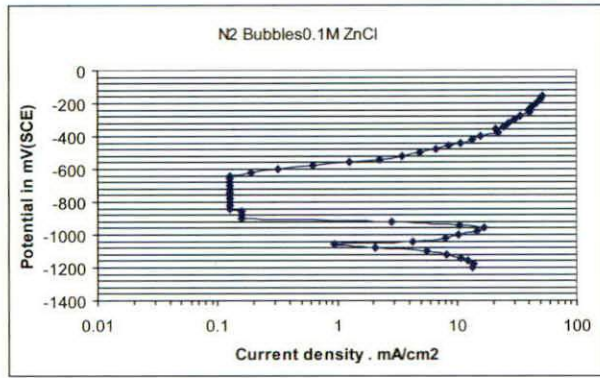Fig.16: Polarisation curve of mild steel in 3.5% NaCl + 0.1M ZnCl₂: , pH= 4.5.

Fig.17: Polarisation curve of mild steel in 3.5% NaCl + 0.1M
ZnCl₂: pH= 6.5.

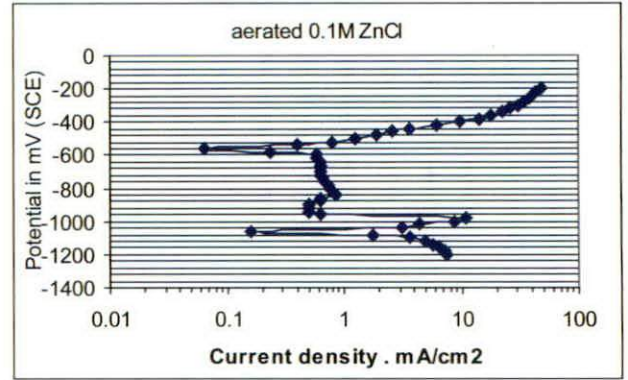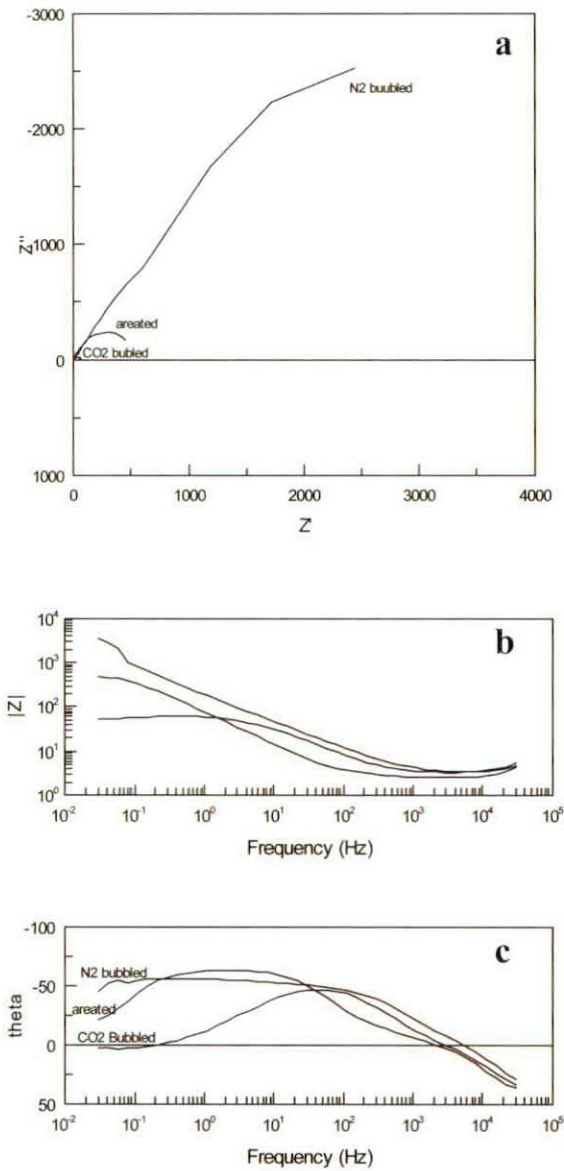Fig.18: Polarisation curve of mild steel in 3.5% NaCl + 0.1M
ZnCl₂: pH= 6.4.

Fig. 19:   0.6 M NaCl 0.1M sodium acetate , a) Nyquist, b)
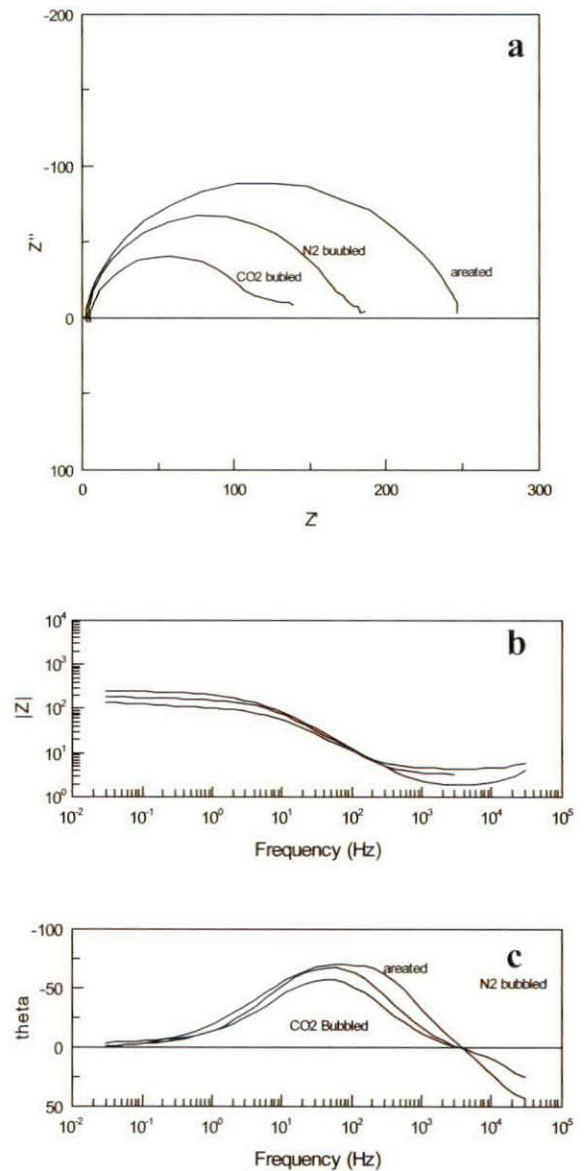bode plot – modulus, C) Bode plot – phase angle.

Fig. 20:   0.6 M NaCl 0.1M acetic acid, a) Nyquist, b) bode
plot – modulus, C) Bode plot – phase angle.

small corrosion resistance observed Rct ≈ 100 $\Omega.cm^{-2}$ and this implies the most rapid corrosion.

3.5% NaCl +0.1M acetic Acid solution

Fig. 20 shows the corrosion behaviour of mild steel in the presence of acetic acid. The common feature taken from this plot is that the corrosion rate values are higher than for the other solution condition. It can be observed that corrosion processes are in agreement with the trends apparent in the polarization data (Figs.7, 8 and 9).

Effect of metal ion inhibitors
3.5% NaCl + 0.1M $CaCl_2$ solution

Fig. 21 shows the impedance response in the presence of calcium chloride. Here there is little improvement in the CO_2 corrosion resistance (Rct ≈ 200-100 $\Omega.cm^{-2}$). There has occurred a significant decrease in the aerated corrosion rate that can be attributed to precipitation of a calcium hydroxide film which increases the charge transfer resistance of the formed protective film.
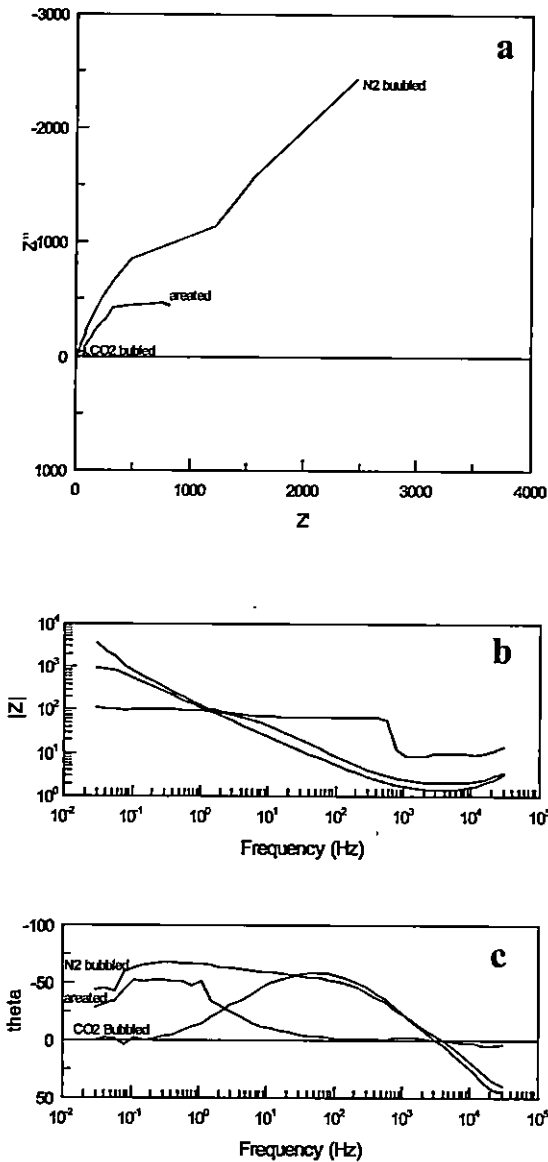
Fig. 21: 0.6 M NaCl 0.1M calcium chloride, a) Nyquist, b) bode plot – modulus, C) Bode plot – phase angle
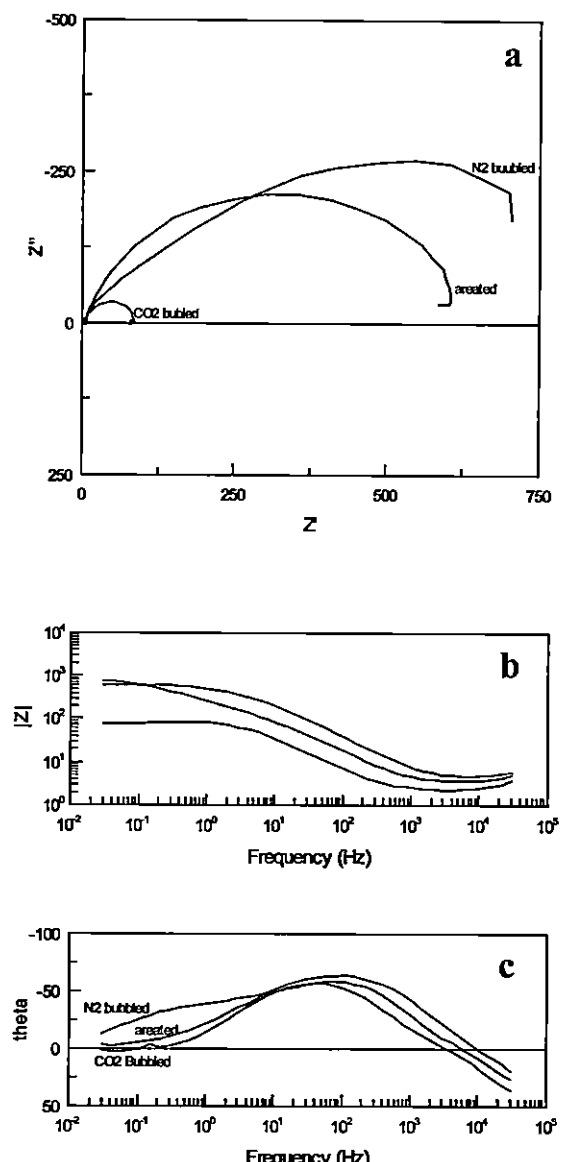
Fig. 22: 0.6 M NaCl 0.1M ZnCl2, a) Nyquist, b) bode plot – modulus, C) Bode plot – phase angle.

3.5% NaCl + 0.1M ZnCl$_2$ solution

Fig. 22 shows impedance response in the presence of zinc chloride. Generally, the corrosion resistance is similar to that in calcium chloride solution, but there is some passivation behaviour, shown by the polarisation curves (Figs. 16, 17 and 18), that is difficult to observe on the impedance plots in (Fig. 22). The reason for that is that passivation behaviour strongly depends on the potential and by scientific principle the impedance as a technique was carried out at the open circuit value for potential.

CONCLUSIONS

1- Mild steel, in the presence of CO$_2$, the highest corrosion rates recorded compared with aerated and N$_2$ bubbled solutions.

2- Acetate enhances the mild steel corrosion rate and this confirms that the presence of acetate add some aggressiveness to the solution.

3- Mostly, There is good agreement between D.C polarization curves results and A.C impedance results accept in case of zinc chloride corrosion measurements; the AC does not help to know clear info about the mechanism happened on the surface.

4- For all solution conditions, the presence of acetic acid gives higher corrosion rate values over solutions containing sodium acetate.

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