

## **CHAPTER-IV**

# **EVALUATION OF CORROSION CHARACTERISTICS OF CARBON STEEL IN GV SOLUTION AND EFFECT OF INHIBITORS**

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## EVALUATION OF CORROSION CHARACTERISTICS OF CARBON STEEL IN GV SOLUTION AND EFFECT OF INHIBITORS

### A) INTRODUCTION :

From the literature survey, it is established that use of inhibitors has been considered as an important criterion for safe and economical performance of the carbon dioxide removal system. The inhibitors studied so far have been categorized into cathodic and anodic depending upon the active group or ion present. Cathodic or film forming inhibitors have an advantage over the anodic inhibitors that their performance steadily increases with concentration. However, in most cases complete protection of the metal is not achieved or the concentration required is high. Additionally most of these inhibitors are pH sensitive, hence their performance is doubtful in a system where variation in pH is essential for optimizing the system.

Anodic inhibitors on the other hand have shown quite a good efficiency at a very low concentration, however, it is most important to maintain their concentration above a certain level otherwise they tend to induce localized corrosion. Many of these inhibitors are oxidizing ions and can perform well in acidic or alkaline media. It is also established (1) that the anodic or passivating inhibitors are sensitive to corrosion potential of the metal.

Many scientists have studied the corrosion of carbon steel material in potassium carbonate solutions in presence and absence of carbon dioxide by weight loss and electrochemical techniques.

As stated in Japanese patent by JGC Corpn. Tokyo ( 2 ), in absence of inhibitor the corrosion rate of CS in 25% potassium carbonate at 100 Deg. C. is 37.8 mpy.

BF Mago (3) has stated that in a boiling solution of potassium carbonate through which carbon dioxide was passed, corrosion rate was 8.46 mm/yr without addition of inhibitors.

Addition of arsenic trioxide to potassium carbonate solution has two advantages :

1. It acts as a catalyst for the absorption/ desorption of carbon dioxide
2. It is a known passivator of CS.

Now, the fact that even without arsenic oxide, the corrosion rate of CS is less than 5 mpy, clearly eliminates the possibility of accurate measurement of loss in weight of test coupons in inhibited potassium carbonate solutions.

The preliminary study carried out by me, on GV solution corrosivity have also given substantial evidences to prove the above fact.

Many scientists have successfully evaluated the performance of various inhibitors in hot potassium carbonate or GV solutions.

Mikhailovskii (4) has stated that surface  $\text{OH}^-$  is formed during the reduction of oxidising anions like chromates, vanadates, tungstates, molybdates, perchlorates, nitrites and peroxy compounds, depending on the ratio of the number of electrons participating in the cathodic

act of the oxidizer reduction to the number of  $\text{OH}^-$  formed. The oxidizer may either activate or passivate the metal.

Fyfe ( 5 ) has stated that in unalloyed steel, stress corrosion cracking (SCC) is prevented in carbon dioxide absorption by an aqueous alkaline arsenite or arsenate ion containing solution by raising the redox potential of the steel by adding ferric, antimony or vanadium ions.

Turner ( 6 ) had found that the measured corrosion potential exceeds that value at which the metal surface is susceptible to intergranular corrosion, then ions are added to or produced in the absorption solution which are capable of increasing the redox potential of the CS. In potassium carbonate solutions which contain 0.1 - 14.0 wt% arsenic ions, the corrosion potential at which the metal surface for intergranular corrosion is assessible lies at -600 mV vs SCE.

Atkins et. al (7) has stated that SCC of CS only took place when electrochemical potential of the steel in contact with the GV solution lay within a well defined range of values. They observed that no cracking under stressed condition was found when testing in solutions at below 70 Deg. C. and there appears to be some sort of corrosion activation at about 70 Deg. C.

Armstrong and Coates (8) stated that the susceptibility of SCC of low CS in caustic solutions has been shown to occur in certain ranges of electrode potentials, being dependent upon solution composition and temperature.

ICI Ltd., London (9) has established that SCC is influenced by corrosion potential.

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Parkins et al (10) defined that the potential range in which cracking occurs depends upon the solution compositions and temperatures, but typically is from about -0.6 to -0.7 V vs SCE. In a private communication I.V. Alemanno (11) has recommended to use the potential measurement method to reduce the SCC susceptibility during the plant in operation.

It may be worth while here to look into macrofeatures associated with the CO<sub>2</sub> removal system. Injection of air into the wetcoke system of CO<sub>2</sub> absorption leads to sufficient solids precipitation and associated operational difficulties. Accumulation of high iron solids are oxidation products due to an increase in general corrosion of the equipment. In uninhibited wetcoke liquor this may be due to the selective dissolution of pearlitic phase in CS. This may often lead to high iron pick up by solution even though explicit evidences of metal loss as may be quantified by routine metal wall thickness measurement, during equipment inspection, are absent (12). Reportedly such form of corrosion is not expected upon using inhibited wetcoke solutions indicating that air injection and inhibitor addition reduce the problem. Increased volume of precipitated solids may be temporary, in such a case, but finally leading to results with lower iron pick up and reducing problems of fouling during plant in operation. An initial spurt in precipitation may safely be correlated to effect of sparging air which increases oxidation rate. The exact phenomenon checking further solids precipitation being unknown, its attribution to inhibitor addition may be expected.

Generally CS is expected to show a ferrite - pearlite structure with varying proportions of pearlite related to the carbon contents. Pearlite, the phase of our interest further comprises of bands of bcc ferrite and iron carbide or cementite (Fe<sub>3</sub>C). Under certain conditions

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of pH and electrode potential and in the presence of certain anions, cementite may dissolve by reduction. This electrochemical behaviour of pearlite was thought to vary with different proportions and varieties of inhibitor additions leading to such reduction as also with varying concentrations of  $O_2$  content of solution (13). Reduced cementite was proposed to yield methane in some cases (14). This loss of cementite may be one of the reasons leading to the phenomenon of pearlite leaching under certain potential ranges which was also thought to be related to the SCC potential (15).

#### **B) VISUAL OBSERVATIONS OF CS SURFACE AND GV SOLUTIONS :**

Observations of the CS surface and GV solutions, with the naked eye, is discussed in this section. Observations are noted before and after the various inhibitors are added to the GV solutions.

GVSL solution prepared in the laboratory was clear without any colouration.

CS surface, as mentioned elsewhere, was shining (prepared up to 240 grit finish) and no visible layer is seen before the experimentation.

Addition of vanadium pentoxide ( $V_2O_5$ ) to the Syn. GVSL solution changes the colour of the solution to light yellow. Any addition of ferrous ions intensifies the yellow colouration instantly. This may be due to oxidation of ferrous to ferric ions by  $V_2O_5$ , which is strongly oxidizing in nature. Aeration of the system after addition of ferric ions does not in any way change the colour of Syn. GVSL solution.  $V_2O_5$  is not completely soluble in Syn. GVSL solution, therefore potassium hydroxide (KOH) was used for dissolution. CS surface after exposure in the Syn. GVSL solution containing  $V_2O_5$  retains its original shine

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and lustre but the surface is slightly dull after exposure in GV solution with  $V_2O_5$  and ferric ions. Pot. dichromate ( $K_2Cr_2O_7$ ), which is very easily soluble in Syn. GVSL solution, gives an orange colour to the GVSL solution, which intensifies with addition of ferrous ions. Aeration does not change the colour of the solution. CS surface is almost as such after exposure in syn. GVSL solution containing  $K_2Cr_2O_7$ , but with ferric ions, the surface is blackened to a great extent.

Ammonium metavanadate containing inhibitors are not easily soluble in Syn. GVSL solution, and therefore KOH was used to dissolve it. It imparts a dark yellow to reddish colouration to GVSL solution which intensifies with addition of ferrous ions to the solution and aeration does not change this. CS surface almost retains its original shine and lustre with or without ferric ion presence.

$K_2Cr_2O_7$  and sodium silicate imparts a greenish colour to the syn. GVSL solution, which intensifies with the addition of ferrous ions and aeration does not change this. CS surface retains its original shine and lustre when exposed to solution containing these inhibitors, but ferric ion addition blackens the surface.

Antimony oxide is also not completely soluble in syn. GVSL solution and therefore KOH is used to dissolve it. The colour of the GV solution does not in any way change due to addition of  $Sb_2O_3$  at any concentration. Addition of ferrous ions imparts light greenish tinge to the solution which turns to golden yellow when the solution is aerated. This is due to oxidation of ferrous to ferric ions. CS surface exposed to Syn. GVSL solution with 0.15%  $Sb_2O_3$  and up to 0.02% ferric ions is blackened to a great extent, but more than 0.02% ferric ion additions, the CS surface retains its original shine and lustre.

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Some photographs of the CS specimen in the solution and out of it are given in Plates - 1, 2 and 3. As can be seen from the photographs, GV solution imparts a darkened surface to the CS but  $Sb_2O_3$  and ferric ions does not change the shine and lustre of the surface and therefore keeps it in as it is condition.

CS after exposure to Syn. GVSL solution without any addition of inhibitors, has a darkened surface on it. Addition of ferric ions not only further intensifies the blackness of the surface but also imparts greenish tinge to the solution, which on aeration turns to intense yellow colouration. CS surface exposed thus is depicted in Plate-1.

Plant lean, semilean and rich solutions (which contains ferrous/ ferric ions) has greenish tinge/ yellow colouration depending upon the ferrous/ ferric contents in the solution. CS exposed to these solutions is imparted with dark black colouration on its surface. After aeration the yellow colouration of the solutions intensifies and the CS surface blackens further.

Plant GVSL solutions collected after  $Sb_2O_3$  additions showed mixed observations. GVSL dated 7.4.90 and 23.5.90 had a greenish tinge and slight precipitations which on aeration turned yellow. Precipitations (ferrous salts) also dissolved after aeration. CS surface acquired a blackish coating after exposure in these solutions. Plant GVSL solutions collected on 31.5.90 and 13.6.90 had intense yellow colouration and aeration does not change this colouration in any way (It is to be mentioned here that aeration rate was increased after 23.5.90). CS surface also retains almost its original shine and lustre after exposure to these solutions.

**C) OBSERVATIONS FROM OPEN CIRCUIT POTENTIAL (OCP) MEASUREMENT (TABLE - 1) :**

c.1) For CS exposed to plant GV solutions :

OCP of CS in lean, semilean and rich solutions collected from plant shows no wider differences, but when temperature is considered, it is seen that OCP of CS in lean, SL at 70 Deg. C. and 85 Deg. C. is more negative than the OCP of CS in rich solution at 102 Deg. C. The temperature at which these solutions were studied is the maximum attainable in practical situation in the plant. The chemical analysis of the solutions (Table-2, p 86) also shows the lower carbonation index value of lean and SL solutions (0.9 and 1.1) than the value of 1.6 for rich solution.

c.2) For CS exposed to Syn. GVSL solution with ferric ions only :

OCP of CS in aerated Syn. GVSL solution is -745 mV, slightly more negative than the OCP of CS in plant GVSL solution (-722 mV). Addition of 0.01%, 0.02%, 0.03% and 0.04% ferric ions to this Syn. GVSL solution does not shift the potential much, in fact it decreases only to -750 to -760 mV range, indicating the non-effect of ferric ions only to act as an inhibitor. It was observed here that ferric ions, which were added in the form of ferrous ions before the solution was aerated, had taken almost two hours of aeration for oxidation to ferric ions.

c.3) For CS exposed to Syn. GVSL solution with 0.1% vanadium pentoxide ( $V_2O_5$ ) and ferric ions :

In absence of ferric ions, OCP of CS in Syn. GVSL solution with 0.1%  $V_2O_5$  gives a value of -330 mV, showing very good shift in potential

when compared with OCP of CS in Syn. GVSL without the inhibitor. Addition of 0.01% ferric ions shifts it to -424 mV showing a negative effect of ferric ions. Any further addition of ferric ions (up to 0.03%) does not shift the potential much. It can be noted here that addition of ferric ions (which is an unavoidable consequence of a CO<sub>2</sub> removal system) decreases the potential by around 90 to 100 mV.

c.4) For CS exposed to Syn. GVSL solution with 0.7% potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.7% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> shows a value of -400 mV, far higher than that value of CS in Syn. GVSL only (-745 mV), showing very good shift in potential. Addition of 0.01, 0.02 and 0.03% ferric ions to this solution shifts the potential to values below -719 mV, showing negative effect of ferric ions. The potential attained after addition of 0.01% ferric ions remains unaffected by further additions of ferric ions to the solution. It was also observed here that ferrous ions on addition are instantaneously oxidized into ferric ions by the strong oxidising property of dichromate ions.

c.5) For CS exposed to Syn. GVSL solution with 0.6% sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and 0.02% potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.6% Na<sub>2</sub>SiO<sub>3</sub> and 0.02% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is -398 mV, showing a very good shift when compared with the value of -745 mV for CS in Syn. GVSL only. Addition of 0.01% ferric ions to this solution shifts OCP to -720 mV showing negative effect of ferric ions. Any further additions of ferric ions up to 0.03%, does not appreciably shifts this potential. Like in the addition of 0.7% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to Syn. GVSL solution, here also, instantaneous oxidation of

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ferrous to ferric ions takes place due to the presence of dichromate ions.

c.6) For CS exposed to Syn. GVSL solution with 1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.25% sodium nitrite ( $\text{NaNO}_2$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 1%  $\text{NH}_4\text{VO}_3$  and 0.25%  $\text{NaNO}_2$  is -329 mV, showing appreciable shift from -745 mV, the OCP value of CS in Syn. GVSL only. Any additions of ferric ions up to 0.03% ferric ions does not change the potential much, in fact it is almost a constant, hovering between -324 to -332 mV values.

c.7) For CS exposed to Syn. GVSL solution with 0.1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.1% potassium antimonyl tartrate ( $\text{KSbC}_4\text{H}_4\text{O}_6$ ) and 0.01% tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) and ferric ions:

OCP of CS in Syn. GVSL solution with 0.1%  $\text{NH}_4\text{VO}_3$ , 0.1%  $\text{KSbC}_4\text{H}_4\text{O}_6$  and 0.01%  $\text{C}_4\text{H}_6\text{O}_6$  is -402 mV, showing appreciable shift from -745 mV, the OCP value of CS in Syn. GVSL only. Additions of 0.01% and 0.02% ferric ions to this solutions does not shift this value further, but with 0.03% ferric ion concentration it falls to -396 mV, still not appreciable shift.

c.8) For CS exposed to Syn. GVSL solution with different concentrations of antimony oxide ( $\text{Sb}_2\text{O}_3$ ) :

OCP of CS in Syn. GVSL solution with 0.075%, 0.1%, 0.13%, 0.14% and 0.15%  $\text{Sb}_2\text{O}_3$  remained between -724 mV to -770 mV, comparable

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to the OCP value of -745 mV for CS in Syn. GVSL solution only, indicating no appreciable shift in potential with the addition of  $\text{Sb}_2\text{O}_3$ . In fact the highest negative value of -770 mV for 0.15%  $\text{Sb}_2\text{O}_3$  shows the accelerating effect of  $\text{Sb}_2\text{O}_3$  additions to Syn. GVSL on CS.

c.9) For CS exposed to Syn. GVSL solution with 0.075% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$  is -745 mV, very much comparable with the value of -745 mV for CS in Syn. GVSL only, showing no effect at all.

Addition of 0.01% and 0.02% ferric ions to Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$ , does not appreciably shift the OCP, but at 0.03% ferric ion concentration it shifts to more positive values of -440 mV, showing better inhibitive effect of the combination. Again at 0.04% ferric ion concentration it decreases by 20 mV to -460 mV showing no appreciable shift.

c.10) For CS exposed to Syn. GVSL solution with 0.1% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.1%  $\text{Sb}_2\text{O}_3$  is -750 mV, again very much comparable with the value of -745 mV for CS in Syn. GVSL only, showing no effect of higher concentrations of  $\text{Sb}_2\text{O}_3$ .

Addition of 0.01% and 0.02% ferric ions to Syn. GVSL solution with 0.1%  $\text{Sb}_2\text{O}_3$  shifts the potential to -728 mV and -727 mV respectively from a value of -750 mV for CS in Syn. GVSL with 0.1%  $\text{Sb}_2\text{O}_3$ , but is not appreciable at all. Further additions of 0.03% and 0.04% ferric

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ions shifts the potential remarkably to around -480 mV and -450 mV respectively, showing increasing trend of shifting potential to more positive values on addition of ferric ions.

c.11) For CS exposed to Syn. GVSL solution with 0.13% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$  is -724 mV, slightly higher value than -745 mV, the OCP for CS in Syn. GVSL only, but not at all appreciable.

Addition of 0.01% and 0.02% ferric ions to Syn. GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$  also does not show any appreciable shift in potential, but at 0.03% ferric ion concentration the potential is shifted to -440 mV and again at 0.04% ferric ion concentration -388 mV, showing very appreciable shifts of 284 mV and 336 mV for 0.03% and 0.04% ferric ion concentrations respectively. In comparison to the GVSL solution only, a decreasing trend is observed with addition of 0.01% ferric ions and an increasing trend towards more positive values is seen thereafter.

c.12) For CS exposed to Syn. GVSL solution with 0.14% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solutions with 0.14%  $\text{Sb}_2\text{O}_3$  is -728 mV, slightly higher value than -745 mV, the OCP for CS in Syn. GVSL only, but very much comparable.

Addition of 0.01% and 0.02% ferric ions does not shift the potential much, but at 0.03% ferric ion concentration, it shifts to -389 mV and

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at 0.04% ferric ion concentration, it is -366 showing very appreciable shifts of 339 mV and 362 mV, respectively for 0.03% and 0.04% ferric ion concentrations.

It can be noted here that after a decrease in OCP from -728 mV to -738 mV with the addition of 0.01% ferric ions, there is a steady increase with 0.02 to 0.04% ferric ion concentrations, albeit not noteworthy with 0.02% ferric ion concentration.

c.13) For CS exposed to Syn. GVSL solution with 0.15% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.15%  $\text{Sb}_2\text{O}_3$  is -770 mV, lower than the value for CS in Syn. GVSL only (-745 mV), showing accelerating tendency with addition of 0.15%  $\text{Sb}_2\text{O}_3$ .

Addition of 0.01% ferric ions shifts this OCP of -770 mV to -430 mV which is not observed with any  $\text{Sb}_2\text{O}_3$  - 0.01% ferric ions combination. A shift of 340 mV is observed here. At 0.02% ferric ion concentration it shifts to -385 mV and at 0.03% ferric ion concentration to -305 mV, showing remarkable shifts in potential values when compared with the OCP of CS in Syn. GVSL only (-745 mV) and with CS in Syn. GVSL with 0.15%  $\text{Sb}_2\text{O}_3$  only (-770 mV). In fact, -305 mV potential value is the best possible positive value obtained with any combination of  $\text{Sb}_2\text{O}_3$  - ferric ion concentration. A shift of 465 mV is observed with 0.15%  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ions. It is also noteworthy that no appreciable shift in potential is observed for any combination of  $\text{Sb}_2\text{O}_3$  - 0.01 and 0.02% ferric ions, but with 0.15%  $\text{Sb}_2\text{O}_3$  - 0.01 and 0.02% ferric ions it shifts from -770 mV to -430 mV and -385 mV respectively. At 0.04% ferric ion concentration, the OCP again decreases to -410 mV, showing a slightly accelerating effect of 0.04% ferric ion concentration.

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**D) OBSERVATIONS FROM CRITICAL CURRENT DENSITY ( $i_{cc}$ ), PASSIVE CURRENT DENSITY ( $i_p$ ), PASSIVE POTENTIAL ( $E_p$ ) AND PRIMARY PASSIVATING POTENTIAL ( $E_{pp}$ ) DERIVED FROM POLARIZATION PLOTS (TABLE -2), FIGURES -1 TO 19 :**

d.1) For CS exposed to plant GV solutions :

Critical current density ( $i_{cc}$  mA/cm<sup>2</sup>) is highest in plant GV semilean solution, when compared with the corresponding values for lean and rich solutions. It is noticeable that an  $i_{cc}$  of 20 mA/cm<sup>2</sup> for semilean solution is 1.3 times higher than that for lean solution and 4.0 times higher than that for rich solution value. The corresponding potential, known as primary passivating potential ( $E_{pp}$  mV) for semilean solution is -120 mV, for lean it is -130 mV and for rich solution is 0 mV. Passive potential ( $E_p$  mV), at which CS material remains passive, for lean and semilean solution is around 360 to 400 mV, but for rich solution it is as far as 600 mV. Passive current density ( $i_p$  mA/cm<sup>2</sup>) at this passive potential point is also very high for rich solution.  $i_p$  of 2.33 mA/cm<sup>2</sup> is observed for rich solution and for lean and semilean solutions it is 0.37 and 0.53 mA/cm<sup>2</sup> respectively. The OCP values of CS in plant GV solutions (between -700 mV and -800 mV) is not at all comparable with their respective  $E_p$  or  $E_{pp}$  values.

d.2) For CS exposed to Syn. GVSL solution with ferric ions :

$i_{cc}$  value for CS in Syn. GVSL solution is 8.33 mA/cm<sup>2</sup>, and after a decrease in this value to 3.56 mA/cm<sup>2</sup> when 0.01% ferric ions are added, it again steadies at 10 mA/cm<sup>2</sup> for 0.02% and 0.03% ferric ion concentration and reaches the peak of 28.33 mA/cm<sup>2</sup> for 0.04% ferric ion concentration.

Corresponding Epp values at these ferric ion concentrations and at these icc values is found to be around -460 mV to -490 mV, comparable with the value for CS in Syn. GVSL only which is -435 mV. Passive current density ( $i_p$  mA/cm<sup>2</sup>) also shows a similar behaviour like critical current density. Passive potential is almost a constant at around +150 mV for all concentrations of ferric ions. Here the OCP values which is around -750 mV for CS in Syn. GVSL only and with 0.01% to 0.04% ferric ion concentrations, is better comparable with Ep and Epp values than that values for CS in plant GV solutions.

Lower icc values for 0.01% ferric ions shows the inhibitive effect of these, but at higher ferric ion concentrations tend to act as accelerating rather than inhibiting for CS. The constant nature of Ep and Epp values also supports the fact that no appreciable effect of ferric ions is obtained.

d.3) For CS exposed to Syn. GVSL solution with 0.1% vanadium pentoxide ( $V_2O_5$ ) and ferric ions :

CS in Syn. GVSL solution with 0.1%  $V_2O_5$  lowers the icc value to 0.24 mA/cm<sup>2</sup> from 8.33 mA/cm<sup>2</sup> icc for CS in Syn. GVSL only, but the addition of 0.01% and 0.02% ferric ions to this increases icc 2 to 4 times and then decreases to almost its original value by the addition of 0.03% ferric ions to the solution.

Corresponding Epp remains constant at around -300 mV for Syn. GVSL only and with 0.01, 0.02 and 0.03% ferric ion concentrations. Passive current density also increases marginally with additions of ferric ions. Ep for all concentrations of ferric ions and for Syn. GVSL only remains constant at -100 mV. The inhibitive effect of 0.1%  $V_2O_5$

is shown in its action of lowering the icc value and Epp value, but the addition of ferric ions increases icc and it does not have any effect on either Ep or Epp values. 0.1%  $V_2O_5$ -ferric ion concentrations tend to accelerate the effect on CS in Syn. GVSL as observed in lower OCP values and increase in the icc and ip values.

d.4) For CS exposed to Syn. GVSL solution with 0.7% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

Critical current density is lowered to 0.04 mA/cm<sup>2</sup> by the addition of 0.7%  $K_2Cr_2O_7$  to Syn. GVSL solution from 8.33 mA/cm<sup>2</sup> in Syn. GVSL only, showing very good inhibiting property of dichromate ions.

Addition of 0.01% ferric ions to this solution increases icc value to 50 mA/cm<sup>2</sup> which is in fact more than 1000 times the value for CS in Syn. GVSL with 0.7%  $K_2Cr_2O_7$ . This increasing trend is somewhat lowered with the additions of 0.02% and 0.03% ferric ions, but it is nowhere near 0.04 mA/cm<sup>2</sup>, the icc value for Syn. GVSL with 0.7%  $K_2Cr_2O_7$ . It is observed that ferric ions in presence of 0.7%  $K_2Cr_2O_7$  tremendously accelerates the effect on CS in Syn. GVSL solution.

Epp values of -590 mV for 0.7%  $K_2Cr_2O_7$  only, also indicates that it is well within the range of OCP value of -400 mV. Ep of -400 mV and OCP of -400 mV also is well comparable and shows that CS will be in passive condition when only 0.7%  $K_2Cr_2O_7$  is present. Addition of ferric ions increases Epp values to -300 to -380 mV range, Ep values increases to +100 to +200 mV range and ip values increases from 0.03 mA/cm<sup>2</sup> for Syn. GVSL with 0.7%  $K_2Cr_2O_7$  to 1.0 to 5.5 mA/cm<sup>2</sup> range, once again showing adverse effect of ferric ion concentrations.

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It is interesting to note here that addition of 0.7%  $K_2Cr_2O_7$  imparts very good inhibition to CS but addition of ferric ions destroys this effect by increasing all values and decreasing OCP values to around -715 mV. Addition of 0.03% ferric ions somewhat arrests the increasing accelerating trend, but still in no way comparable to the values of Syn. GVSL with 0.7%  $K_2Cr_2O_7$ .

d.5) For CS exposed to Syn. GVSL solution with 0.6% sodium silicate ( $Na_2SiO_3$ ) and 0.02% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

CS in Syn. GVSL solution with 0.6%  $Na_2SiO_3$  and 0.02%  $K_2Cr_2O_7$  shows an icc of 1.07 mA/cm<sup>2</sup>, nearly 7 times lower than the icc for CS in Syn. GVSL only. ip is also much lower at 0.12 mA/cm<sup>2</sup> (1.78 mA/cm<sup>2</sup> for Syn. GVSL only), but the addition of ferric ions increases both icc and ip to much higher values, when compared with icc and ip for Syn. GVSL only or with the above mentioned inhibitors. This indicates that although the inhibitors alone are capable of lowering the current values, the addition of ferric ions destroys this property and accelerates the corrosion process. The shift in the values of OCP at different ferric ion concentration in the range of -700 mV from around -400 mV for CS in Syn. GVSL with inhibitors, also supports this point. Epp values, when ferric ions are added are also more negative when compared with the value obtained using  $Na_2SiO_3$  and  $K_2Cr_2O_7$  only, but Ep value remains constant at -100 mV for all ferric ion concentrations.

It is noted here that addition of 0.6%  $Na_2SiO_3$  and 0.02%  $K_2Cr_2O_7$  imparts good inhibition of CS but addition of ferric ions alters this property altogether.

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d.6) For CS exposed to Syn. GVSL solution with 1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.25% sodium nitrite ( $\text{NaNO}_2$ ) and ferric ions:

CS in Syn. GVSL solution with 1%  $\text{NH}_4\text{VO}_3$  and 0.25%  $\text{NaNO}_2$  shows an icc value of  $0.24 \text{ mA/cm}^2$  much lower than the value of  $8.33 \text{ mA/cm}^2$  for CS in Syn. GVSL only and comparable with the value of  $0.24 \text{ mA/cm}^2$  for CS in Syn. GVSL with 0.1%  $\text{V}_2\text{O}_5$ . Addition of ferric ions does not alter the icc much. In fact  $i_p$ ,  $E_{pp}$  and  $E_p$  values also does not show any appreciable alteration. It can be noted here that OCP values for CS in Syn. GVSL solutions with and without ferric ions are not comparable to  $E_p$  values for the same, showing a difference of more than 300 mV, OCP values are almost comparable with  $E_{pp}$  values rather than  $E_p$  values. From the values obtained it can be seen that addition of ferric ions to Syn. GVSL solution containing  $\text{NH}_4\text{VO}_3$  and  $\text{NaNO}_2$  does not in any way change the current values or shift the potential characteristics.

d.7) For CS exposed to Syn. GVSL solution with 0.1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), 0.1% potassium antimonyl tartrate ( $\text{KSbC}_4\text{H}_4\text{O}_6$ ), and 0.01% tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) :

Critical current density for CS in Syn. GVSL solution with 0.1%  $\text{NH}_4\text{VO}_3$ , 0.1%  $\text{KSbC}_4\text{H}_4\text{O}_6$  and 0.01%  $\text{C}_4\text{H}_6\text{O}_6$  is  $0.66 \text{ mA/cm}^2$ , much lower than the icc value of  $8.33 \text{ mA/cm}^2$  for CS in Syn. GVSL only, showing better inhibiting property of the inhibitor combinations mentioned above.

Addition of 0.01 and 0.02% ferric ions does not alter this value of icc, but addition of 0.03% ferric ions lowers it further to  $0.09 \text{ mA/cm}^2$  showing good effect of 0.03% ferric ion concentration. The

same trend is shown in the  $i_p$  values.  $E_{pp}$  and  $E_p$  for 0.03% ferric ions are definitely more negative, and therefore more comparable with the respective OCP value, than the other ferric ion combinations, but it is still not noteworthy shift in potentials. Like in the  $i_{cc}$  and  $i_p$  values for 0.01% and 0.02% with the inhibitor combinations mentioned,  $E_{pp}$  and  $E_p$  values also does not shift much. This shows the ineffectiveness of the inhibitors with or without ferric ions to the Syn. GVSL solution.

d.8) For CS in Syn. GVSL solution with different concentrations of antimony oxide ( $Sb_2O_3$ ) :

CS in GVSL solution with additions of 0.075%  $Sb_2O_3$  and 0.1%  $Sb_2O_3$  shows a falling trend in the  $i_{cc}$  values. The same trend is followed in  $i_p$  values, but further additions of  $Sb_2O_3$  to attain a concentration of 0.13% and 0.14% shows a tremendous (> ten fold) increase in  $i_{cc}$  values and 2 to 10 times increase in  $i_p$  values. At 0.15%  $Sb_2O_3$ , there is again a fall of  $i_{cc}$  and  $i_p$  values but in no way comparable to the value for Syn. GVSL only, 0.075% or 0.1%  $Sb_2O_3$  values. The  $E_{pp}$  and  $E_p$  values for all the combinations are much farther from the OCP values which is always more than -725 mV for all  $Sb_2O_3$  concentrations. The  $E_p$  values for 0.13 and 0.14%  $Sb_2O_3$  is the least obtained (-350 mV and -310 mV respectively).

Almost constant values of  $i_{cc}$  and  $i_p$  with the addition of 0.075% and 0.1%  $Sb_2O_3$  and increase in the values of these with 0.13, 0.14 and 0.15%  $Sb_2O_3$  concentrations and the comparison of  $E_{pp}$  and  $E_p$  values, and the constant nature of OCP values together shows that  $Sb_2O_3$  is incapable of changing passive characteristics of CS in Syn. GVSL solution.

d.9) For CS exposed to Syn. GVSL with 0.075% antimony oxide ( $Sb_2O_3$ ) and ferric ions :

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CS in Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$  shows an  $i_{cc}$  value of 7.67 mA/cm<sup>2</sup> comparable with the value of 8.33 mA/cm<sup>2</sup> for CS in Syn. GVSL only. Addition of 0.01% ferric ions increases this value to around 9.0 mA/cm<sup>2</sup> showing an accelerating trend, but at 0.02, 0.03 and 0.04% ferric ion concentration there is a gradual decrease in value up to 0.07 mA/cm<sup>2</sup>. Same trend is shown in the  $i_p$  values also, where for 0.075%  $\text{Sb}_2\text{O}_3$  it is 1.06 mA/cm<sup>2</sup> and for 0.04% ferric ions with 0.075%  $\text{Sb}_2\text{O}_3$  it is only 0.03 mA/cm<sup>2</sup>. This shows the positive effect of 0.075%  $\text{Sb}_2\text{O}_3$  in combination with 0.02% or more ferric ion concentrations.

$E_p$  values remains a constant up to 0.02% ferric ions, but at 0.03% and 0.04% ferric ion concentration it comes closer to OCP values of -440 mV and -460 mV ( $E_p$  of -300 mV and -330 mV for 0.03% and 0.04% ferric ions).

$E_{pp}$  values for 0.01% and 0.02% ferric ions are more negative, but more positive values are obtained for 0.03% and 0.04% concentration of ferric ions.

The decreasing nature of  $i_{cc}$  and  $i_p$  values from 0.02% ferric ions onwards, the more negative values of  $E_p$  at 0.03% and 0.04% ferric ions, more positive values of  $E_{pp}$  at 0.03 and 0.04% ferric ions and the shift in OCP from 0.03% ferric ions onwards shows that 0.075%  $\text{Sb}_2\text{O}_3$  with more than 0.02% ferric ions is capable of lowering the critical current density as well as shifting the potential to move nearer the  $E_p$  values and therefore has good passivating properties.

d.10) For CS exposed to Syn. GVSL with 0.1% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

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Critical current density (icc) of CS in Syn. GVSL solution with 0.1%  $\text{Sb}_2\text{O}_3$  is 5.56 mA/cm<sup>2</sup> slightly lower than the value for GVSL solution only i.e. without antimony and ferric ions. Addition of 0.01% ferric ions to the solution containing 0.1%  $\text{Sb}_2\text{O}_3$  increases icc value by more than five times showing tremendous accelerating effect, but further addition of ferric ions to make 0.02% in the solution decreases this value to around 15 mA/cm<sup>2</sup> and trend continues with 0.03% and 0.04% ferric ions. Lowest icc value of 0.064 mA/cm<sup>2</sup> is obtained with 0.04% ferric ions. Same trend is shown by ip values where an increase in the ip value is observed with 0.01% ferric ions and then a gradual decrease of this to attain 0.019 mA/cm<sup>2</sup> value for 0.04% ferric ions.

Ep values show a shift towards more positive side with additions of 0.01% and 0.02% ferric ions, but with 0.03% and 0.04% ferric ions it shifts closer to OCP values of -480 mV and -450 mV (Ep of -350 mV for both 0.03% and 0.04% ferric ions). Epp values for 0.01% and 0.02% ferric ions like in Ep values are nowhere closer to the OCP values, but for 0.03% and 0.04% ferric ions it is comparable with the OCP values.

Decrease in icc and ip values of GVSL solutions with 0.1%  $\text{Sb}_2\text{O}_3$  containing 0.03% and 0.04% ferric ions, comparable values of Ep and OCP at this concentrations and the shift in Ep values towards OCP value shows that 0.1%  $\text{Sb}_2\text{O}_3$  with 0.03% or 0.04% ferric ions is capable of lowering the icc value as well as shifting the potential towards Ep value thereby depicting its good passivating properties.

d.11) For CS exposed to Syn. GVSL with 0.13% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

CS in Syn. GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$  shows an icc value of 64.44 mA/cm<sup>2</sup> more than seven times higher than that for GVSL solution without any inhibitor addition. The accelerating effect of 0.13%  $\text{Sb}_2\text{O}_3$  is clearly seen here.

Addition of 0.01% and 0.02% ferric ions to GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$  increases the icc value to 111.11 mA/cm<sup>2</sup> and 100 mA/cm<sup>2</sup> respectively, showing again further acceleration of the corrosion process. But at 0.03% ferric ions concentration this is reduced remarkably to 0.51 mA/cm<sup>2</sup> depicting very good inhibiting property of the combination. Further addition of ferric ions to achieve 0.04% ferric ions does not change this value of icc, clearly showing that additional ferric ions does not either accelerate or retard the corrosion phenomena.  $i_p$  values also behaves the same way, the only difference being the value of 0.033 mA/cm<sup>2</sup> for 0.04% ferric ions (0.05 mA/cm<sup>2</sup> for 0.03% ferric ions), showing a further decrease in the value.

$E_p$  values up to 0.02% ferric ions does not shift significantly hovering between +300 mV and +400 mV but at 0.03% and 0.04% ferric ions it shifts closer to the OCP values of -440 mV and -388 mV respectively ( $E_p$  of -280 mV and -230 mV for 0.03% and 0.04% respectively).

$E_{pp}$  values for 0.01% and 0.02% ferric ions is in no way comparable to the OCP's of the CS in these solutions, but for 0.03% and 0.04% ferric ions is comparable with their respective OCP values.

Tremendous decrease in icc and  $i_p$  values for GVSL solutions containing 0.03% and 0.04% ferric ions, shift in the OCP values towards  $E_{pp}$  values and comparable values of OCP with  $E_p$  values,

clearly indicate the passivating properties of 0.13%  $\text{Sb}_2\text{O}_3$  in combination with 0.03% and 0.04% ferric ions.

d.12) For CS exposed to Syn. GVSL solution with 0.14% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

Critical current density ( $i_{cc}$ ) for CS in Syn. GVSL solution with 0.14%  $\text{Sb}_2\text{O}_3$  shows a value of 57.78 mA/cm<sup>2</sup>, far higher than the value of 8.33 mA/cm<sup>2</sup> which is for CS in GVSL solution without any addition of  $\text{Sb}_2\text{O}_3$ , clearly showing the accelerating effect of 0.14%  $\text{Sb}_2\text{O}_3$  addition. The trend of increase in  $i_{cc}$  values continue with the addition of 0.01% ferric ions (67.78 mA/cm<sup>2</sup>) and 0.02% ferric ions (96.67 mA/cm<sup>2</sup>), again showing accelerating effect. Further addition of ferric ions to achieve a concentration of 0.03% drastically reduces the  $i_{cc}$  value to only 0.51 mA/cm<sup>2</sup> showing very good inhibiting property of the combination. Addition to achieve 0.04% ferric ions slightly increases the  $i_{cc}$  value to 0.64 mA/cm<sup>2</sup> but still gives good inhibiting property.  $i_p$  values also show the same trend, an increase of values up to 0.02% ferric ions and a decrease at 0.03% ferric ion and then a slight increase again at 0.04% ferric ions.

$E_p$  values up to 0.02% ferric ions does not shift at all, but at 0.03% and 0.04% of ferric ions it shifts closer to the OCP values of -389 mV and -366 mV respectively ( $E_p$  values for 0.03% and 0.04% ferric ion are -250 mV and -290 mV respectively).

$E_{pp}$  values up to 0.02% ferric ions is not at all comparable to its OCP value. The  $E_{pp}$  values for 0.03% and 0.04% ferric ions are in fact more negative than their corresponding OCP values.

Remarkable decrease in the values of  $i_{cc}$  and  $i_p$ , shift in  $E_p$  values comparable with OCP values, more negative values of  $E_{pp}$  when

compared with their respective OCP values, for GVSL solution with 0.14%  $\text{Sb}_2\text{O}_3$  and 0.03% and 0.04% ferric ions concentration, shows very good passivating properties of the combinations.

It is to be noted here that the trend of almost comparable values of icc and ip up to 0.13%  $\text{Sb}_2\text{O}_3$  containing 0.03% and 0.04% ferric ions is slightly reversed, in that there is a slight increase in both the values with 0.14%  $\text{Sb}_2\text{O}_3$  and 0.04% ferric ions when compared with 0.03% ferric ion values.

d.13) For CS exposed to Syn. GVSL solution with 0.15% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

CS in Syn. GVSL solution with 0.15%  $\text{Sb}_2\text{O}_3$  shows an icc value of 23.89 mA/cm<sup>2</sup> much higher value when compared with the icc value of 8.33 mA/cm<sup>2</sup> for GVSL solution without any addition of inhibitor, but less than that value for 0.13%  $\text{Sb}_2\text{O}_3$  and 0.14%  $\text{Sb}_2\text{O}_3$  containing GVSL solution.

Addition of 0.01% ferric ions drastically reduces the icc value to 0.14 mA/cm<sup>2</sup>. This is in sharp contrast to the values obtained with other  $\text{Sb}_2\text{O}_3$  concentrations where icc values increases from 0.075%  $\text{Sb}_2\text{O}_3$  to 0.13%  $\text{Sb}_2\text{O}_3$  and then somewhat reduces for 0.14%  $\text{Sb}_2\text{O}_3$ . This behaviour is followed with further concentrations of ferric ions i.e. 0.02% and 0.03%. For these concentrations of ferric ions, the values of icc is found to be the lowest attainable with any combination of  $\text{Sb}_2\text{O}_3$  -ferric ions.

The icc value of 0.068 mA/cm<sup>2</sup> for 0.15%  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ions is in fact the lowest amongst all other combinations. But at 0.04% ferric ion concentration icc increases to 0.11 mA/cm<sup>2</sup> showing an

accelerating effect. The same trend, as the case of  $i_{cc}$ , is followed in the values for  $i_p$ . Here also the values of  $i_p$  (0.007) mA/cm<sup>2</sup> for 0.02% and 0.03% of ferric ions are the lowest amongst all Sb<sub>2</sub>O<sub>3</sub> - ferric ion combinations.

Like the pattern followed in  $i_{cc}$  and  $i_p$  values,  $E_{pp}$  and  $E_p$  values also follows the same.  $E_{pp}$  values for all 0.15% Sb<sub>2</sub>O<sub>3</sub> and ferric ion combinations falls either equal to or more negative to the OCP s of the corresponding systems, showing that attainment of  $E_{pp}$  is achieved by all the combinations.

$E_p$  values for 0.01% and 0.02% ferric ion concentrations (-320 mV and -350 mV) are comparable with the OCP s of the corresponding system (-430 mV and -385 mV), but the  $E_p$  value of -350 mV for 0.15% Sb<sub>2</sub>O<sub>3</sub> and 0.03% ferric ions is in fact less than the OCP of CS in the system (-305 mV). This shows that for achieving this OCP it is shifted through the  $E_p$  value of -350 mV.

The trend is again reversed with the addition of 0.04% ferric ions, where the  $E_{pp}$  value is more negative than OCP value and the  $E_p$  value is just comparable with the OCP value for the system.

Remarkable decrease in the values of  $i_{cc}$  and  $i_p$  with 0.15% Sb<sub>2</sub>O<sub>3</sub> and 0.01% ferric ion concentration onwards, the lowest attained  $i_{cc}$  and  $i_p$  values for 0.02% and 0.03% ferric ion concentrations, almost equal or more negative values of  $E_{pp}$ 's to the OCP s of the system with all ferric ion. Concentrations and highly comparable values of  $E_p$  and OCP for all systems shows this combination as good passivators of CS in Syn. GVSL solutions. Amongst these combinations, 0.15% Sb<sub>2</sub>O<sub>3</sub> with 0.03% ferric ions shows the best possible results that can be achieved. The less

negative value of OCP when compared with  $E_p$  value is to be noted here, since this is the only combination which gives this result.

**E) OBSERVATION FROM CORROSION CURRENT DENSITY VALUES OBTAINED FROM POLARIZATION PLOTS (TABLE - 3) :**

e.1) For CS exposed to plant GV solution :

$I_{Corr}$  in  $\text{mA}/\text{cm}^2$  for CS in GV rich solution is highest (when compared with GV lean and SL solution collected from plant). These experiments were conducted at 70 Deg. C., 85 Deg. C. and 102 Deg. C. for lean, semi lean and rich solutions respectively.

e.2) For CS exposed to Syn. GVSL solution with ferric ions only :

$I_{Corr}$  value for CS in Syn. GVSL solution at 85 Deg. is 0.19  $\text{mA}/\text{cm}^2$ , but this value decreases with the addition of 0.01% ferric ions to 0.006  $\text{mA}/\text{cm}^2$ , but further additions of ferric ions increases this value and for 0.04% ferric ions it reaches up to 0.223  $\text{mA}/\text{cm}^2$ , showing negative effect of additional ferric ions on the value of  $I_{Corr}$ .

e.3) For CS exposed to Syn. GVSL solution with 0.1% vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) and ferric ions :

$I_{Corr}$  for CS in Syn. GVSL solution with 0.1%  $\text{V}_2\text{O}_5$  increases to 0.209  $\text{mA}/\text{cm}^2$  from the value of 0.019  $\text{mA}/\text{cm}^2$  for CS in GVSL only, indicating tremendous increase in its value, but further additions of 0.01% and 0.02% ferric ions does not change the  $I_{Corr}$  much. At 0.03% ferric ions the value attains a minimum of 0.126  $\text{mA}/\text{cm}^2$ , still very high.

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e.4) For CS exposed to Syn. GVSL solution with 0.7% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

I Corr value for CS in Syn. GVSL solution with 0.7%  $K_2Cr_2O_7$  of  $0.021 \text{ mA/cm}^2$  is almost same as that for CS in GVSL only ( $0.019 \text{ mA/cm}^2$ ). Addition of 0.01 to 0.03% ferric ions disturbs this equality and increases this value to around 0.5 to  $0.6 \text{ mA/cm}^2$ , showing negative effect of the addition of ferric ions.

e.5) For CS exposed to Syn. GVSL solution with 0.6% sodium silicate ( $Na_2SiO_3$ ) and 0.02% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

0.6%  $Na_2SiO_3$  and 0.02%  $K_2Cr_2O_7$  in Syn. GVSL solution gives CS an I Corr of  $0.016 \text{ mA/cm}^2$  comparable to the value of  $0.019 \text{ mA/cm}^2$  for CS in Syn. GVSL only. Addition of 0.01% ferric ions increases this to  $0.139 \text{ mA/cm}^2$  and again to  $0.404 \text{ mA/cm}^2$  with 0.02% ferric ions which then decreases marginally to  $0.307$  with 0.03% ferric ions.

e.6) For CS exposed to Syn. GVSL solution with 1% ammonium metavanadate ( $NH_4VO_3$ ) and 0.25% sodium nitrite ( $NaNO_2$ ) and ferric ions :

CS in Syn. GVSL solution with 1% amm. metavanadate and 0.25%  $NaNO_2$  gives an I Corr of  $0.17 \text{ mA/cm}^2$  higher than that for CS in Syn. GVSL only ( $0.019 \text{ mA/cm}^2$ ). Addition of 0.01% ferric ions and 0.02% ferric ions marginally lowers this to around 0.12 to  $0.13 \text{ mA/cm}^2$ , but at 0.03% ferric ions lowers this tremendously to  $0.022 \text{ mA/cm}^2$  comparable with I Corr for CS in Syn. GVSL only.

e.7) For CS exposed to Syn. GVSL solution with 0.1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.1% potassium antimonyl tartrate ( $\text{KSbC}_4\text{H}_4\text{O}_6$ ) and 0.01% tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) and ferric ions:

I Corr. for CS in Syn. GVSL solution with 0.1%  $\text{NH}_4\text{VO}_3$ , 0.1%  $\text{KSbC}_4\text{H}_4\text{O}_6$  and 0.01% tartaric acid is 0.073 mA/cm<sup>2</sup>, slightly on the higher side when compared to the value of 0.019 mA/cm<sup>2</sup> for CS in Syn. GVSL only. Addition of 0.01%, 0.02% and 0.03% ferric ions does not alter this value much showing no effect of ferric ions.

e.8) For CS exposed to Syn. GVSL solution with different concentrations of antimony oxide ( $\text{Sb}_2\text{O}_3$ ) :

Addition of 0.075%  $\text{Sb}_2\text{O}_3$  in Syn. GVSL increases the I Corr value only marginally to 0.026 mA/cm<sup>2</sup> from 0.019 mA/cm<sup>2</sup> which is the value for CS in Syn. GVSL only. At 0.1%  $\text{Sb}_2\text{O}_3$  the I Corr value is 0.153 mA/cm<sup>2</sup> and this value steadily increases to a max. value of 0.48 mA/cm<sup>2</sup> for 0.13%  $\text{Sb}_2\text{O}_3$ , then decreases to 0.2 mA/cm<sup>2</sup> for 0.14%  $\text{Sb}_2\text{O}_3$  and to a value of 0.056 mA/cm<sup>2</sup> for 0.15%  $\text{Sb}_2\text{O}_3$ . It is observed here that I Corr increases with the additions of  $\text{Sb}_2\text{O}_3$  up to 0.13% and then decreases for further concentration of 0.14% and 0.15%  $\text{Sb}_2\text{O}_3$ .

e.9) For CS exposed to Syn. GVSL solution with 0.075% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

I Corr for CS in Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$  is 0.026 mA/cm<sup>2</sup>. Addition of 0.01% and 0.02% ferric ions does not affect this value much, but addition of 0.03% ferric ions decreases the value to 0.006 from 0.026 mA/cm<sup>2</sup> (four times decrease).

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Addition of 0.04% ferric ions increases this marginally to 0.010 mA/cm<sup>2</sup>. It is to be noticed here that the lowest value of I Corr (0.006 mA/cm<sup>2</sup>) is obtained with 0.03% ferric ions.

e.10) For CS exposed to Syn. GVSL solution with 0.1% antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) and ferric ions :

I Corr for CS in Syn. GVSL solution with 0.1% Sb<sub>2</sub>O<sub>3</sub> is 0.153 mA/cm<sup>2</sup>, which is very much higher than 0.019 mA/cm<sup>2</sup> for CS in Syn. GVSL only. This value is also far higher than the value for 0.075% Sb<sub>2</sub>O<sub>3</sub> in GVSL solution. Addition of 0.01% and 0.02% ferric ions does not alter this value of 0.153 mA/cm<sup>2</sup> much, but at 0.03% ferric ions I Corr decreases to as low as 0.027 mA/cm<sup>2</sup> and again to 0.013 mA/cm<sup>2</sup> at 0.04% ferric ions. The same observation as in 0.075% Sb<sub>2</sub>O<sub>3</sub> is repeated here, but the I Corr value increases tremendously for 0.1% Sb<sub>2</sub>O<sub>3</sub> in GVSL solution. Also at 0.04% ferric ions I Corr value is the lowest.

e.11) For CS exposed to Syn. GVSL solution with 0.13% antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) and ferric ions :

CS in Syn. GVSL with 0.13% Sb<sub>2</sub>O<sub>3</sub> shows an I Corr of 0.48 mA/cm<sup>2</sup> which is very high when compared with the I Corr value of 0.019 mA/cm<sup>2</sup> for CS in GVSL only. Addition of 0.01% ferric ions again increases this value to 0.59 mA/cm<sup>2</sup> and that for 0.02% ferric ions it is 0.72 mA/cm<sup>2</sup>. After reaching a maximum of 0.72 mA/cm<sup>2</sup> at 0.02% ferric ions, at 0.03% ferric ions it falls to 0.14 mA/cm<sup>2</sup> and to 0.061 mA/cm<sup>2</sup> for 0.04% ferric ions.

e.12) For CS exposed to Syn. GVSL solution with 0.14% antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) and ferric ions :

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I Corr value for CS in Syn. GVSL solution with 0.14%  $\text{Sb}_2\text{O}_3$  is 0.20 mA/cm<sup>2</sup> far less when compared with the value of 0.48 mA/cm<sup>2</sup> for CS in GVSL with 0.13%  $\text{Sb}_2\text{O}_3$ , but higher when compared with the value of 0.019 mA/cm<sup>2</sup> for CS in GVSL only.

Addition of 0.01% and 0.02% ferric ions marginally increases this value to 0.27 mA/cm<sup>2</sup>, but at 0.03% ferric ions it decreases to 0.043 mA/cm<sup>2</sup> and at 0.04% ferric ions it is 0.020 mA/cm<sup>2</sup>.

The increase in the I Corr value up to 0.02% ferric ions and the decrease thereafter is noteworthy.

The lowest value of I Corr is obtained with 0.04% ferric ions as is the case with 0.1% and 0.13%  $\text{Sb}_2\text{O}_3$ .

It is also interesting to note here that after the I Corr has increased up to 0.13%  $\text{Sb}_2\text{O}_3$  addition, in this case it has started to decrease.

e.13) For CS exposed to Syn. GVSL solution with 0.15% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

I Corr for CS in Syn. GVSL with 0.15% is 0.056 mA/cm<sup>2</sup>, higher when compared with the value of 0.019 for CS in GVSL only, but far lower than the I Corr values for 0.1%  $\text{Sb}_2\text{O}_3$  (0.153 mA/cm<sup>2</sup>), 0.13%  $\text{Sb}_2\text{O}_3$  (0.48 mA/cm<sup>2</sup>) and 0.14% (0.20 mA/cm<sup>2</sup>). Only the value for 0.075%  $\text{Sb}_2\text{O}_3$  is lower than this value.

Addition of 0.01% ferric ions lowers this value to 0.006 mA/cm<sup>2</sup> and at 0.02% ferric ions it reaches 0.003 mA/cm<sup>2</sup>. This is in contrast with the other  $\text{Sb}_2\text{O}_3$  systems where at 0.01 and 0.02% ferric ion addition there was either no increase or slight increase in I Corr Value.

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At 0.03% ferric ion addition the value of I Corr further decreases to a low of 0.0007 mA/cm<sup>2</sup> and then at 0.04% ferric ions it increases to 0.014 mA/cm<sup>2</sup>. The value at 0.03% ferric ions is lowest when compared with I Corr for all the combinations of Sb<sub>2</sub>O<sub>3</sub> /Ferric ions tried in the system.

It is to be noted here that at 0.04% ferric ions there is an increase in I Corr value.

**F) OBSERVATIONS FROM POLARIZATION RESISTANCE (Rp), CORROSION RATE (CR) AND INHIBITOR EFFICIENCY (IE) VALUES (TABLE - 4) :**

f.1) For CS exposed to plant GV solutions :

Polarization resistance values for CS in lean, semi lean and rich solutions are in decreasing order as expected. It is to be noted here that these experiments were carried out at 70 Deg. C., 85 Deg. C. and 102 Deg. C. for lean, semi lean and rich solutions respectively. Consequently the corrosion rates calculated from polarization plots are in increasing order from lean to rich. This may be due to higher temperature and higher carbonation index.

f.2) For CS exposed to Syn. GVSL solution with ferric ions only:

Rp value of 63.1 Ohm.cm is obtained for CS in Syn. GVSL solution without ferric ions and inhibitor. Addition of 0.01% and 0.02% ferric ions does not change this value much but at 0.03% concentration of ferric ions it increases to 108.2 Ohm.cm and at 0.04% concentration of ferric ions it again decreases to 12.4 Ohm.cm.

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Corrosion rate of CS in Syn. GVSL without ferric ions and any inhibitor is 8.25 mpy, but the addition of ferric ions at 0.01% reduces this to 2.82 (efficiency of 65.8%), at 0.02% ferric ions 5.7 mpy (efficiency of 30.9%), at 0.03% ferric ions 4.6 mpy (efficiency of 44.2%) and at 0.04% ferric ions 1.2 mpy (efficiency of 85.5%). There is very good inhibition at 0.01% ferric ions, but it falls to lower values with further additions of ferric ions except at 0.04% concentration of ferric ions.

f.3) For CS exposed to Syn. GVSL solution with 0.1% vanadium pentoxide ( $V_2O_5$ ) and ferric ions :

The addition of 0.1%  $V_2O_5$  to CS in Syn. GVSL solution increases the Rp value to 175.2 Ohm.cm and also increases the corrosion rate to 93.1 mpy.

Addition of 0.01, 0.02 and 0.03% ferric ions decreases the Rp values further, showing a negative effect of the addition. Only at 0.03% concentration of ferric ions there is a slight increase in Rp as compared to the same at 0.02% concentration of ferric ions.

Corrosion rates also increases with the additions of 0.01% and 0.02% ferric ions showing negative efficiency, but at 0.03% concentration of ferric ions there is a decrease in corrosion rate from 93.1 mpy to 56.2 mpy, giving an inhibitor efficiency of 39.6%.

f.4) For CS exposed to Syn. GVSL solution with 0.7% Potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

Addition of 0.7%  $K_2Cr_2O_7$  to CS in Syn. GVSL solution increases the Rp value to 217 Ohm.cm, showing a higher value than that for CS

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in Syn. GVSL solution without any inhibitor (630 Ohm.cm.), but additions of 0.01%, 0.02% and 0.03% ferric ions reduces this to around 10 Ohm.cm. clearly showing the accelerating effect.

Corrosion rate for CS in Syn. GVSL solution with 0.7%  $K_2Cr_2O_7$  is 9.27 mpy, which is almost comparable with the value of 8.25 for CS in Syn. GVSL without any inhibitor. Additions of ferric ions (0.01% to 0.03%) increases this to more than 150 mpy giving negative efficiency of -1700% and more. It is noted here that ferric ion addition increases the corrosion rate of CS tremendously in presence of  $K_2Cr_2O_7$  in Syn. GVSL solution.

f.5) For CS exposed Syn. GVSL solution with 0.6% sodium silicate ( $Na_2SiO_3$ ) and 0.02% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

Addition of 0.6%  $Na_2SiO_3$  and 0.02%  $K_2Cr_2O_7$  to CS in Syn. GVSL solution increases the Rp value to 194 Ohm. cm which is higher than 63 Ohm.cm, the value for CS in Syn. GVSL solution without any inhibitor. Additions of 0.01%, 0.02% and 0.03% ferric ions to the solution decreases this Rp value to around 25 Ohm.cm.

Corrosion rate of CS in Syn. GVSL solution with the above mentioned inhibitors is 7.2 mpy which is comparable with that for CS in GVSL solution without any inhibitor (8.25 mpy), but addition of 0.01% ferric ions accelerates this effect by increasing the corrosion rate to 61.8 mpy, at 0.02 % concentration of ferric ion it increases to 180 mpy and at 0.03% concentration of ferric ions it increases to 136.7 mpy, showing very high negative % efficiencies for these combinations.

- f.6) For CS exposed to Syn. GVSL solution with 1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.25% sodium nitrite ( $\text{NaNO}_2$ ) and ferric ions :

Addition of 1%  $\text{NH}_4\text{VO}_3$  and 0.25%  $\text{NaNO}_2$  decreases the  $R_p$  value to 38.4 Ohm.cm from 63 Ohm.cm, which is the  $R_p$  value for CS in Syn. GVSL without any inhibitor. Additions of 0.01 and 0.02% ferric ions slightly increases this value, but at 0.03% ferric ion concentration an  $R_p$  value of 99.5 Ohm.cm is shown, giving better inhibiting property.

Corrosion rate of CS in Syn. GVSL with the above mentioned inhibitors is 76.8 mpy which is high when compared with the corrosion rate of CS in Syn. GVSL solution without any inhibitor (8.25 mpy). Further additions of 0.01 and 0.02% ferric ions marginally decreases this to around 50 mpy, giving an efficiency of more than 25%. At ferric ion concentration of 0.03%, corrosion rate decreases to 9.8 mpy giving an efficiency of 87.2%.

- f.7) For CS exposed to Syn. GVSL solution with 0.1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and 0.1% potassium antimonyl tartrate ( $\text{KSbC}_4\text{H}_4\text{O}_6$ ) and 0.01% tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) and ferric ions :

Addition of 0.1%  $\text{NH}_4\text{VO}_3$  and 0.1%  $\text{KSbC}_4\text{H}_4\text{O}_6$  and 0.01%  $\text{C}_4\text{H}_6\text{O}_6$  increases  $R_p$  value to 92 Ohm.cm from 63 Ohm.cm which is the value for CS in Syn. GVSL solution without any inhibitor. Addition of 0.01 and 0.02% ferric ions to this does not change this value much, but

at 0.03% concentration of ferric ions it is lowered to a value of around 60.8 Ohm. cm.

Corrosion rate of CS in Syn. GVSL containing the above mentioned inhibitors is 32.7 mpy, which is higher than that for CS in Syn. GVSL solution without any inhibitors which is 8.25 mpy. Addition of ferric ions increases this rate (except in the case of 0.02% concentration of ferric ions where there is a slight decrease in corrosion rate giving inhibitor efficiency of 2.14%) giving negative efficiency.

f.8) For CS exposed to Syn. GVSL solution with different concentration of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) :

Addition of 0.075%  $\text{Sb}_2\text{O}_3$  in Syn. GVSL solution decreases the Rp value to 45.7 Ohm.cm from the value of 63.0 Ohm.cm. which is for CS in Syn. GVSL solution without any inhibitor. This value of Rp goes on decreasing with further concentrations of  $\text{Sb}_2\text{O}_3$  of 0.1% and 0.13%. At 0.13%  $\text{Sb}_2\text{O}_3$  concentration Rp value is the lowest at 6.9 Ohm.cm, but at 0.14% concentration of  $\text{Sb}_2\text{O}_3$  it shows increasing trend at 11.6 Ohm.cm and at 0.15%  $\text{Sb}_2\text{O}_3$  concentration it reaches 29.8 Ohm.cm, showing better property at higher concentrations of  $\text{Sb}_2\text{O}_3$ .

Corrosion rates also show the same behaviour as shown in I Corr and Rp values. It steadily increases up to 0.13%  $\text{Sb}_2\text{O}_3$  concentrations and then decreases and reaches a values of 25.2 mpy for 0.15%  $\text{Sb}_2\text{O}_3$  concentrations.

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f.9) For CS exposed to Syn. GVSL with 0.075% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

Addition of 0.075%  $\text{Sb}_2\text{O}_3$  to Syn. GVSL solution gives Rp value of 45.7 Ohm.cm which is lower than 63.0 Ohm.cm which is the value for CS in Syn. GVSL without any inhibitor. As seen in the Rp values of CS in Syn. GVSL solution with concentrations of 0.01% and 0.02% ferric ions where there is no much change, with the presence of 0.075%  $\text{Sb}_2\text{O}_3$  and 0.01% and 0.02% also there is no much change, albeit there is an increasing tendency. At a concentration of 0.03% ferric ions there is a tremendous increase in Rp value where it reaches 510 Ohm.cm, contrary to the value of 108.2 Ohm.cm for CS in Syn. GVSL solution with 0.03% ferric ions only.

At 0.04% ferric ions with 0.075%  $\text{Sb}_2\text{O}_3$  there is a fall in Rp value (172.7 Ohm.cm), still very high when compared with the Rp value of 12.4 Ohm.cm. for CS in Syn. GVSL solution with 0.03% ferric ions only.

Corrosion rate of CS in Syn. GVSL with the above mentioned inhibitor is 11.8 mpy, slightly higher than that value (8.25 mpy) for CS in Syn. GVSL solution without any inhibitor. Addition of 0.01% and 0.02% ferric ions reduces the corrosion rate efficiently for CS in Syn. GVSL solution without any inhibitor, but in presence of 0.075%  $\text{Sb}_2\text{O}_3$ , it is slightly increased for 0.01% ferric ion concentration giving an efficiency of -4.24% and a slight decrease at 0.02% ferric ion concentration giving an efficiency of 16.9%.

At 0.03% ferric ion concentration with 0.075%  $\text{Sb}_2\text{O}_3$ , there is a tremendous decrease in corrosion rate to 2.61 mpy, giving an efficiency of 77.9% which is far higher than that for CS in Syn. GVSL solution with 0.03% ferric ions only. At 0.04% ferric ion concentration there is an increase in corrosion rate in presence of 0.075%  $\text{Sb}_2\text{O}_3$  (IE of 60.4%) in contrast to the value for CS in Syn. GVSL solution with 0.04% ferric ions only (IE of 85.5%).

It is seen that  $R_p$  is maximum and corrosion rate is minimum for CS in Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$  and 0.03% ferric ions.

f.10) For CS exposed to Syn. GVSL with 0.1% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

Addition of 0.1%  $\text{Sb}_2\text{O}_3$  in Syn. GVSL solution gives  $R_p$  value of 21.4 Ohm.cm, which is lower than the value of 63.0 Ohm.cm, the value for CS in Syn. GVSL without any inhibitor. Addition of 0.01% and 0.02% ferric ion to this further decreases  $R_p$  value to 18.2 Ohm.cm and 12.3 Ohm.cm showing negative effect. When these values are compared with the values of CS in Syn. GVSL solution with 0.01% ferric ion concentration (57.3 Ohm.cm) and with 0.02% ferric ion concentration (81.5 Ohm.cm), it is seen that decrease is comparable with 0.01% ferric ion concentration but not with 0.02% ferric ion concentration.  $R_p$  value of 335 Ohm.cm is obtained for 0.1%  $\text{Sb}_2\text{O}_3$  with 0.03% ferric ions which is very high than 108.2 Ohm.cm, the value for CS in Syn. GVSL solution with 0.03% ferric ions only. This was also the case with 0.075%  $\text{Sb}_2\text{O}_3$  with 0.03% ferric ions.

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With 0.04% ferric ion concentration in presence of 0.1%  $\text{Sb}_2\text{O}_3$  there is a fall in Rp value to 221 Ohm.cm, but still very high when compared with the value of 12.4 Ohm.cm for CS in Syn. GVSL solution with 0.04% ferric ions only.

Corrosion rate of CS in Syn. GVSL with 0.1%  $\text{Sb}_2\text{O}_3$  is 58.4 mpy, very high when compared with 8.25 mpy, value for CS in Syn. GVSL solution without any inhibitor. Addition of 0.01% and 0.02% ferric ions increases this corrosion rate marginally giving inhibitor efficiencies of -9.25% and -16.4% respectively. This is in sharp contrast with the efficiencies obtained with CS in Syn. GVSL solution with 0.01% and 0.02% ferric ion concentrations where 65.8% and 30.9% efficiencies are obtained.

At 0.03% ferric ion concentration in presence of 0.1%  $\text{Sb}_2\text{O}_3$ , corrosion rate falls to 12.14 mpy giving an efficiency of 79.2% far higher than that for CS in Syn. GVSL solution with 0.03% ferric ions only (44.2%). At 0.04% ferric ion concentration, both the system attain good comparability with more than 85% efficiency.

Like in 0.075%  $\text{Sb}_2\text{O}_3$  with 0.03% and 0.04% ferric ion concentration, in this case also maximum efficiency is achieved at this concentrations.

f.11) For CS exposed to Syn. GVSL solution with 0.13% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

Addition of 0.13%  $\text{Sb}_2\text{O}_3$  in Syn. GVSL solution, Rp value of 6.9 Ohm.cm is obtained which is lowest value obtained for GVSL solutions

with  $\text{Sb}_2\text{O}_3$  and is also very low when compared with 63 Ohm.cm, which is the  $R_p$  value of CS in Syn. GVSL solution without any inhibitor.

It is also observed that there is a steady fall in  $R_p$  values starting from CS in Syn. GVSL without any inhibitor, in GVSL with 0.075%  $\text{Sb}_2\text{O}_3$  and in GVSL with 0.1%  $\text{Sb}_2\text{O}_3$  and the lowest  $R_p$  value in CS in GVSL with 0.13%  $\text{Sb}_2\text{O}_3$ . The same trend is followed with corrosion rate values, in which case a steady rise is followed up to CS in Syn. GVSL solution, where it reaches a maximum of 213 mpy.

Addition of 0.01% and 0.02% ferric ions further reduces the  $R_p$  value to 4.54 and 4.12 Ohm.cm respectively, comparable to the decrease in  $R_p$  value (not to the  $R_p$  value itself) for CS in Syn. GVSL solution with 0.01% ferric ion concentration, but not comparable with the increase in  $R_p$  value for CS in Syn. GVSL solution with 0.02% ferric ion concentration. At 0.03% ferric ion concentration in presence of 0.13%  $\text{Sb}_2\text{O}_3$  there is increase in  $R_p$  value which is also very low when compared with  $R_p$  value of 108.2 Ohm.cm for CS in Syn. GVSL solution with 0.03% ferric ions only. At 0.04% ferric ion concentration maximum  $R_p$  value of 32.9 Ohm.cm is obtained which is higher than that for CS in Syn. GVSL solution with 0.04% ferric ions only (12.4 Ohm.cm).

Corrosion rate also increases when 0.01% and 0.02% ferric ions are added to the system containing 0.13%  $\text{Sb}_2\text{O}_3$  giving negative efficiencies of -22.5% and -49.8%. This was also the case with 0.1%  $\text{Sb}_2\text{O}_3$  with 0.01% and 0.02% ferric ion concentration.

This is also in sharp contrast with the efficiencies obtained with CS in Syn. GVSL solution with 0.01% and 0.02% ferric ion concentrations where 65.8% and 30.9% efficiencies are obtained.

At 0.03% ferric ion concentration in presence of 0.13%  $\text{Sb}_2\text{O}_3$ , corrosion rate falls to 62.9 mpy giving an efficiency of 70.5%, far higher than that for CS in Syn. GVSL solution with 0.03% ferric ions only (44.2%). At 0.04% ferric ion concentrations, both the system attain good comparability with more than 85% efficiency.

Maximum inhibitor efficiency is achieved with 0.13%  $\text{Sb}_2\text{O}_3$  with 0.03% and 0.04% ferric ion concentrations, as was the case with 0.075% and 0.1%  $\text{Sb}_2\text{O}_3$  containing solutions.

f.12) For CS exposed to Syn. GVSL solution with 0.14% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

Addition of 0.14%  $\text{Sb}_2\text{O}_3$  to CS in Syn. GVSL solution gives a Rp value of 11.6 Ohm.cm, lower when compared with the value of 63 Ohm.cm for CS in Syn. GVSL solution without inhibitor, but higher when compared with the value of 6.9 Ohm.cm obtained for CS in Syn. GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$ . It is observed, that after a fall in Rp values upto 0.13%  $\text{Sb}_2\text{O}_3$  concentrations, there is a rise in Rp value from 0.14%  $\text{Sb}_2\text{O}_3$  concentration. This is also true to corrosion rate values, where there is a rise in the rates up to 0.13%  $\text{Sb}_2\text{O}_3$  concentrations and a fall to 89.2 mpy with 0.14%  $\text{Sb}_2\text{O}_3$  concentration.

Addition of 0.01% and 0.02% ferric ions further reduces Rp value to 8.8 and 4.3 Ohm.cm respectively, comparable to the decrease in Rp value for CS in Syn. GVSL solution with 0.01% ferric ion concentration, but not comparable with the increase in Rp value for

CS in Syn. GVSL solution with 0.02% ferric ion concentration. At 0.03% ferric ion concentration, in presence of 0.14%  $\text{Sb}_2\text{O}_3$ , there is increase in the Rp value which is also very low when compared with the Rp value of 108.2 Ohm.cm for CS in Syn. GVSL solution with 0.03% ferric ions only. At 0.04% ferric ions concentration maximum Rp value of 25.6 Ohm.cm is obtained, which is higher than that for CS in Syn. GVSL solution with 0.04% ferric ions only (12.4 Ohm.cm).

Corrosion rate also increases when 0.01% and 0.02% ferric ions are added to the system containing 0.14%  $\text{Sb}_2\text{O}_3$  giving negative efficiencies of -12.1% and -35.7%. This is similar to observations for 0.1%  $\text{Sb}_2\text{O}_3$  and 0.13%  $\text{Sb}_2\text{O}_3$  with 0.01% and 0.02% ferric ion concentration. This is also in sharp contrast with the efficiencies obtained with CS in Syn. GVSL solution with 0.01% and 0.02% ferric ion concentrations where 65.8% and 30.9% efficiencies are obtained. At 0.03% ferric ion concentration in presence of 0.14%  $\text{Sb}_2\text{O}_3$  corrosion rate falls to 19.1 mpy giving an efficiency of 78.6%, far higher than that for CS in Syn. GVSL solution with 0.03% ferric ions only (44.2%). At 0.04% ferric ion concentration in Syn. GVSL solution with 0.14%  $\text{Sb}_2\text{O}_3$  90% efficiency is obtained which is slightly higher than that for CS in Syn. GVSL solution with 0.04% ferric ions only (85.5%).

Maximum inhibitor efficiency is achieved with 0.14%  $\text{Sb}_2\text{O}_3$  with 0.03% and 0.04% ferric ion concentrations. The trend of decreasing Rp value up to 0.13%  $\text{Sb}_2\text{O}_3$ , and increasing corrosion rates up to 0.14%  $\text{Sb}_2\text{O}_3$  is reversed at 0.14%  $\text{Sb}_2\text{O}_3$  concentrations. 90% efficiency is obtained with 0.14%  $\text{Sb}_2\text{O}_3$  with 0.04% ferric ions, which is maximum achieved in all the concentrations of  $\text{Sb}_2\text{O}_3$  up to 0.14%.

f.13) For CS exposed to Syn. GVSL solution with 0.15% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

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Addition of 0.15%  $\text{Sb}_2\text{O}_3$  in Syn. GVSL solution gives an  $R_p$  value of 29.8 Ohm.cm, lower when compared with the value of 63 Ohm.cm for CS in Syn. GVSL solution without inhibitor, but higher when compared with the value of 11.6 Ohm.cm. obtained for CS in Syn. GVSL solution with 0.14%  $\text{Sb}_2\text{O}_3$ . It is observed here that the tendency of  $R_p$  to increase from 0.14%  $\text{Sb}_2\text{O}_3$  concentration is followed with further increase in  $R_p$  value. This is also true with corrosion rate values, where there is further decrease to 25.2 mpy for 0.15%  $\text{Sb}_2\text{O}_3$  concentration from 89.2 mpy (for 0.14%  $\text{Sb}_2\text{O}_3$  concentration).

Addition of 0.01% ferric ions increases  $R_p$  value to 505.6 Ohm.cm. This is in sharp contrast to the values for any combinations of  $\text{Sb}_2\text{O}_3$  - 0.01% ferric ions and also is not comparable with the decrease in  $R_p$  for CS in GVSL with 0.01% ferric ions only. Only with this concentration of  $\text{Sb}_2\text{O}_3$  this is achieved. At 0.02% ferric ion concentration in presence of 0.15%  $\text{Sb}_2\text{O}_3$ ,  $R_p$  further increases to 529.2 Ohm.cm. This is also in sharp contrast to the other combination of  $\text{Sb}_2\text{O}_3$  - 0.02% ferric ions and also is not comparable with the slight increase in  $R_p$  for CS in GVSL with 0.02% ferric ions. At 0.03% ferric ion concentration highest  $R_p$  value of 1976.3 Ohm.cm is achieved. This rise in  $R_p$  is comparable with  $R_p$  for 0.075%  $\text{Sb}_2\text{O}_3$ , 0.1%  $\text{Sb}_2\text{O}_3$  with 0.03% ferric ions respectively but the tremendously higher value is more than 3-5 times than these values for 0.075% and 0.1%  $\text{Sb}_2\text{O}_3$  values, with 0.03% ferric ions. At 0.04% ferric ions in presence of 0.15%  $\text{Sb}_2\text{O}_3$  there is a decrease in  $R_p$  value to 253.9 Ohm.cm, but is still higher than that for any combinations of  $\text{Sb}_2\text{O}_3$  - 0.04% ferric ions. The fall in  $R_p$  at 0.04% ferric ions is in line with other  $\text{Sb}_2\text{O}_3$  - 0.04% Combination and also with CS in GVSL without any inhibitor and with 0.04% ferric ions only, except in the case for 0.13%  $\text{Sb}_2\text{O}_3$  and 0.14%  $\text{Sb}_2\text{O}_3$  with 0.04% ferric ions where there is a slight increase in  $R_p$  values.

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Corrosion rate decreases with the additions of 0.01% and 0.02% ferric ions, in sharp contrast to other  $\text{Sb}_2\text{O}_3$  - 0.01% and 0.02% ferric ion systems. But the decrease is comparable with the corrosion rates obtained for CS in GVSL without any inhibitor. For CS in GVSL with 0.15%  $\text{Sb}_2\text{O}_3$  and 0.01% and 0.02% ferric ions an efficiency of 89.4% and 94.4% is achieved when all other combinations of  $\text{Sb}_2\text{O}_3$  - 0.01% and 0.02% ferric ions achieves negative to very low efficiencies.

At 0.03% ferric ion concentration in presence of 0.15%  $\text{Sb}_2\text{O}_3$ , corrosion rate of 0.29 mpy is achieved, which is the lowest obtained for any combination of  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ions, giving an inhibitor efficiency of 98.8% which is highest achieved. When compared with the efficiency of 44.2% for CS in GVSL solution without any inhibitor, but with 0.03% ferric ions it is seen that it is very high. For all other  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ion concentration 70 - 80% efficiency is achieved.

At 0.04% ferric ion concentration in presence of 0.15%  $\text{Sb}_2\text{O}_3$ , corrosion rate increases to 6.4 mpy giving an efficiency of 74.6%, lower when compared with other  $\text{Sb}_2\text{O}_3$  - 0.04% ferric ions combination (except with 0.075%  $\text{Sb}_2\text{O}_3$ ).

This efficiency is also lower when compared with the value of 85.5% for CS in Syn. GVSL with 0.04% ferric ion only.

Higher efficiency of 89.4% at 0.01% ferric ion concentration and highest efficiency of 98.8% at 0.03% ferric ion concentration and highest Rp value of 1976.3 Ohm.cm at 0.03% at 0.04% ferric ion concentration are some of the main observations for CS in Syn. GVSL solution with 0.15%  $\text{Sb}_2\text{O}_3$ .

**G) OBSERVATIONS FROM GRAPHS DEPICTING OCP VS ZONAL CHARACTERISTICS TAKEN FROM POLARIZATION DATA (FIGURES - 20 TO 30) :**

g.1) CS in Syn. GVSL solution with ferric ions only :

OCP of CS in aerated Syn. GVSL solution without any inhibitor or ferric ions is -745 mV and this value falls in the free corrosion zone, far away from flade potential FP or passivation zone. Addition of 0.01%, 0.02%, 0.03% and 0.04% ferric ions to Syn. GVSL does not appreciably shift the potential and all values for this lies in the free corrosion zone only. It is noted here that there is widening of FP zone towards passivation zone at 0.04% ferric ion concentration. This behaviour of OCP with the additions of ferric ions shows the non effect of it on CS in Syn. GVSL solution.

g.2) For CS exposed to Syn. GVSL solution with 0.1% vanadium pentoxide ( $V_2O_5$ ) and ferric ions :

In the absence of ferric ions, OCP of CS in Syn. GVSL solution with 0.1%  $V_2O_5$  is -330 mV and falls in the free corrosion zone. When compared with the OCP of CS in Syn. GVSL solution (-745 mV) it is seen that the shift in OCP by the addition of 0.1%  $V_2O_5$  is noteworthy, but still lies in the free corrosion zone only. Addition of 0.01%, 0.02% and 0.03% ferric ions to this solution shifts it to more negative values and therefore stays in free corrosion zone itself. Thus, the effect of ferric ion addition is accelerating in nature.

g.3) For CS exposed to Syn. GVSL solution with 0.7% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.7%  $K_2Cr_2O_7$  is -400 mV and it falls in the flade potential zone (FP zone), where susceptibility to SCC is maximum. Shift in OCP is large, when compared with the OCP of CS in Syn. GVSL only ( -745 mV) but it is enough only to shift it to FP zone.

Addition of 0.01%, 0.02% and 0.03% ferric ions shifts it to more negative values, comparable to -745 mV, value for CS in Syn. GVSL only and in the corrosion zone thereby showing the accelerating effect of ferric ions in présence of 0.7%  $K_2Cr_2O_7$ .

g.4) For CS exposed to Syn. GVSL solution with 0.6% sodium silicate ( $Na_2SiO_3$ ) and 0.02% potassium dichromate ( $K_2Cr_2O_7$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.6%  $Na_2SiO_3$  and 0.02%  $K_2Cr_2O_7$  is -398 mV and it falls in the free corrosion zone in the graph. Shift in OCP is large, as compared to the OCP of CS in Syn. GVSL only (-745 mV) but still it lies in the free corrosion zone.

Addition of 0.01%, 0.02% and 0.03% ferric ions shifts the OCP to more negative values and therefore stays in the free corrosion zone. Accelerating effect of ferric ions is seen here.

g.5) For CS exposed to Syn. GVSL with 1% ammonium metavanadate ( $NH_4VO_3$ ) and 0.25% sodium nitrite ( $NaNO_2$ ) and ferric ions :

OCP of CS in Syn. GVSL with 1%  $NH_4VO_3$  and 0.25%  $NaNO_2$  is -329 mV and it falls in the border line of free corrosion and FP zone, showing very good shift when compared with the OCP of CS in Syn. GVSL only (-745 mV) but not enough to push it to the passivation zone. Addition of 0.01% ferric ions shows the OCP (-324 mV) in FP

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zone due to the widening of the FP zone. Same is true with 0.02% ferric ion concentration. At 0.03% ferric ion concentration it falls in the free corrosion zone due to the narrowing of the FP zone. OCP of CS does not change much with the addition of ferric ions.

g.6) For CS exposed to Syn. GVSL solution with 0.1% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ), 0.1% Potassium antimonyl tartrate ( $\text{KSbC}_4\text{H}_4\text{O}_6$ ) and 0.01% tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) and ferric ions:

OCP of CS in Syn. GVSL solution with 0.1%  $\text{NH}_4\text{VO}_3$ , 0.1%  $\text{KSbC}_4\text{H}_4\text{O}_6$  and 0.01%  $\text{C}_4\text{H}_6\text{O}_6$  is -402 mV, very much falling in the free corrosion zone, even though noteworthy shift is observed when compared with the OCP of CS in Syn. GVSL only (-745 mV). Addition of 0.01%, 0.02% and 0.03% does not change the potentials much and all OCP values for this falls in the free corrosion zone.

Widening of the FP zone at 0.03% ferric ion concentration is noted which brings the OCP closer to it.

g.7) For CS exposed to Syn. GVSL solution with 0.075% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.075%  $\text{Sb}_2\text{O}_3$  is -745 mV, falling in the free corrosion zone, showing no shift in potential when compared with OCP of CS in Syn. GVSL only (-745 mV). At 0.01% and 0.02% ferric ion concentrations there is again no change in OCP and it also falls in the free corrosion zone. It is noted here that there is a widening of FP zone towards free corrosion zone at 0.01% ferric ion concentration.

At 0.03% ferric ion concentration the OCP shifts to -440 mV and falls in the FP zone and at 0.04% ferric ion concentration it is -460 mV.

and again goes in the free corrosion zone, albeit very near to FP zone. It is observed here that after the widening of FP zone at 0.01% ferric ion concentration, the FP zone narrows down steadily towards passivation zone at higher ferric ion concentration. Shift in OCP is observed for 0.03% and 0.04% ferric ion concentrations in presence of 0.075%  $\text{Sb}_2\text{O}_3$ , but is still not enough to push it to passivation zone.

g.8) For CS exposed to Syn. GVSL solution with <sup>0.01%</sup>0.01% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. solution with <sup>0.01%</sup>0.01%  $\text{Sb}_2\text{O}_3$  is -750 mV, falling in the free corrosion zone, showing no shift in potential when compared with OCP of CS in Syn. GVSL only (-745 mV). At 0.01% and 0.02% ferric ion concentrations there is no shift in OCP and both the values fall in the free corrosion zone. It is observed that at 0.01% ferric ion concentration there is narrowing down of FP zone towards passivation zone, but the passivation zone itself goes to more positive values. At 0.02% ferric ion concentration both the zones stay as such. At 0.03% ferric ion concentration shift of OCP to -480 mV is observed, but still is in the free corrosion zone. At this concentration of ferric ions, the passivation zone narrows down towards FP zone and it is seen that due to this, FP zone becomes small. At 0.04% ferric ion concentration OCP is -450 mV and falls in the border line of FP zone and free corrosion zone. It is noted here that noteworthy shifts in OCP are observed at 0.03% and 0.04% ferric ion concentrations and the narrowing down of the FP zone is also observed at these concentrations.

g.9) For CS exposed to Syn. GVSL solution with 0.13% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.13%  $\text{Sb}_2\text{O}_3$  is -724 mV, falling in the free corrosion zone, showing very slight shift in potential when

compared with OCP of CS in Syn. GVSL only (-745 mV). At 0.01% and 0.02% ferric ion concentrations there is very negligible shift in OCP showing -737 mV and -710 mV respectively, and these values falls well in the free corrosion zone. At 0.03% ferric ion concentration and OCP value of -440 mV is observed falling in the FP zone. It is also seen that FP zone widens towards free corrosion zone at this concentration, the passivation zone also widens towards FP zone. At 0.04% ferric ion concentration again the OCP is shifted to -388 mV but it falls in the free corrosion zone, very near to FP zone. This is due to the narrowing of the FP zone towards passivation zone at 0.04% ferric ion concentration. Passivation zone at this concentration also narrows down away from FP zone. Shift in OCP at 0.03% and 0.04% ferric ion concentration in presence of 0.13%  $Sb_2O_3$  is observed, but it falls in or very near to FP zone.

g.10) For CS exposed to Syn. GVSL solution with 0.14% antimony oxide ( $Sb_2O_3$ ) and ferric ions :

OCP of CS in Syn. GVSL with 0.14%  $Sb_2O_3$  is -728 mV, falling in the free corrosion zone, showing very slight shift in potential when compared with the OCP of CS in Syn. GVSL only (-746 mV).

At 0.01% and 0.02% ferric ion concentrations there is no appreciable shift in OCP and the values fall well in the free corrosion zone. It is noted here that there is narrowing of the FP zone towards passivation zone at 0.02% ferric ion concentration, but the passivation zone itself narrows down away from the FP zone. At 0.03% ferric ion concentration OCP of -389 mV and at 0.04% ferric ion concentration OCP of -366 mV is shown, showing very appreciable shifts, but still falling in the FP zone. It is observed here that at 0.03% ferric ion concentration there is widening of FP zone towards free

corrosion zone and the same is observed for passivation zone which widens towards FP zone. Shift in OCP at 0.03% and 0.04% ferric ion concentration in presence of 0.14%  $\text{Sb}_2\text{O}_3$  is observed, but it falls well in the FP zone.

g.11) For CS exposed to Syn. GVSL solution with 0.15% antimony oxide ( $\text{Sb}_2\text{O}_3$ ) and ferric ions :

OCP of CS in Syn. GVSL solution with 0.15%  $\text{Sb}_2\text{O}_3$  is -770 mV, falling in the free corrosion zone and showing slight shift towards more negative value, when compared with OCP of CS in GVSL only (-745 mV). At 0.01% ferric ion concentration OCP of -430 mV is observed and it falls in the borderline of FP and free corrosion zone. It is observed here that there is narrowing of FP zone towards passivation zone and the passivation zone widens towards FP zone, making FP zone very narrow when compared with FP zones of other  $\text{Sb}_2\text{O}_3$  - 0.01% ferric ions combinations. At 0.02% ferric ion concentration the shift in OCP continues and shows a value of -385 mV and it falls in the border line of FP and passivation zone. Here there is a slight widening of FP zone towards free corrosion zone. At 0.03% ferric ion concentration an OCP of -305 mV is observed and it falls well in the passivation zone. Here also there is a slight narrowing of FP zone towards passivation zone. At 0.04% ferric ion concentration, OCP of -410 mV is obtained which falls in the FP zone, nearer to the border line of FP and passivation zone, showing negative effect of this.

It is noteworthy here that shifts in potential is observed from 0.01% ferric ion onwards and these OCP's fall either in the FP or passivation zones. This is not the case with other  $\text{Sb}_2\text{O}_3$  - ferric ion combination. Very narrow FP zone is also interesting in this case.

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Only with 0.03% the OCP is well in the passivation zone. This is not achieved in any other combination of  $\text{Sb}_2\text{O}_3$  - ferric ions.

#### **H) OBSERVATIONS FROM PHOTOMICROGRAPHS OF PEARLITE LEACHING STUDY (PLATES 4 TO 14) :**

Results of microstructural observations to study selective leaching of any particular phase in CS exposed to GVSL solution with and without additives are presented as per following nomenclature.

h.1) Plates 4 and 5 depicts general microstructure of the investigated material at 250 X and 625 X magnification respectively :

Lower magnification shows overall appearance with dark areas of pearlitic and brighter areas of ferrite when viewed in bright field. No pits are observed as the specimen was ground to sufficient depth and polished carefully before etching. Bulk grains show slight elongation probably due to rolling during manufacture of plate material.

At higher magnification the darker pearlite areas clearly show presence of iron carbide ( $\text{Fe}_3\text{C}$ ) i.e., cementite particles.

h.2) Plates 6, 7 and 8 gives appearance of CS specimen surface exposed to aerated GVSL solution without inhibitor additions:

Plate 6 (mag 250 X) shows brownish appearance of pearlite leached areas and dark spotty areas where no leaching has occurred. The non metallic elongated inclusions in rolling direction are preferentially attacked leaving blackish brown craters. On set of pitting on parent metal other than on these inclusions are also visible.

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Dark field view at identical magnification confirms presence of dark pearlite leached areas and golden brown craters of localised attack containing corrosion products. Pits are also visible clearly. Plate 8 at a higher magnification (625 X) established the presence of corrosion products in localised pits and craters upon closer observation.

h.3) Plate 9, 10 and 11 depicts results of CS specimen exposed to 0.1 % antimony oxide and 0.03 % ferric ions in aerated GVSL solution :

The pearlitic phase in plate 9 (mag. 250 X ) appears mildly etched with darker colour. Non metallic inclusion and localised features are not severely affected as seen in its almost unchanged morphology. Plate 10 (mag 625 X) shows initiation of localised attack adjacent to these features. The fact that these features are not substantially attacked during the course of this exposure is brought out clearly in Plate 11 (mag. 625 X ) which shows a dark field image without corrosion products.

h.4) Plates 12, 13 and 14 shows effect on CS surface exposed to 0.15 % antimony oxide and 0.03 % ferric ions in aerated GVSL solution :

Very mild etching effects of this solution is noticed on the pearlitic phase, Plate 12 (mag 250 X). The non metallic inclusion and localised features are remarkably unaffected as seen in Plate 13 (mag 625 X). Dark field imaging (Plate 14 mag 250 X) shows intact nature of spotty carbide, indicating the presence of pearlite on the surface. Minor leaching is however observed specially in areas adjacent to elongated inclusions.

**I) OBSERVATIONS FROM POLARIZATION RESISTANCE AND DOUBLE LAYER CAPACITANCE VALUES FROM AC IMPEDANCE STUDY (FIGURES - 31 TO 42, TABLE - 5) :**

i.1) Effect of ferric ion concentration, antimony oxide ( $\text{Sb}_2\text{O}_3$ ) concentration and aeration on polarization resistance ( $R_p$ ) of CS in Syn. GVSL solution :

CS in Syn. GVSL solution (without aeration) and without any  $\text{Sb}_2\text{O}_3$  or any ferric ions shows an  $R_p$  of 357 Ohm.cm, which on addition of increasing concentrations of ferric ions from 0.01% to 0.04% decreases steadily, attaining a value of 71 Ohm.cm at 0.04% ferric ion concentration. Hence, it may be noted that for CS in Syn. GVSL solution without aeration and  $\text{Sb}_2\text{O}_3$  and increasing ferric ion concentrations, corrosion process is accelerated.

CS in Syn. GVSL solution (with aeration) and without any  $\text{Sb}_2\text{O}_3$  or any ferric ions shows an  $R_p$  of 777 Ohm.cm which on addition of 0.01% ferric ions is reduced to 173 Ohm.cm. Further additions 0.02% and 0.03% ferric ions moves this value to around 35 Ohm.cm and with 0.04% ferric ion concentration it is again reduced to 93 Ohm.cm. An increase in the  $R_p$  value is noted for GVSL solution with aeration when compared with the values for GVSL solution without aeration, with or without ferric ions. Only exception to this is at 0.01% ferric ion concentration where a slight decrease in  $R_p$  is shown.

CS in Syn. GVSL solution (without aeration) and with 0.15%  $\text{Sb}_2\text{O}_3$  without any ferric ions shows an  $R_p$  of 434 Ohm.cm which on addition of 0.01% ferric ions decreases to 282 Ohm.cm and then increases to 568 Ohm.cm at 0.02% ferric ion concentration. Thereafter a steady decrease in  $R_p$  occurs up to 0.04% ferric ion concentration.

CS in Syn. GVSL solution (with aeration) with 0.15%  $\text{Sb}_2\text{O}_3$  shows an  $R_p$  of 518 Ohm.cm which is slightly more than the value for GVSL without aeration. After a decrease in  $R_p$  at 0.01% concentration of ferric ions and an increase at 0.02% ferric ions, there is a tremendous increase in  $R_p$  (12353 Ohm.cm) at 0.03% ferric ion concentration which again decreases considerably at 0.04% ferric ion concentration.  $R_p$  for CS in Syn. GVSL solution without and with aeration with or without ferric ions does not change much except for 0.15%  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ions combination.

It is seen here that at 0.01% ferric ion concentration without or with aeration, without or with  $\text{Sb}_2\text{O}_3$ ,  $R_p$  decreases considerably, when compared with the value of  $R_p$  of Syn. GVSL without ferric ions.

Effect of aeration is also considerable and it is noticeable in the increasing values of  $R_p$  for GVSL solution with aeration.

Effect of 0.15%  $\text{Sb}_2\text{O}_3$  and aeration on the  $R_p$  value can also be noticed in the increasing values of this. In fact for 0.15%  $\text{Sb}_2\text{O}_3$  with 0.03% ferric ions and aeration gives the highest  $R_p$  value.

Adverse effect of excess of ferric ions ( $> 0.03\%$ ) is also seen by low  $R_p$  values with or without  $\text{Sb}_2\text{O}_3$ .

At 0.15%  $\text{Sb}_2\text{O}_3$  up to 0.02% ferric ions there is no effect on  $R_p$  with or without aeration.

Inhibitor efficiency for 0.15%  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ion combination calculated from  $R_p$  values shows a value of 97.18%.

i.2) Effect of ferric ion concentration, antimony oxide ( $\text{Sb}_2\text{O}_3$ ) concentration and aeration on double layer capacitance (Cdl) of CS in Syn. GVSL solution :

CdL value for CS in Syn. GVSL solution (without aeration) and without  $\text{Sb}_2\text{O}_3$  or ferric ions is 5772 microfarads which on addition of 0.01% and 0.02% ferric ions increases rapidly, but at 0.03% and at 0.04% ferric ion concentration decreases again. It may be noted here that for CS in Syn. GVSL solution without aeration and  $\text{Sb}_2\text{O}_3$  and different ferric ion concentrations, corrosion process is accelerated as shown by its higher Cdl values.

CS in Syn. GVSL solution (with aeration) and without  $\text{Sb}_2\text{O}_3$  or any ferric ions gives Cdl value of 2393 microfarads, less than the value for without aeration. Increasing concentrations of ferric ions increases the Cdl value, only at 0.04% ferric ion concentration there is again a fall in Cdl value. A decrease in Cdl value is noted for GVSL solution with aeration when compared with the values for GVSL solution without aeration, with or without ferric ions. Only exception is at 0.01% ferric ion concentration, where there is an increase in Cdl. value.

CS in Syn. GVSL solution (without aeration) and with 0.15%  $\text{Sb}_2\text{O}_3$  without any ferric ions shows Cdl of 4941 microfarads. Increasing concentrations of ferric ions increases this value up to 0.03% ferric ions and at 0.04% ferric ions Cdl decreases further.

CS in Syn. GVSL solution (with aeration) with 0.15%  $\text{Sb}_2\text{O}_3$  shows Cdl value of 4388 microfarads almost comparable with the value for GVSL without aeration. After an increase in Cdl value at 0.01% ferric ion concentration there is a decrease at 0.02% ferric ion concentration

and again at 0.03% ferric ion it attains a lowest value of 222 microfarads. This low value of Cdl is again tremendously increased at 0.04% ferric ion concentration.

It is seen that Cdl increase is considerable at 0.01% ferric ion addition without or with aeration.

Effect of aeration is also observed considerably at 0.02% and 0.03% ferric ion concentration. Effect of 0.15%  $Sb_2O_3$  and aeration is noticed when the values of Cdl are compared with that for GVSL without  $Sb_2O_3$ . In fact, for 0.15%  $Sb_2O_3$  and 0.03% ferric ions with aeration gives the lowest Cdl value. Accelerating effect of excess ferric ions, i.e. greater than 0.03%, is seen in the high Cdl value with  $Sb_2O_3$  after lowest Cdl value is obtained at 0.03% ferric ion concentration.

**J) OBSERVATIONS FROM EXPERIMENTS CARRIED OUT USING PLANT GVSL SOLUTIONS OBTAINED AFTER DOSAGE OF ANTIMONY OXIDE ( $Sb_2O_3$ ) (FIGURES - 2 AND 3, TABLE - 6) :**

In the plant, antimony oxide ( $Sb_2O_3$ ) was added to the potassium hydroxide solution prepared for making GV solution in the GV pit. Considering the bulk solution of GV, 345 kgs of  $Sb_2O_3$ , within a span of four months, was added so that GV bulk solution always contains more than 0.1%  $Sb_2O_3$ . After the addition of  $Sb_2O_3$ , potassium carbonate and arsenic trioxide was added to get a lean solution. Lean GV solution from the  $CO_2$  regeneration section was then mixed with this solution on stream to get a lean solution of GV with 0.8 to 0.9 carbonation index, which was then pumped to  $CO_2$  absorber tower top.

After a few days, sample of GVSL is taken out from GVSL section and a few more samples of GVSL taken at various intervals of days.

OCP and polarization studies were conducted in the laboratory by usual procedures using these solutions. Experiments were conducted without aeration of the GVSL solution and then with aeration. GVSL solution chemical analysis was done (Table-6) and various parameters were obtained from the studies.

OCP s of CS in these solutions are given in Table -1, critical current density (icc), passive current density (ip), passive potential (Ep) and primary passivating potential (Epp) obtained from potentiodynamic polarization plots (Figures -2 and 3) are depicted in Table -2.

Anodic Tafel, cathodic Tafel parameters and corrosion current value (I Corr) are given in Table -3. Polarization resistance (Rp), corrosion rate and inhibitor efficiency was calculated from these data and is given in Table -4.

j.1) Plant GVSL solutions with antimony oxide ( $Sb_2O_3$ ) :

j.1.a) GVSL solution dated 7-4-90 :

CS in GVSL solution dated 7-4-90 had an OCP of -748 mV in without aerated condition. When aerated, the OCP shifted to -570 mV showing positive effect of aeration. GVSL solution was turbid before aeration and greenish tinge was also observed. This solution had turned yellowish when aerated and it may be due to the oxidation of ferrous to ferric ions.

Complete effect of antimony oxide and ferric ions is not observed here. Critical current density (icc) in without aerated condition is very high at  $19.44 \text{ mA/cm}^2$  and it decreases to  $1.24 \text{ mA/cm}^2$  after aeration, showing good low ring of critical current density. Primary passivating

potential ( $E_{pp}$ ) stays constant at -350 mV for both. Passive current density ( $i_p$ ) also behaves in a same way as  $i_{cc}$ .

Passive potential ( $E_p$ ) shifts after aeration to -220 mV from -300 mV without aeration. OCP of -540 mV obtained after aeration is still nowhere near  $E_p$  but comparable with  $E_{pp}$  value, when compared with  $E_p$  and  $E_{pp}$  values for without aeration.

Corrosion current density ( $I_{Corr}$ ) values also behaves in a similar way, 0.885 mA/cm<sup>2</sup> without aeration, decreasing to 0.10 mA/cm<sup>2</sup> after aeration, showing good inhibiting property of antimony oxide ( $Sb_2O_3$ ), ferric ions and aeration.

Polarization resistance ( $R_p$ ) does not change much even after aeration. Corrosion rate of 396 mpy is obtained for CS in GVSL without aeration, which on aeration decreases to 44.5 mpy giving efficiency of 88.76%.

j.1.b) GVSL solution dated 23-5-90 :

CS in GVSL solution dated 23-5-90 shows an OCP of -718 mV in without aerated condition, but after aeration it shifted to -275 mV, showing very good effect of  $Sb_2O_3$  and ferric ions. It was observed here that solution collected from the plant was greenish in colour and turbid in nature, very characteristic of ferrous ions in the solution. On aeration this is oxidized to ferric ions and therefore exhibits passive characteristics in conjunction with  $Sb_2O_3$ .

$i_{cc}$  value in without aerated condition shows a high of 72.2 Ohm.cm<sup>2</sup> which on aeration drops to a low of 0.21 Ohm.cm<sup>2</sup>.  $i_p$  value also shows similar behaviour. The tremendous decrease in

icc and ip values after aeration shows that  $Sb_2O_3$  and ferric ions with aeration depicts very good inhibiting properties.

$E_{pp}$  for both the condition only marginally differs, but still for after aerated condition it is on the more positive side.  $E_p$  value for CS in GVSL in without aerated condition is 450 mV and is no way comparable to its OCP of -718 mV, but in after aerated condition  $E_p$  shows a value of -200 mV, very much comparable to the OCP of -275 mV for the system. Shift in  $E_p$  value to -200 mV from 450 mV is noticed and it is due to the presence of  $Sb_2O_3$  and ferric ions.

$i_{Corr}$  for CS in GVSL (without aeration) shows a value of 0.599 mA/cm<sup>2</sup> which on aeration is lowered to 0.14 mA/cm<sup>2</sup> showing a decrease which can be correlated to the presence of  $Sb_2O_3$  and ferric ions exhibiting good inhibiting properties.

$R_p$  increases to 14.8 Ohm.cm after aeration from 4.02 Ohm.cm without aeration.  $R_p$  increase is not much and shows that there is still scope of inhibition of CS in the system.

Corrosion rate of CS for without aerated condition shows 267 mpy, decreasing in trend when compared with the value of 396 mpy for CS in GVSL dated 7-4-90. This rate on aeration shows a value of 62.2 mpy giving an efficiency of 76.7%. Efficiency is found to be decreasing when compared with the value of 88.76% for GVSL dated 7-4-90.

Lower icc value, lower ip value, lower corrosion rate and comparable values of OCP and  $E_p$  for CS in GVSL after aerated condition are the main observations for sample dated 23-5-90.

**j.1.c) GVSL solution dated 31-5-90 :**

The observation of turbidity in the GVSL solution dated 7-4-90 and 23-5-90 and the change in colouration of the solution after aeration, OCP values of around -700 mV for the solutions and the shift in it after aeration, higher  $i_{cc}$ ,  $i_p$  and  $I_{Corr}$  values and non comparable  $E_{pp}$  and  $E_p$  values with OCP values for both solutions, higher corrosion rates for CS in as such GVSL solutions and the decrease in it after aeration, points that more aeration is required in the plant.

After increase in the aeration in the plant, sample of GVSL solution was collected after one week (on 31-5-90) and experiments were carried out.

GVSL solution dated 31-5-90 was found to be yellowish in colour and no turbidity was also seen. Analysis of the same also showed traces of ferrous ions in it.

OCP of CS in GVSL solution dated 31-5-90 is -330 mV without aeration, which is more positive than the OCP of CS in GVSL solution dated 7-4-90 and 23-5-90. After aeration the OCP of -330 mV shifted to -185 mV, still showing good inhibiting property. OCP of -330 mV and -185 mV shows that  $Sb_2O_3$  and ferric ions and also aeration possesses very good property of shifting potentials.

$i_{cc}$  value in without aerated condition is as low as  $1.31 \text{ mA/cm}^2$  and on aeration it decreases only to  $1.06 \text{ mA/cm}^2$ .  $i_p$  values also does not show much difference in both conditions.

$E_{pp}$  for CS in without aerated condition is -280 mV and after aeration is -275 mV, both are very much comparable with their respective

OCP's. Infact for after aeration OCP of -185 mV is far positive than the Epp value. Ep of -170 mV in without aerated condition and -100 mV for after aeration is also very much comparable with their respective OCP s, but the shift in potential is very remarkable in both the conditions.

I Corr for CS in GVSL (without aeration) shows a value of 0.27 mA/cm<sup>2</sup> which on aeration decreases to 0.053 mA/cm<sup>2</sup>.

I Corr of 0.27 mA/cm<sup>2</sup> is found to be the lowest in comparison with the I Corr values for GVSL selected on 7-4-90 and 23-5-90. After aeration also the value is found to be the lowest.

Rp for CS in GVSL without aeration is 22.67 Ohm.cm and after aeration increases to 37.7 Ohm.cm. Corrosion rate for CS in GVSL without aeration is 120.2 mpy which is lowered to 23.7 mpy after aeration. Values of Rp and corrosion rate are highest and lowest respectively when these values are compared with the values for GVSL dated 7-4-90 and 23-5-90, showing higher passivation characteristics of GVSL solution collected on 31-5-90. Inhibitor efficiency calculated from corrosion rate values works out to be 80.28%.

Lower icc values, ip values and corrosion rates for CS in aerated and non aerated condition shows the effect of Sb<sub>2</sub>O<sub>3</sub>, ferric ions on the passivation characteristics. Epp and Ep values for both which are also very comparable with their respective OCP s shows that the shift in potential is also noteworthy.

j.1.d) GVSL solution dated 13-6-90 :

GVSL solution collected on 13-6-90 was found to be Yellowish in colour and no turbidity was also observed. OCP of CS in this solution without aeration is -291 mV and after aeration it shifted to -195 mV. More positive OCP of CS in the solution with or without aeration, when compared with other GVSL solutions collected from plant showed the inhibitive characteristics of  $Sb_2O_3$  and ferric ions present in the GVSL solution.

icc for CS in GVSL without aeration is  $2.11 \text{ mA/cm}^2$  which when aerated shows a value of  $0.67 \text{ mA/cm}^2$ . ip values of  $0.07$  and  $0.04 \text{ mA/cm}^2$  are shown for without aeration and after aeration respectively. Aeration of the GVSL solution still lowers icc and ip values. This was not the case with GVSL collected on 31-5-90, where it lowers only marginally. icc and ip values obtained are lowest after aeration when compared with the values for GVSL solutions collected on previous dates.

Epp values for without aeration and after aeration does not differ much ( $-265 \text{ mV}$  without aeration and  $-270 \text{ mV}$  after aeration), but are very much comparable with their respective OCP s. Ep values of  $-150 \text{ mV}$  for both conditions are also very much comparable with OCP s. OCP of CS for aerated condition is  $195 \text{ mV}$  and Ep for the same is  $-150 \text{ mV}$  and it shows that it is best comparable potentials so far achieved.

I Corr for CS in GVSL without aeration is  $0.17 \text{ mA/cm}^2$  and after aeration was found to be  $0.0038 \text{ mA/cm}^2$ . Both values are lowest obtained when compared with the I Corr values for other GVSL solutions collected on previous dates.

Rp for CS in GVSL without aeration is  $28.9 \text{ ohm. cm}$  which on aeration tremendously increases to  $349.1 \text{ Ohm.cm}$ . only with this solution this

much increase in  $R_p$  is observed. In all other previous three cases increase in  $R_p$  is marginal.

Corrosion rate of 77.3 mpy for without aeration is also lowered to 1.68 mpy after aeration.

The lowering of corrosion rate by much a large margin is observed only in this solution and inhibitor efficiency was found to be 97.83%, highest obtained so far and comparable with the efficiency for CS in synthetic GVSL solution with 0.15%  $Sb_2O_3$  and 0.03% ferric ions.

Lower  $i_{cc}$ ,  $i_p$  and corrosion rates for CS in aerated and non aerated condition, comparable  $E_{pp}$  and  $E_p$  values with the OCP s, highest  $R_p$  values and an efficiency of 97.83% shows very good passivation properties of  $Sb_2O_3$ , and ferric ions in GVSL solution.

#### **K) BRIEF SUMMARY**

The establishment of the use of inhibitors especially anodic, from literature survey in the GV solution to lower corrosion related problems in  $CO_2$  removal system and the study by electrochemical methods of these inhibitors are some salient features of the introduction part. It is also noted that weight loss studies is also not helpful for accurate measurements of corrosion rates since even without inhibitors the corrosion rate is very low. The important criteria for stress corrosion cracking is the redox potential of CS in the solution was also established. Inhibitors shifting this potential towards more positive values are also studied. SCC potential of CS in a typical GV solution was found out to be -0.6 to -0.7 V vs SCE. The importance of potential measurement during the plant in operation is also stressed.

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The lower OCP value of CS in plant lean and semilean solution than in rich solution at lower temperature is noteworthy. Lower carbonation index of lean and semilean solution is also interesting.

Addition of 0.01 to 0.04% ferric ions to Syn. GV semi lean solution does not in any way effect the OCP of CS.

0.1% vanadium pentoxide addition to Syn GVSL shifts the potential substantially, but presence of ferric ions again shifts it to more negative values. The same trend is followed with larger shifts with 0.7% potassium dichromate and also with 0.6% sodium silicate and 0.02% potassium dichromate. With 1% ammonium metavanadate and 0.2% sodium nitrite in GVSL solution there is a shift in potential, but ferric ions addition to this does not change this. Same can be said about 0.1% ammonium metavanadate with 0.1% potassium antimonyl tartrate and 0.01% tartaric acid.

OCP of CS in Syn. GVSL solution with different concentrations of antimony trioxide ( $Sb_2O_3$ ) does not in any way shift the potential, showing that only  $Sb_2O_3$  is incapable of this. Addition of ferric ions to this, especially with more than 0.02% ferric ions the shift in potential is enormous and is maximum with the combination of 0.15%  $Sb_2O_3$  and 0.03% ferric ions, where an OCP of -305 mV is obtained. It is also noted here that only with 0.15%  $Sb_2O_3$  and the minimum concentration of ferric ions, i.e. 0.01%, appreciable shift in OCP is observed.

Critical current density for plant semi lean is higher than that value for lean and rich solutions. Passive potential in all the three solutions is also found to be far away from OCP values, having positive value.

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In Syn. GVSL solution with ferric ions, icc values increases with additions of ferric ions except in the case of 0.01% ferric ions. Constant Ep and Epp values for all ferric ion concentrations also supports the fact that no appreciable effect is obtained.

0.1% vanadium pentoxide with ferric ions in Syn. GVSL solution increases critical current density and primary passive potential and passive potential is not affected or shifted at all.

Addition of 0.7% potassium dichromate and ferric ions in Syn. GVSL increases the icc value by more than 1000 times to that value for CS in Syn. GVSL with only 0.7% potassium dichromate alone. Passive potential and OCP value for 0.7% pot. dichromate in Syn. GVSL is well comparable, but ferric ion presence destroys this character and Ep & Epp are not at all comparable with their respective OCP's. The same observations are infact applicable to inhibitor combinations of 0.6% sodium silicate and 0.02% pot. dichromate.

For the inhibitor combinations of 1% ammonium metavanadate with 0.25% sodium nitrite in Syn. GVSL icc, Epp, Ep and ip values does not show any appreciable alteration with the addition of ferric ions, but the OCP's are comparable only with Epp rather than Ep. Same can be said about the values for inhibitor combination of 0.1% amm. metavanadate with 0.1% pot. antimonyl tartrate and 0.01% tartaric acid. In this, there is some change in icc and ip values with additions of ferric ions, but it is not noteworthy.

Additions of antimony trioxide (0.075 to 0.15%) to Syn. GVSL tremendously increases icc value. Epp and Ep values also are not at all comparable with OCP's.

In presence of ferric ions, especially with more than 0.01% ferric ions and any concentration of  $Sb_2O_3$  (more than 0.075%) decreases icc value tremendously. Epp values are well within the value of OCP and for the combination of 0.15%  $Sb_2O_3$  and 0.03% ferric ions Ep value is more negative than the OCP value of -305 mV. The trend of shifting of potential increases with increasing concentrations of  $Sb_2O_3$  and reaches to -305 mV for 0.15%  $Sb_2O_3$  - 0.03% ferric ion combination. Lowest icc value of 0.068 mA/cm<sup>2</sup> is obtained with this. Epp value for all combinations is very much comparable with OCP s. The accelerating effect of 0.04% ferric ions with 0.15%  $Sb_2O_3$  is to be noted here. Corrosion current density (I Corr) for CS in plant GV rich solution at 102 Deg. C. is found to be highest. Polarization resistance (Rp) and corrosion rate of CS in plant GV rich solution, consequently is also lower and higher respectively than the value for lean and semi lean solution. This may be due to higher temperature and high carbonation index of rich solution.

I Corr for CS in Syn. GVSL solution increases with the additions of ferric ions except with 0.01% ferric ions. Rp increase is observed at 0.03% ferric ion concentration. Corrosion rate decreases sharply at 0.01% ferric ion concentration giving an efficiency of 65.8% and at 0.04% ferric ion concentration it is 85.5%, showing very good inhibiting property.

With 0.1% vanadium pentoxide in Syn. GVSL solution very low I Corr value is observed and additions of ferric ions does not change this value much. Rp for 0.1% vanadium pentoxide only is high, but corrosion rate is also very high. Only at 0.03% ferric ion concentration there is a decrease in corrosion rate giving an efficiency of 39.6%.

0.7% pot. dichromate addition in Syn. GVSL solution gives a low I Corr to CS, but addition of ferric ions destroys this property and

increases I Corr tremendously. Rp also behaves in a similar way in reverse manner. Corrosion rate consequently increases with further additions of ferric ions showing negative efficiencies to the order of -1700% and more. The same observations is applicable to the inhibitor combination of 0.6% sodium silicate and 0.02% pot. dichromate.

The inhibitor combination of 1% amm. metavanadate and 0.25% sodium nitrite in Syn. GVSL solution shows high value of I Corr. Addition of ferric ions does not change this much, except at 0.03% ferric ions where there is a lowering of I Corr. Rp also behaves like I Corr, in that there is an increase at 0.03% ferric ion concentration. Corrosion rates are decreased marginally with the additions of ferric ions, but at 0.03% ferric ion concentrations it attains lowest corrosion rate showing an efficiency of 87.2%.

Addition of the combination of 1% ammonium metavanadate, 0.1% pot. antimonyl tartrate and 0.01% tartaric acid gives a slightly higher value of I Corr, and this value is not altered with the additions of ferric ions. Lower Rp values and higher corrosion rates are observed with additions of ferric ions giving negative efficiencies.

I Corr value with additions of  $Sb_2O_3$  in Syn. GVSL solution increases with increasing concentrations of  $Sb_2O_3$  up to 0.13%  $Sb_2O_3$  after which it decreases up to 0.15%  $Sb_2O_3$ . Rp, consequently decreases up to 0.13%  $Sb_2O_3$  additions and then increases up to 0.15%  $Sb_2O_3$ . The same is true for corrosion rate values.

Addition of ferric ions to Syn. GVSL solution containing  $Sb_2O_3$  decreases I Corr tremendously, especially at more than 0.02% ferric ion concentrations. This is true for all concentrations of  $Sb_2O_3$  studied.

Even at 0.01% and 0.02% ferric ion concentrations low I Corr values are observed. With 0.075%  $Sb_2O_3$  and 0.03% ferric ion concentration an I Corr value of 0.006 mA/cm<sup>2</sup> is obtained. At the same concentration higher Rp value of 510 Ohm.cm is shown. Corrosion rates also behaves in a similar way up to 0.02% ferric ion addition giving low efficiencies but at 0.03% ferric ions it shows an efficiency of 77.9%. There is acceleration of corrosion process at 0.04% ferric ions since Rp decreases and corrosion rate increases. Same observations are repeated at other  $Sb_2O_3$  concentrations (0.1%, 0.13%, 0.14%), where after achieving negative efficiencies at 0.01% and 0.02% ferric ion concentrations, there is tremendous decrease in I Corr, increase in Rp and decrease in corrosion rate, giving very high (more than 80%) inhibitor efficiencies.

For 0.15%  $Sb_2O_3$  this behavior is somewhat altered since there is positive efficiencies even with 0.01% and 0.02% ferric ion concentrations. Only with 0.15%  $Sb_2O_3$  this is achieved. For 0.01% ferric ions itself an efficiency of 89.4% is obtained which increases with further additions of ferric ions and reaches a maximum of 98.8% for 0.03% ferric ion concentration.

Rp is also highest at 1976.3 Ohm.cm at 0.03% ferric ion concentration. Corrosion rate is found to be lowest at 0.29 mpy, lowest obtained for any combination of  $Sb_2O_3$  - ferric ions.

It is also interesting that there is a slight acceleration at 0.04% ferric ion concentration as is the case with other  $Sb_2O_3$  - ferric ion combination with the exception of some.

OCP's of CS in Syn. GVSL solution without and with addition of ferric ions falls in the free corrosion zone (FC) in the zonal characteristics graph, showing that no passivity is achieved by ferric ions alone.

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With 0.1% vanadium pentoxide the OCP is nearer to the flade potential zone (FP) and any additions of ferric ions shifts it to deeper into the FC Zone.

0.7% pot. dichromate addition to syn. GVSL solution shifts the OCP to FP Zone showing good inhibiting property, but addition of ferric ions shifts it to more negative values and the refore to FC Zone. Same is observed for the inhibitor combination of 0.6% sodium silicate and 0.02% pot. dichromate. In this case with the inhibitors alone it is still in the FC zone.

For 1% amm. metavanadate and 0.25% sod. nitrite inhibitor combination in syn. GVSL solution, OCP lies in the borderline of FP & FC zone. There is no appreciable difference with the additions of ferric ions, since it always lies in FC zone. Same observations stands good for the inhibitor combinat ion of 0.1% amm. metavanadate, 0.1% pot. antimonyl tartrate and 0.01% tartaric acid with ferric ions.

With 0.075%  $Sb_2O_3$  and 0.01% and 0.02% ferric ion concentrations in Syn. GVSL solution, the OCP always falls in the FC zone since there is no shift in potential. This observations holds good for even 0.1%, 0.13% and 0.14%  $Sb_2O_3$  concentrations. At 0.03% and 0.04% ferric ion concentrations with the above mentioned concentrations of  $Sb_2O_3$  (upto 0.14%) there is appreciable shift in OCP's and it always falls either near or in FP zone.

For 0.15%  $Sb_2O_3$  in Syn. GVSL solution and 0.01% and 0.02% ferric ion concentration the shift in OCP is noteworthy and it falls in the borderline of FP and FC zone. At 0.03% ferric ion concentration it is well within passivation zone, but at 0.04% ferric ion concentration OCP again is pushed to the borderline of FP and passivation zone,

showing negative effect of higher concentration of ferric ions. Only with 0.15%  $\text{Sb}_2\text{O}_3$  the OCP for 0.01% and 0.02% ferric concentrations such shift is observed which lies in the FP zone in the zonal characteristics graph.

General microstructure of the investigated CS material shows dark areas of pearlitic and brighter areas of ferrite at low magnification and at higher magnification pearlite areas clearly show cementite particles. CS exposed to GVSL without any inhibitor shows pearlite leached areas and onset of pitting is also observed. At higher magnification presence of corrosion products in the pits was established. With 0.10%  $\text{Sb}_2\text{O}_3$  and 0.03% ferric ions in GVSL, CS material's pearlitic phase appears mildly etched and localised features are not severely affected. Corrosion products are also not seen at higher magnification. With 0.15%  $\text{Sb}_2\text{O}_3$  and 0.03% ferric ion concentration, the effect is limited to very mild etching. Inclusions and localised features are remarkably unaffected. Intact nature of spotty carbide at higher magnification is observed.

From AC impedance studies done for CS in GVSL solution without and with aeration and  $\text{Sb}_2\text{O}_3$  (0.15%) and ferric ions, polarisation resistance and double layer capacitance values were calculated. This was done using nyquist and bode plots.

Ferric ion additions up to 0.04% decreases  $R_p$  considerably, showing that the corrosion process is accelerated. This was noticed in without aerated condition. After aeration and in presence of ferric ions  $R_p$  is found to be higher than that for non aerated condition, but there is again decrease in  $R_p$  with increasing concentration of ferric ions.

Addition of 0.15%  $\text{Sb}_2\text{O}_3$  to Syn. GVSL solution without aeration and increasing concentration of ferric ions decreases  $R_p$  values except

at 0.02% concentration. Addition of 0.15%  $\text{Sb}_2\text{O}_3$  to Syn. GVSL solution with aeration and increasing concentration of ferric ions up to 0.03% increases  $R_p$  value. It is observed here that at 0.01% and at 0.04% ferric ion concentration there is decrease in  $R_p$  values. For 0.15%  $\text{Sb}_2\text{O}_3$  - 0.03% ferric ions an  $R_p$  of 12353 Ohm.cm. is obtained. It is also interesting that at 0.01% ferric ion concentration for any condition  $R_p$  decreases considerably.

Same observations hold good for Cdl values. Wherever there is increase in  $R_p$  there is decrease in Cdl. In Syn. GVSL with 0.15%  $\text{Sb}_2\text{O}_3$  and 0.03% ferric ion concentration with aeration Cdl value of 222 microfarads is obtained. Increase in the concentration of ferric ions also pushes the Cdl value higher as is observed with 0.04% ferric ions. No effect on Cdl is observed for any condition at 0.01% ferric ion concentration.

Antimony oxide addition in the plant on stream was done in such a way that GV bulk solution always contains around 0.1%  $\text{Sb}_2\text{O}_3$ . Experiments carried out using GVSL solutions collected at various intervals of days and with and without aeration showed that there was definite changes in its electrochemical characteristics. Four GVSL solutions collected within a span of around two months had shown higher OCP values, lower  $i_{cc}$  and  $i_p$  values,  $E_{pp}$  and  $E_p$  in almost all cases are very much comparable with OCP s of CS. There is also a marked difference in these values with and without aeration of GVSL solution. Insufficient aeration of GVSL solution in the plant had shown lower OCP and higher  $i_{cc}$  and  $i_p$  values at first but after aeration in the plant and the experiments without aeration showed that these values were much lower than the conventional values, showing the effect of  $\text{Sb}_2\text{O}_3$  and ferric ions.

I Corr had also decreased drastically, but Rp value is not effected much showing scope of further inhibition up to 23.05.90. Corrosion rates had reduced after aeration, showing inhibitor efficiencies of around 80.0%. But for sample collected on 13.06.90 showed an Rp of 349.1 Ohm.cm. after aeration and corrosion rate of only 1.68 mpy (I.E. of 97.83%), which is comparable with the results of CS in Syn. GVSL with 0.15% Sb<sub>2</sub>O<sub>3</sub> and 0.03% ferric ions.

**TABLE 1: OPEN CIRCUIT POTENTIALS OF CARBON STEEL IN DIFFERENT GV SOLUTIONS**

Sr. No.	Condition	OCP IN mV
1	GV A II Semi lean - 70 Deg. C.	-734
2	GV A II Semi lean - 85 Deg. C.	-722
3	GV A II Rich - 102 Deg. C.	-686
4	GVSL A II dt. 7-4-90 without aeration	-748
5	GVSL A II dt. 7-4-90 with aeration	-570
6	GVSL A II dt. 23-5-90 without aeration	-718
7	GVSL A II dt. 23-5-90 with aeration	-275
8	GVSL A II dt. 31-5-90 without aeration	-330
9	GVSL A II dt. 31-5-90 with aeration	-185
10	GVSL A II dt. 13-6-90 without aeration	-291
11	GVSL A II dt. 13-6-90 with aeration	-195
12	<u>GVSL</u> + 0.1% W/V Vanadium pentoxide ✓	-330
13	Sol.(12) + 100 mg/l ferric ions	-424
14	Sol.(12) + 200 mg/l ferric ions	-431
15	Sol.(12) + 300 mg/l ferric ions	-427
16	GVSL + 0.7 % W/V Potassium dichromate ✓	-400
17	Sol.(16) + 100 mg/l ferric ions	-719
18	Sol.(16) + 200 mg/l ferric ions	-719
19	Sol.(16) + 300 mg/l ferric ions	-715
20	GVSL + 0.6% W/V Sodium silicate ✓ + 0.02 % W/V Potassium dichromate	-398
21	Sol.(20) + 100 mg/l ferric ions	-720
22	Sol.(20) + 200 mg/l ferric ions	-715
23	Sol.(20) + 300 mg/l ferric ions	-711

GVSL

**Table-1 (Contd.)**

<b>Sr. No.</b>	<b>Condition</b>	<b>OCP IN mV</b>
24	GVSL + 1 % W/V Ammonium metavanadate + 0.25 % W/V Sodium nitrite	-329
25	Sol.(24) + 100 mg/l ferric ions	-324
26	Sol.(24) + 200 mg/l ferric ions	-332
27	Sol.(24) + 300 mg/l ferric ions	-329
28	GVSL + 0.1 % W/V Ammonium metavanadate + 0.1 % W/V Potassium antimonyl tartrate + 0.01 % W/V Tartaric acid	-402
29	Sol.(28) + 100 mg/l ferric ions	-402
30	Sol.(28) + 200 mg/l ferric ions	-425
31	Sol.(28) + 300 mg/l ferric ions	-396
32	Synthetic GVSL Solution	-745
33	Sol.(32) + 100 mg/l ferric ions	-750
34	Sol.(32) + 200 mg/l ferric ions	-750
35	Sol.(32) + 300 mg/l ferric ions	-750
36	Sol.(32) + 400 mg/l ferric ions	-760
37	GVSL + 0.075 % W/V Antimony trioxide	-745
38	Sol.(37) + 100 mg/l ferric ions	-750
39	Sol.(37) + 200 mg/l ferric ions	-750
40	Sol.(37) + 300 mg/l ferric ions	-440
41	Sol.(37) + 400 mg/l ferric ions	-460
42	GVSL + 0.1 % W/V Antimony trioxide	-750
43	Sol.(42) + 100 mg/l ferric ions	-728
44	Sol.(42) + 200 mg/l ferric ions	-729
45	Sol.(42) + 300 mg/l ferric ions	-480
46	Sol.(42) + 400 mg/l ferric ions	-450

**Table-1 (Contd.)**

<b>Sr. No.</b>	<b>Condition</b>	<b>OCP IN mV</b>
47	GVSL + 0.13 % W/V Antimony trioxide	-724
48	Sol.(47) + 100 mg/l ferric ions	-737
49	Sol.(47) + 200 mg/l ferric ions	-710
50	Sol.(47) + 300 mg/l ferric ions	-440
51	Sol.(47) + 400 mg/l ferric ions	-388
52	GVSL + 0.14% W/V Antimony trioxide	-728
53	Sol.(52) + 100 mg/l ferric ions	-738
54	Sol.(52) + 200 mg/l ferric ions	-735
55	Sol.(52) + 300 mg/l ferric ions	-389
56	Sol.(52) + 400 mg/l ferric ions	-366
57	GVSL + 0.15% W/V Antimony trioxide	-770
58	Sol.(57) + 100 mg/l ferric ions	-430
59	Sol.(57) + 200 mg/l ferric ions	-385
60	Sol.(57) + 300 mg/l ferric ions	-305
61	Sol.(57) + 400 mg/l ferric ions	-410

**TABLE 2: CRITICAL CURRENT DENSITY, PASSIVE CURRENT DENSITY, PASSIVE POTENTIAL AND PRIMARY PASSIVATING POTENTIAL VALUES FOR CS IN GV SOLUTION**

Sr. No.	Condition	icc mA	ip mA	Ep mV	Epp mV
1	GV A II Semi lean - 70 Deg. C.	14.44	0.37	400	-130
2	GV A II Semi lean - 85 Deg. C.	20.00	0.53	360	-120
3	GV A II Rich - 102 Deg. C.	5.00	2.33	600	0
4	GVSL A II dt. 7-4-90 without aeration	19.44	4.56	300	-350
5	GVSL A II dt. 7-4-90 with aeration	1.24	0.12	-200	-350
6	GVSL A II dt. 23-5-90 without aeration	72.20	2.78	450	-380
7	GVSL A II dt. 23-5-90 with aeration	0.21	0.03	-200	-320
8	GVSL A II dt. 31-5-90 without aeration	1.31	0.06	-170	-280
9	GVSL A II dt. 31-5-90 with aeration	1.06	0.05	-100	-275
10	GVSL A II dt. 13-6-90 without aeration	2.11	0.07	-150	-265
11	GVSL A II dt. 13-6-90 with aeration	0.67	0.04	-150	-270
12	GVSL + 0.1% W/V Vanadium pentoxide	0.24	0.09	-100	-300
13	Sol.(12) + 100 mg/l ferric ions	0.80	0.14	-100	-310
14	Sol.(12) + 200 mg/l ferric ions	0.42	0.13	-100	-310
15	Sol.(12) + 300 mg/l ferric ions	0.17	0.11	-100	-290
16	GVSL + 0.7 % W/V Potassium dichromate	0.04	0.03	-400	-590
17	Sol.(16) + 100 mg/l ferric ions	50.00	5.56	100	-330
18	Sol.(16) + 200 mg/l ferric ions	36.10	5.56	100	-300
19	Sol.(16) + 300 mg/l ferric ions	45.60	1.22	200	-380

**Table-2 (Contd.)**

Sr. No.	Condition	lcc mA	Ip mA	Ep mV	Epp mV
20	GVSL + 0.6% W/V Sodium silicate + 0.02 % W/V Potassium dichromate	1.01	0.12	-100	-315
21	Sol.(20) + 100 mg/l ferric ions	19.44	4.44	-100	-370
22	Sol.(20) + 200 mg/l ferric ions	27.78	3.89	-100	-400
23	Sol.(20) + 300 mg/l ferric ions	19.44	2	-100	-385
24	GVSL + 1 % W/V Ammonium metavanadate + 0.25 % W/V Sodium nitrite	0.24	0.12	60	-320
25	Sol.(24) + 100 mg/l ferric ions	0.26	0.13	0	-370
26	Sol.(24) + 200 mg/l ferric ions	0.21	0.11	0	-350
27	Sol.(24) + 300 mg/l ferric ions	0.19	0.12	0	-300
28	GVSL + 0.1 % W/V Ammonium metavanadate + 0.1 % W/V Potassium antimonyl tartrate + 0.01 % W/V Tartaric acid	0.66	0.19	-150	-310
29	Sol.(28) + 100 mg/l ferric ions	0.59	0.17	-150	-305
30	Sol.(28) + 200 mg/l ferric ions	0.77	0.22	-150	-305
31	Sol.(28) + 300 mg/l ferric ions	0.09	0.08	-200	-350
32	Synthetic GVSL Solution	8.33	1.78	200	-435
33	Sol.(32) + 100 mg/l ferric ions	3.56	0.69	150	-470
34	Sol.(32) + 200 mg/l ferric ions	10.00	2.11	150	-490
35	Sol.(32) + 300 mg/l ferric ions	10.00	2.11	150	-480
36	Sol.(32) + 400 mg/l ferric ions	28.33	5.56	150	-460
37	GVSL + 0.075 % W/V Antimony trioxide	7.67	1.06	200	-475
38	Sol.(37) + 100 mg/l ferric ions	9.00	0.61	200	-550

**Table-2 (Contd.)**

<b>Sr. No.</b>	<b>Condition</b>	<b>icc mA</b>	<b>ip mA</b>	<b>Ep mV</b>	<b>Epp mV</b>
39	Sol.(37) + 200 mg/l ferric ions	1.04	0.14	200	-520
40	Sol.(37) + 300 mg/l ferric ions	0.08	0.02	-300	-450
41	Sol.(37) + 400 mg/l ferric ions	0.07	0.03	-330	-430
42	GVSL + 0.1 % W/V Antimony trioxide	5.56	0.67	200	-490
43	Sol.(42) + 100 mg/l ferric ions	31.11	6.44	300	-300
44	Sol.(42) + 200 mg/l ferric ions	15.56	3.83	300	-330
45	Sol.(42) + 300 mg/l ferric ions	0.10	0.26	-350	-425
46	Sol.(42) + 400 mg/l ferric ions	0.64	0.019	-350	-450
47	GVSL + 0.13 % W/V Antimony trioxide	64.44	1.6	400	-350
48	Sol.(47) + 100 mg/l ferric ions	111.11	13.33	300	-310
49	Sol.(47) + 200 mg/l ferric ions	100.00	10.22	300	-340
50	Sol.(47) + 300 mg/l ferric ions	0.51	0.052	-280	-440
51	Sol.(47) + 400 mg/l ferric ions	0.50	0.033	-230	-350
52	GVSL + 0.14% W/V Antimony trioxide	57.78	8.67	300	-310
53	Sol.(52) + 100 mg/l ferric ions	67.78	10.22	300	-350
54	Sol.(52) + 200 mg/l ferric ions	96.67	12.22	300	-260
55	Sol.(52) + 300 mg/l ferric ions	0.51	0.037	-250	-450
56	Sol.(52) + 400 mg/l ferric ions	0.64	0.06	-290	-385
57	GVSL + 0.15% W/V Antimony trioxide	23.89	2.22	200	-470
58	Sol.(57) + 100 mg/l ferric ions	0.14	0.019	-320	-430
59	Sol.(57) + 200 mg/l ferric ions	0.078	0.007	-350	-460
60	Sol.(57) + 300 mg/l ferric ions	0.068	0.007	-350	-430
61	Sol.(57) + 400 mg/l ferric ions	0.11	0.017	-360	-470

**TABLE3: ANODIC TAFEL, CATHODIC TAFEL AND CORROSION CURRENT DENSITY VALUES FOR CS IN GV SOLUTIONS**

Sr. No.	Condition	Ba mV/DEC	Bc mV/DEC	I Corr mA/cm <sup>2</sup>
1	GV A II Semi lean - 70 Deg. C.	86.6	101.3	0.0097
2	GV A II Semi lean - 85 Deg. C.	161.7	114.1	0.0294
3	GV A II Rich - 102 Deg. C.	5448.0	151.1	0.1286
4	GVSL A II dt. 7-4-90 without aeration	2025.0	162.7	0.8880
5	GVSL A II dt. 7-4-90 with aeration	26.4	138.0	0.1000
6	GVSL A II dt. 23-5-90 without aeration	183.0	68.5	0.5990
7	GVSL A II dt. 23-5-90 with aeration	56.0	181.9	0.1400
8	GVSL A II dt. 31-5-90 without aeration	251.0	255.6	0.2700
9	GVSL A II dt. 31-5-90 with aeration	86.6	79.9	0.0532
10	GVSL A II dt. 13-6-90 without aeration	174.7	257.3	0.1734
11	GVSL A II dt. 13-6-90 with aeration	148.4	33.6	0.0038
12	GVSL + 0.1% W/V Vanadium pentoxide	5645.0	875.5	0.2090
13	Sol.(12) + 100 mg/l ferric ions	10975.0	565.5	0.2330
14	Sol.(12) + 100 mg/l+ 200 mg/l ferric ions	12734.0	395.9	0.2390
15	Sol.(12) + 100 mg/l+ 300 mg/l ferric ions	1344.0	335.8	0.1260
16	GVSL + 0.7 % W/V Potassium dichromate	193.3	180.1	0.0210
17	Sol.(16) + 100 mg/l ferric ions	2258.0	105.2	0.5350
18	Sol.(16) + 200 mg/l ferric ions	699.4	96.2	0.3760
19	Sol.(16) + 300 mg/l ferric ions	503.8	86.4	0.5820
20	GVSL + 0.6% W/V Sodium silicate + 0.02 % W/V Potassium dichromate	165.0	106.0	0.0160
21	Sol.(20) + 100 mg/l ferric ions	400.0	88.0	0.1390
22	Sol.(20) + 200 mg/l ferric ions	9488.0	97.0	0.4040
23	Sol.(20) + 300 mg/l ferric ions	746.0	91.0	0.3070

**Table-3 (Contd.)**

Sr. No.	Condition	Ba mV/DEC	Bc mV/DEC	I Corr mA/cm <sup>2</sup>
24	GVSL + 1 % W/V Ammonium metavanadate + 0.25 % W/V Sodium nitrite	298.4	252.9	0.1720
25	Sol.(24) + 100 mg/l ferric ions	187.8	198.7	0.1140
26	Sol.(24) + 200 mg/l ferric ions	296.2	182.4	0.1290
27	Sol.(24) + 300 mg/l ferric ions	142.0	66.4	0.0220
28	GVSL + 0.1 % W/V Ammonium metavanadate + 0.1 % W/V Potassium antimonyl tartrate + 0.01 % W/V Tartaric acid	398.0	216.0	0.0730
29	Sol.(28) + 100 mg/l ferric ions	844.3	322.0	0.1310
30	Sol.(28) + 200 mg/l ferric ions	326.0	227.0	0.0720
31	Sol.(28) + 300 mg/l ferric ions	8961.0	185.0	0.1440
32	Synthetic GVSL Solution	142.3	29.2	0.0190
33	Sol.(32) + 100 mg/l ferric ions	47.0	38.3	0.0060
34	Sol.(32) + 200 mg/l ferric ions	49.7	38.6	0.0130
35	Sol.(32) + 300 mg/l ferric ions	57.7	38.8	0.0100
36	Sol.(32) + 400 mg/l ferric ions	132.2	100.8	0.2230
37	GVSL + 0.075 % W/V Antimony trioxide	183.1	62.8	0.0260
38	Sol.(37) + 100 mg/l ferric ions	80.0	58.0	0.0280
39	Sol.(37) + 200 mg/l ferric ions	72.7	63.5	0.0220
40	Sol.(37) + 300 mg/l ferric ions	194.8	91.0	0.0060
41	Sol.(37) + 400 mg/l ferric ions	90.1	64.1	0.0100
42	GVSL + 0.1 % W/V Antimony trioxide	7767.0	68.6	0.1530
43	Sol.(42) + 100 mg/l ferric ions	268.0	67.4	0.1430
44	Sol.(42) + 200 mg/l ferric ions	86.8	70.0	0.1520

**Table-3 (Contd.)**

Sr. No.	Condition	Ba mV/DEC	Bc mV/DEC	I Corr mA/cm <sup>2</sup>
45	Sol.(42) + 300 mg/l ferric ions	954.4	236.3	0.0270
46	Sol.(42) + 400 mg/l ferric ions	155.7	101.9	0.0130
47	GVSL + 0.13 % W/V Antimony trioxide	565.9	77.6	0.4800
48	Sol.(47) + 100 mg/l ferric ions	250.1	70.7	0.5900
49	Sol.(47) + 200 mg/l ferric ions	482.6	70.0	0.7200
50	Sol.(47) + 300 mg/l ferric ions	204.0	72.4	0.1400
51	Sol.(47) + 400 mg/l ferric ions	270.0	50.0	0.0610
52	GVSL + 0.14% W/V Antimony trioxide	226.4	61.3	0.2000
53	Sol.(52) + 100 mg/l ferric ions	145.9	57.1	0.2200
54	Sol.(52) + 200 mg/l ferric ions	269.8	68.2	0.2700
55	Sol.(52) + 300 mg/l ferric ions	38.8	37.5	0.0430
56	Sol.(52) + 400 mg/l ferric ions	17.7	26.7	0.0200
57	GVSL + 0.15% W/V Antimony trioxide	128.5	47.7	0.0560
58	Sol.(57) + 100 mg/l ferric ions	142.3	111.6	0.0060
59	Sol.(57) + 200 mg/l ferric ions	46.5	134.6	0.0030
60	Sol.(57) + 300 mg/l ferric ions	42.2	73.7	0.0007
61	Sol.(57) + 400 mg/l ferric ions	258.3	106.6	0.0140

**TABLE 4: POLARIZATION RESISTANCE, CORROSION RATE AND INHIBITOR EFFICIENCY VALUES FOR CS IN GV SOLUTIONS**

Sr. No.	Condition	Rp ohm.cm	Corrosion Rate (MPY)	IE %
1	GV A II Semi lean - 70 Deg. C.	233.0	4.3	-
2	GV A II Semi lean - 85 Deg. C.	109.7	13.1	-
3	GV A II Rich - 102 Deg. C.	55.2	57.3	-
4	GVSL A II dt. 7-4-90 without aeration	8.2	396.0	-
5	GVSL A II dt. 7-4-90 with aeration	10.7	44.5	88.8
6	GVSL A II dt. 23-5-90 without aeration	4.0	267.0	-
7	GVSL A II dt. 23-5-90 with aeration	14.8	62.2	76.7
8	GVSL A II dt. 31-5-90 without aeration	22.7	120.2	-
9	GVSL A II dt. 31-5-90 with aeration	37.7	23.7	80.3
10	GVSL A II dt. 13-6-90 without aeration	28.9	77.3	-
11	GVSL A II dt. 13-6-90 with aeration	349.1	1.7	97.8
12	GVSL + 0.1% W/V Vanadium pentoxide	175.2	93.1	-
13	Sol.(12) + 100 mg/l ferric ions	111.3	104.0	-11.7
14	Sol.(12) + 200 mg/l ferric ions	77.5	107.0	-14.9
15	Sol.(12) + 300 mg/l ferric ions	102.9	56.2	39.6
16	GVSL + 0.7 % W/V Potassium dichromate	217.0	9.3	-
17	Sol.(16) + 100 mg/l ferric ions	9.1	238.7	-2475.0
18	Sol.(16) + 200 mg/l ferric ions	10.9	167.5	-1707.0
19	Sol.(16) + 300 mg/l ferric ions	6.1	259.3	-2697.0
20	GVSL + 0.6% W/V Sodium silicate + 0.02 % W/V Potassium dichromate	193.9	7.2	-

**Table-4 (Contd.)**

Sr. No.	Condition	Rp ohm.cm	Corrosion Rate (MPY)	IE %
21	Sol.(20) + 100 mg/l ferric ions	25.0	61.8	-758.0
22	Sol.(20) + 200 mg/l ferric ions	11.5	180.0	-2400.0
23	Sol.(20) + 300 mg/l ferric ions	12.7	136.7	-1799.0
24	GVSL + 1 % W/V Ammonium metavanadate + 0.25 % W/V Sodium-nitrite	38.4	76.8	-
25	Sol.(24) + 100 mg/l ferric ions	40.8	51.0	33.6
26	Sol.(24) + 200 mg/l ferric ions	42.2	57.6	25.0
27	Sol.(24) + 300 mg/l ferric ions	99.5	9.8	87.2
28	GVSL + 0.1 % W/V Ammonium metavanadate + 0.1 % W/V Potassium antimonyl tartrate + 0.01 % W/V Tartaric acid	92.0	32.7	-
29	Sol.(28) + 100 mg/l ferric ions	86.2	58.3	-78.3
30	Sol.(28) + 200 mg/l ferric ions	90.0	32.0	2.1
31	Sol.(28) + 300 mg/l ferric ions	60.8	64.1	-96.0
32	Synthetic GVSL Solution	63.1	8.3	-
33	Sol.(32) + 100 mg/l ferric ions	57.3	2.8	65.8
34	Sol.(32) + 200 mg/l ferric ions	81.5	5.7	30.9
35	Sol.(32) + 300 mg/l ferric ions	108.2	4.6	44.2
36	Sol.(32) + 400 mg/l ferric ions	12.4	1.2	85.8
37	GVSL + 0.075 % W/V Antimony trioxide	45.7	11.8	-
38	Sol.(37) + 100 mg/l ferric ions	59.1	12.3	-4.2
39	Sol.(37) + 200 mg/l ferric ions	74.5	9.81	6.9
40	Sol.(37) + 300 mg/l ferric ions	510.4	2.6	77.9

**Table-4 (Contd.)**

Sr. No.	Condition	Rp ohm.cm	Corrosion Rate (MPY)	IE %
41	Sol.(37) + 400 mg/l ferric ions	172.7	4.7	60.4
42	GVSL + 0.1 % W/V Antimony trioxide	21.4	58.4	-
43	Sol.(42) + 100 mg/l ferric ions	18.2	63.8	-9.3
44	Sol.(42) + 200 mg/l ferric ions	12.3	68.0	-16.4
45	Sol.(42) + 300 mg/l ferric ions	335.8	12.1	79.2
46	Sol.(42) + 400 mg/l ferric ions	221.0	6.0	89.7
47	GVSL + 0.13 % W/V Antimony trioxide	6.9	213.0	-
48	Sol.(47) + 100 mg/l ferric ions	4.5	261.0	-22.5
49	Sol.(47) + 200 mg/l ferric ions	4.1	319.0	-49.8
50	Sol.(47) + 300 mg/l ferric ions	18.3	62.9	70.5
51	Sol.(47) + 400 mg/l ferric ions	32.9	27.3	87.2
52	GVSL + 0.14% W/V Antimony trioxide	11.6	89.2	-
53	Sol.(52) + 100 mg/l ferric ions	8.8	100.0	-12.1
54	Sol.(52) + 200 mg/l ferric ions	4.3	121.0	-35.7
55	Sol.(52) + 300 mg/l ferric ions	21.5	19.1	78.6
56	Sol.(52) + 400 mg/l ferric ions	25.6	8.9	90.0
57	GVSL + 0.15% W/V Antimony trioxide	29.8	25.2	-
58	Sol.(57) + 100 mg/l ferric ions	505.6	2.7	89.4
59	Sol.(57) + 200 mg/l ferric ions	529.2	1.4	94.4
60	Sol.(57) + 300 mg/l ferric ions	1976.3	0.3	98.8
61	Sol.(57) + 400 mg/l ferric ions	253.9	6.4	74.6

**TABLE 5:  
POLARIZATION RESISTANCE Rp (Ohm. Cm) VALUES FROM IMPEDANCE SPECTRA**

Ferric Ion Concn.	GVSL Solution without Aeration	GVSL Solution with Aeration	GVSL Solution with 0.15% Sb <sub>2</sub> O <sub>3</sub> and without Aeration	GVSL Solution with 0.15% Sb <sub>2</sub> O <sub>3</sub> and with Aeration
0.0%	357	777	434	518
0.01%	250	173	282	253
0.02%	187	362	568	469
0.03%	180	340	224	12353
0.04%	71	93	172	87

**DOUBLE LAYER CAPACITANCE Cdl (MICROFARADS) VALUES FROM IMPEDANCE SPECTRA**

0.0%	5772	2393	4941	4388
0.01%	11995	19474	13753	52030
0.02%	92336	25316	32279	22193
0.03%	53614	33591	50036	222
0.04%	33967	14054	19008	32279

**TABLE-6 : CHEMICAL ANALYSIS OF PLANT GVSL SOLUTIONS :**

Sampling Date	K <sub>2</sub> CO <sub>3</sub> g/l	KHCO <sub>3</sub> g/l	As <sub>2</sub> O <sub>3</sub> g/l	As <sub>2</sub> O <sub>5</sub> g/l	Iron mg/l	Carbonation Index
07-4-90	196.90	60.19	110.41	24.40	362	1.175
23-5-90	188.08	75.34	77.92	22.90	200	1.217
31-5-90	174.62	87.93	74.65	21.63	458	1.258
13-6-90	184.12	75.27	71.35	21.24	375	1.220

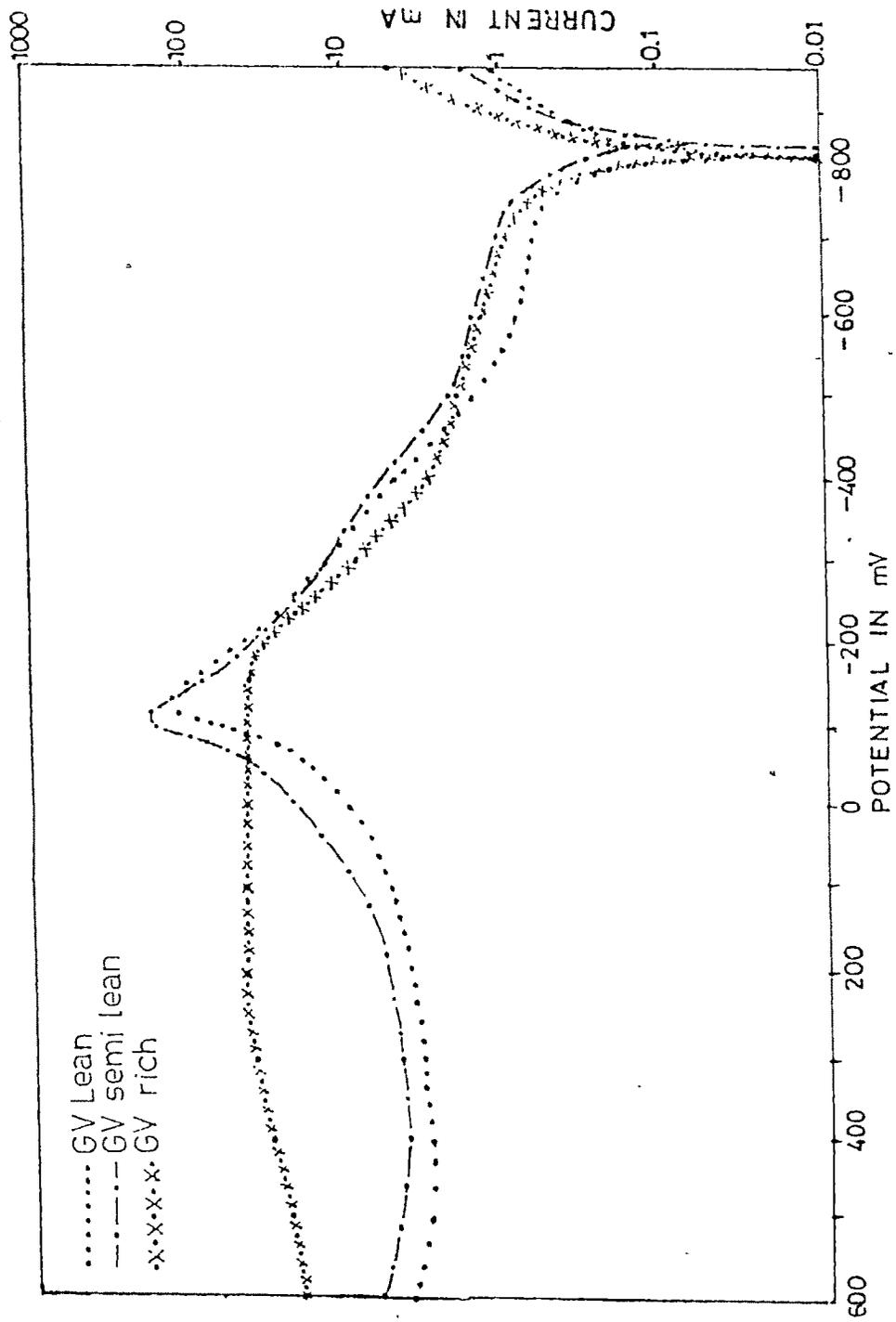


FIG.1 :POTENTIODYNAMIC POLARIZATION SCANS OF CS IN PLANT GV SOLUTIONS

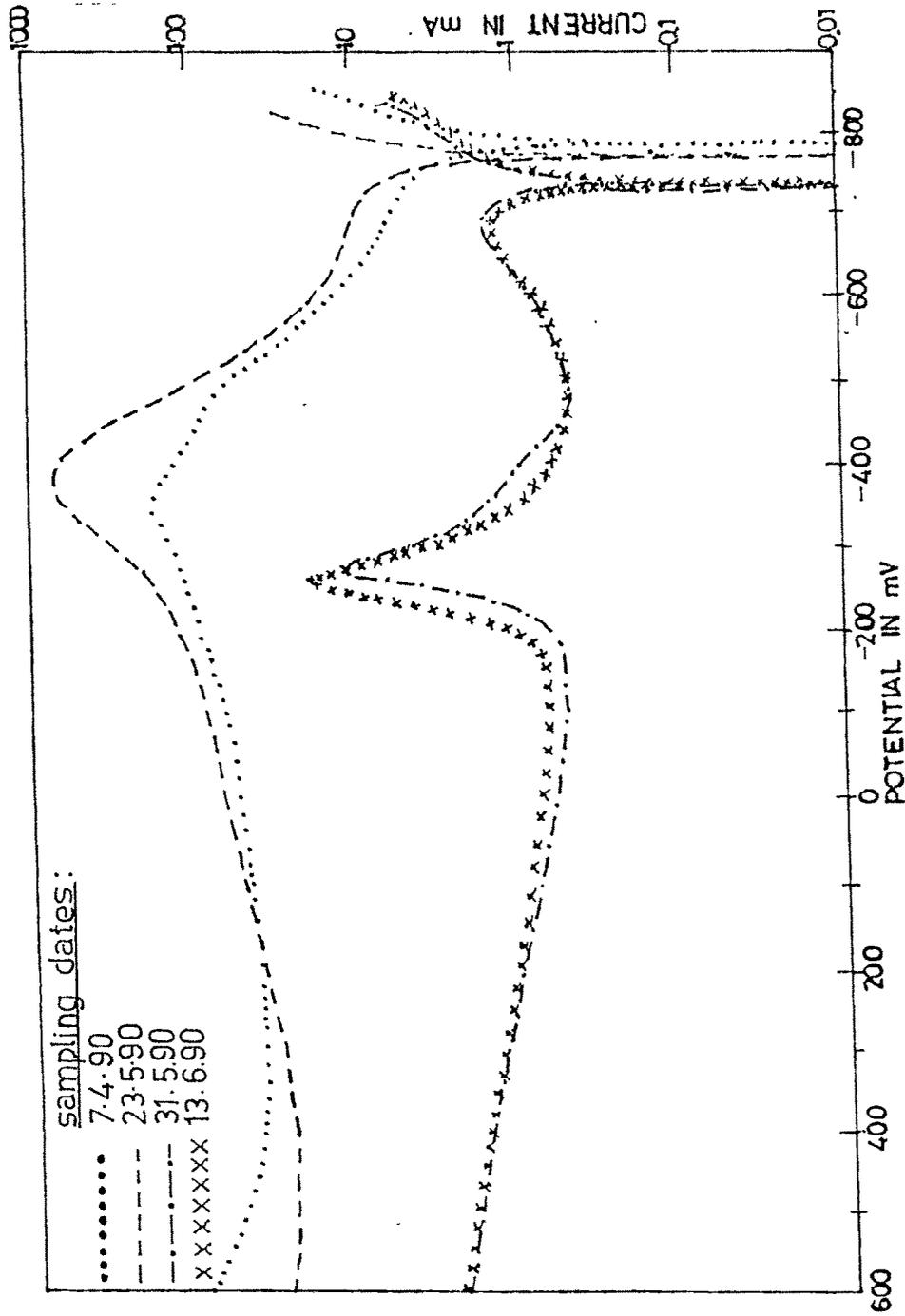


FIG. 2 : POTENTIODYNAMIC POLARIZATION SCANS OF CS IN PLANT GVSL SOLUTION (WITHOUT AERATION)

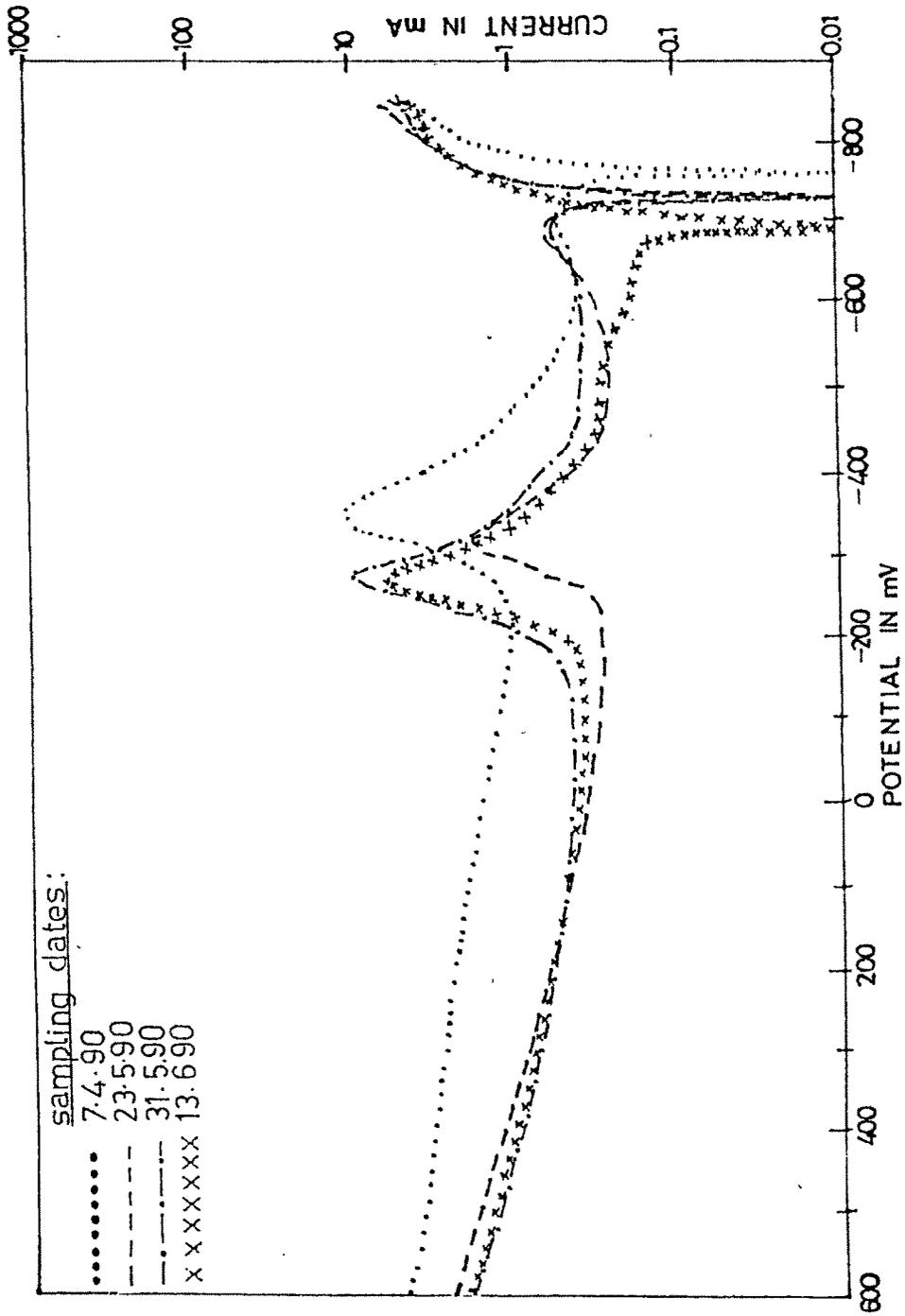


FIG. 3 : POTENTIODYNAMIC POLARIZATION SCANS OF CS IN PLANT GVSL SOLUTION (WITH AERATION)

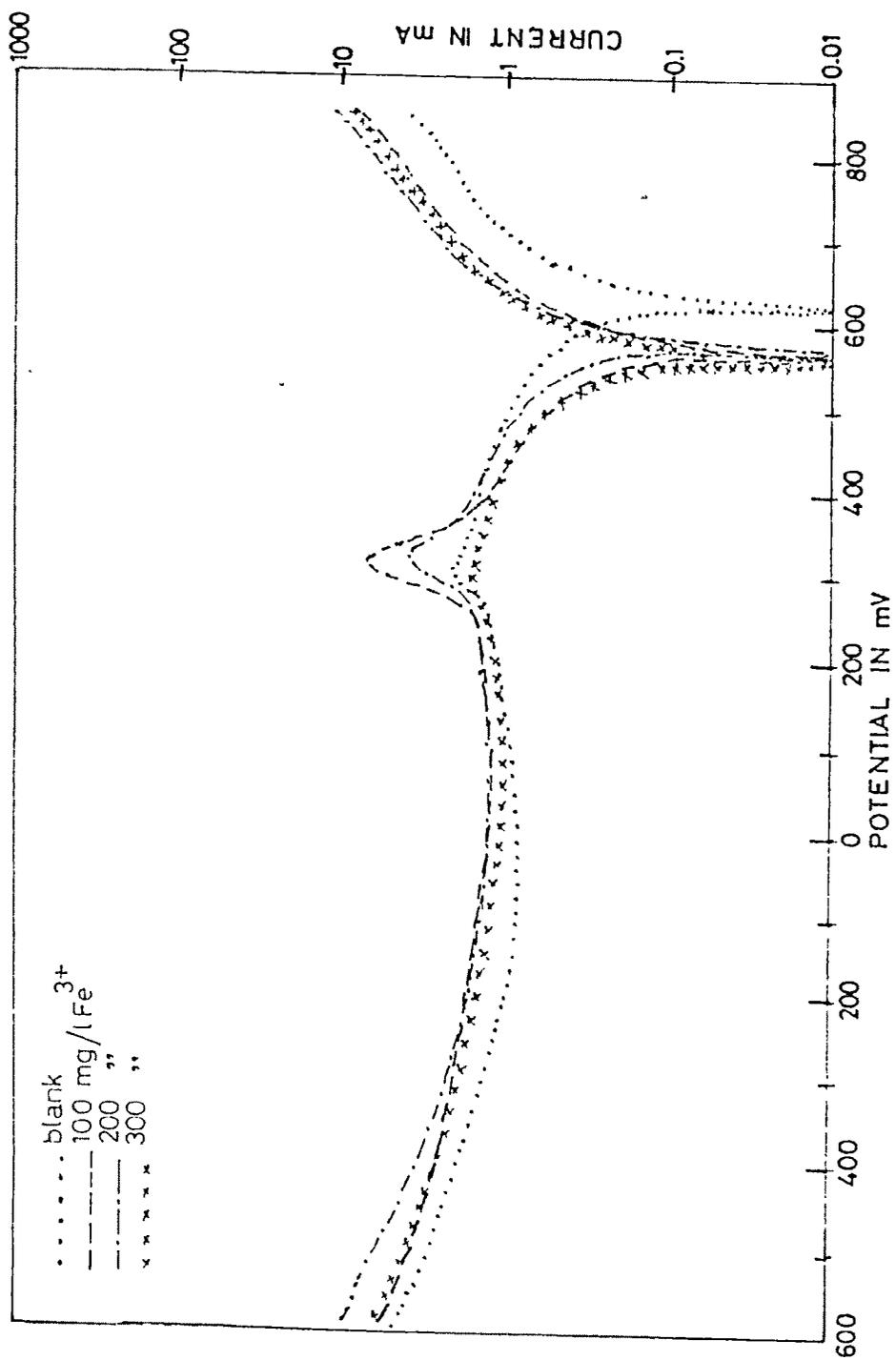


FIG.4 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.1% VANADIUM PENTOXIDE

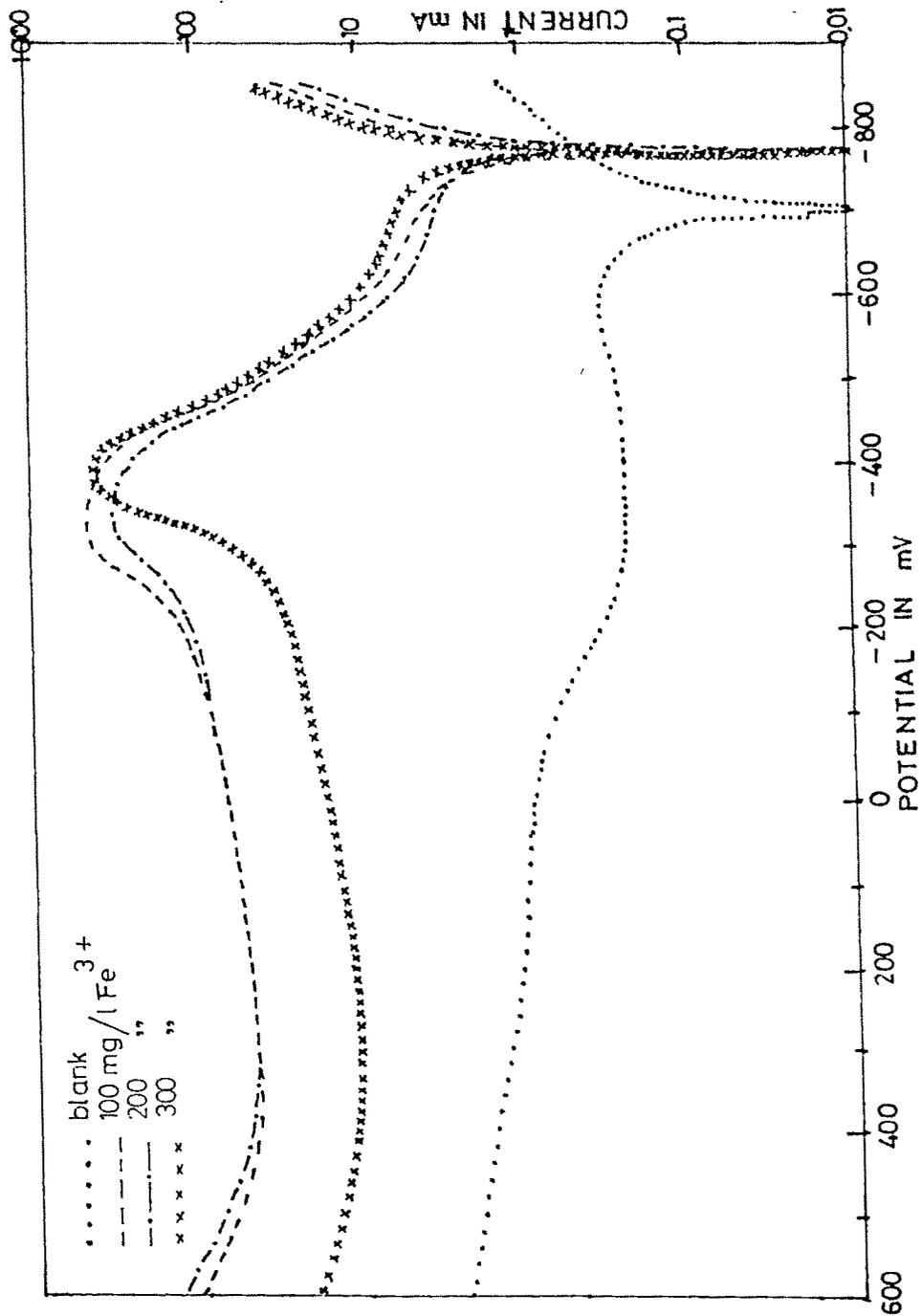


FIG.5 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.7% POT. DICHROMATE

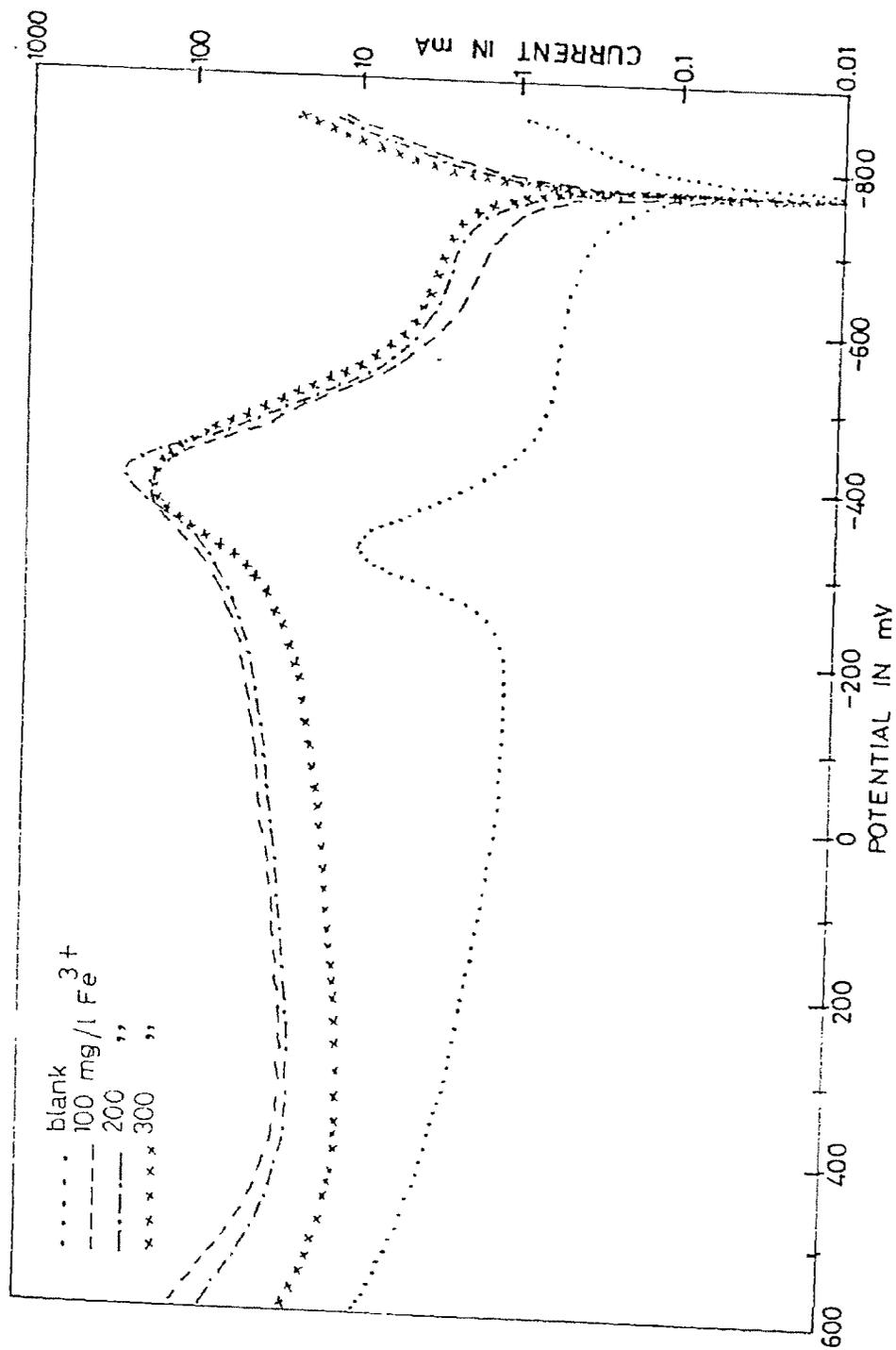


FIG.6 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.6% SOD. SILICATE AND 0.02% POT. DICHROMATE

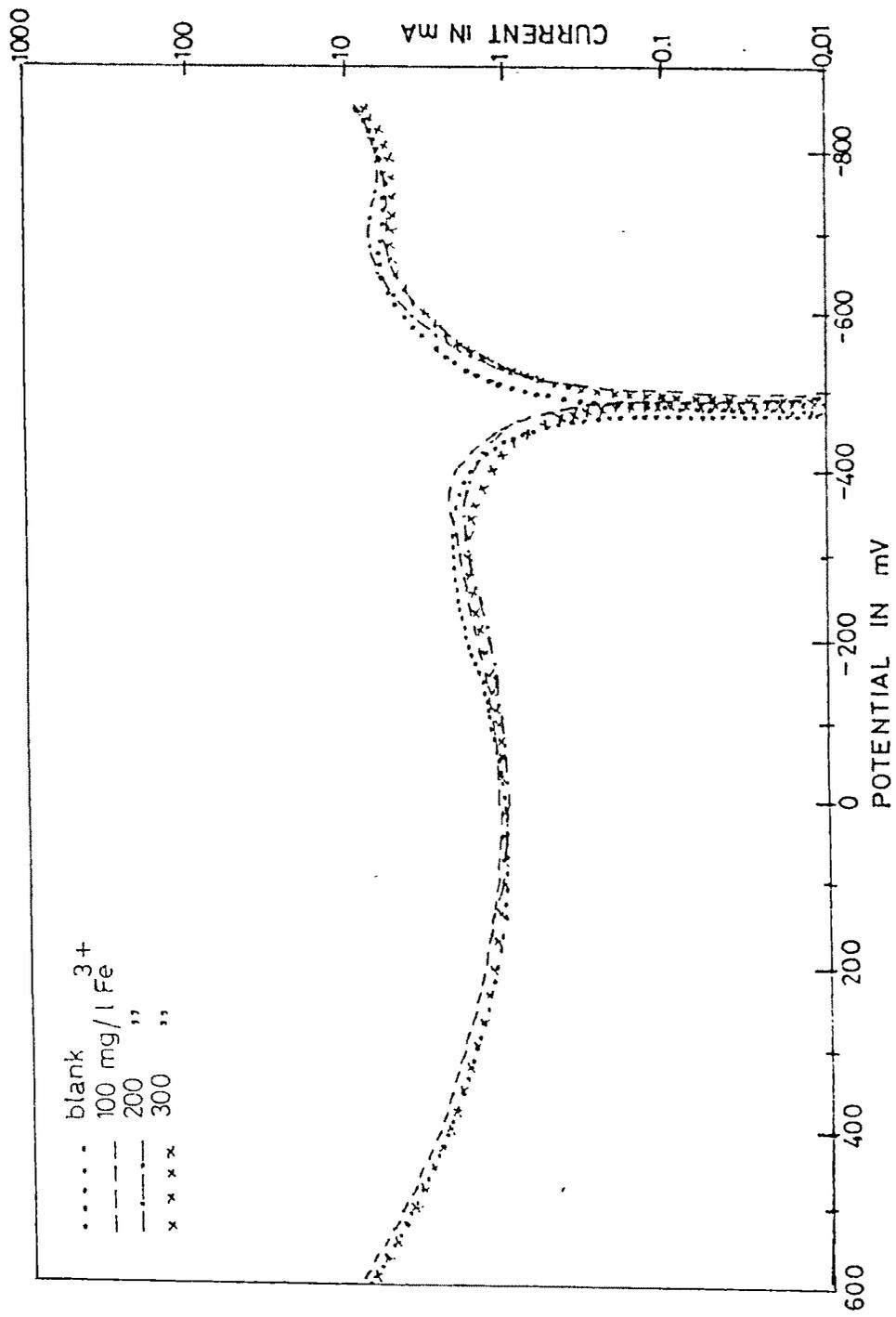


FIG.7 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 1% AMM. METAVANDATE  
 AND 0.25% SOD. NITRITE

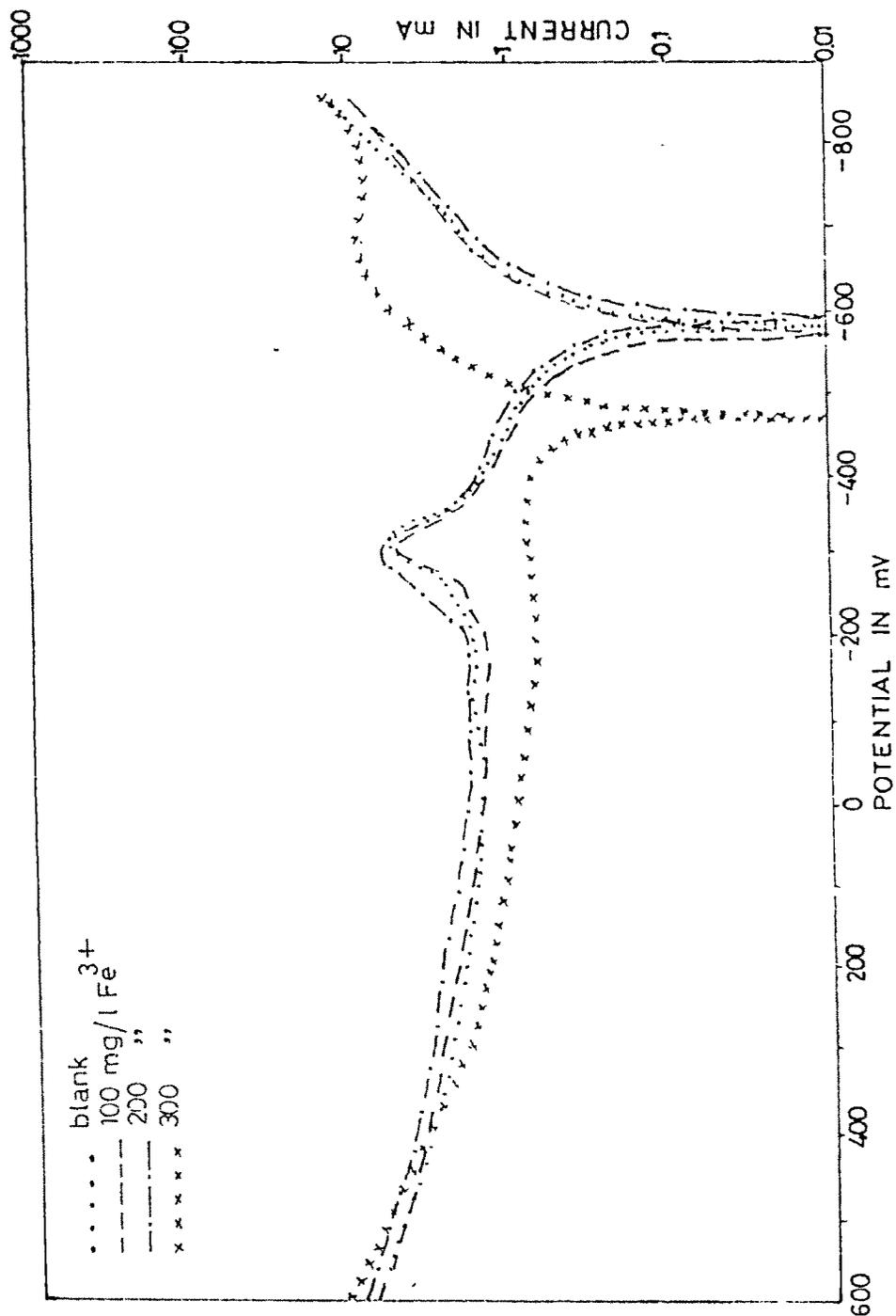


FIG.8 : EFFECT ON FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.1% AMM.  
 METAVANDATE, 0.1% POT. ANT. TARTRATE AND 0.01% TARTARIC  
 ACID

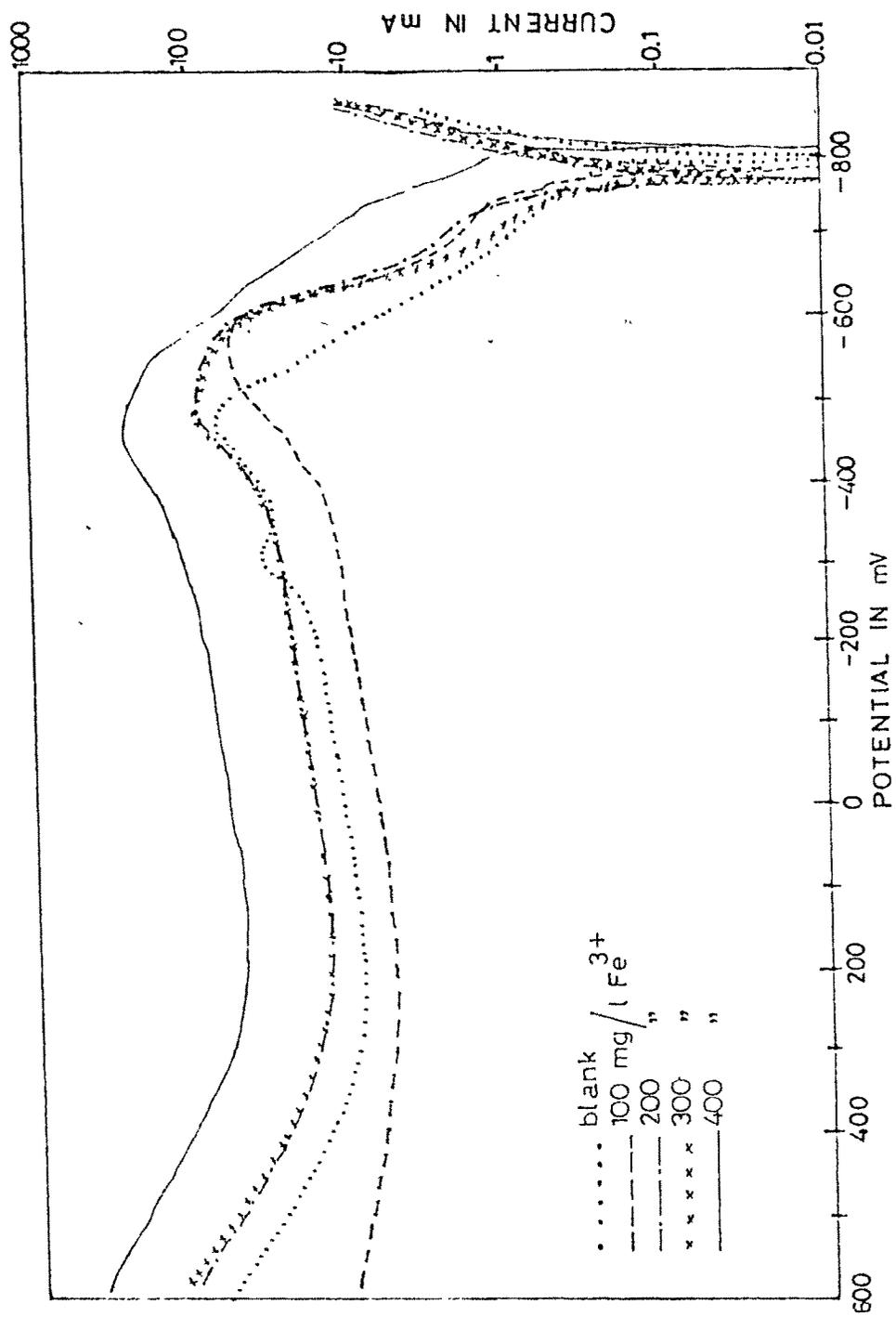


FIG.9 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS OF CS IN 0.1N GVSL SOLUTION

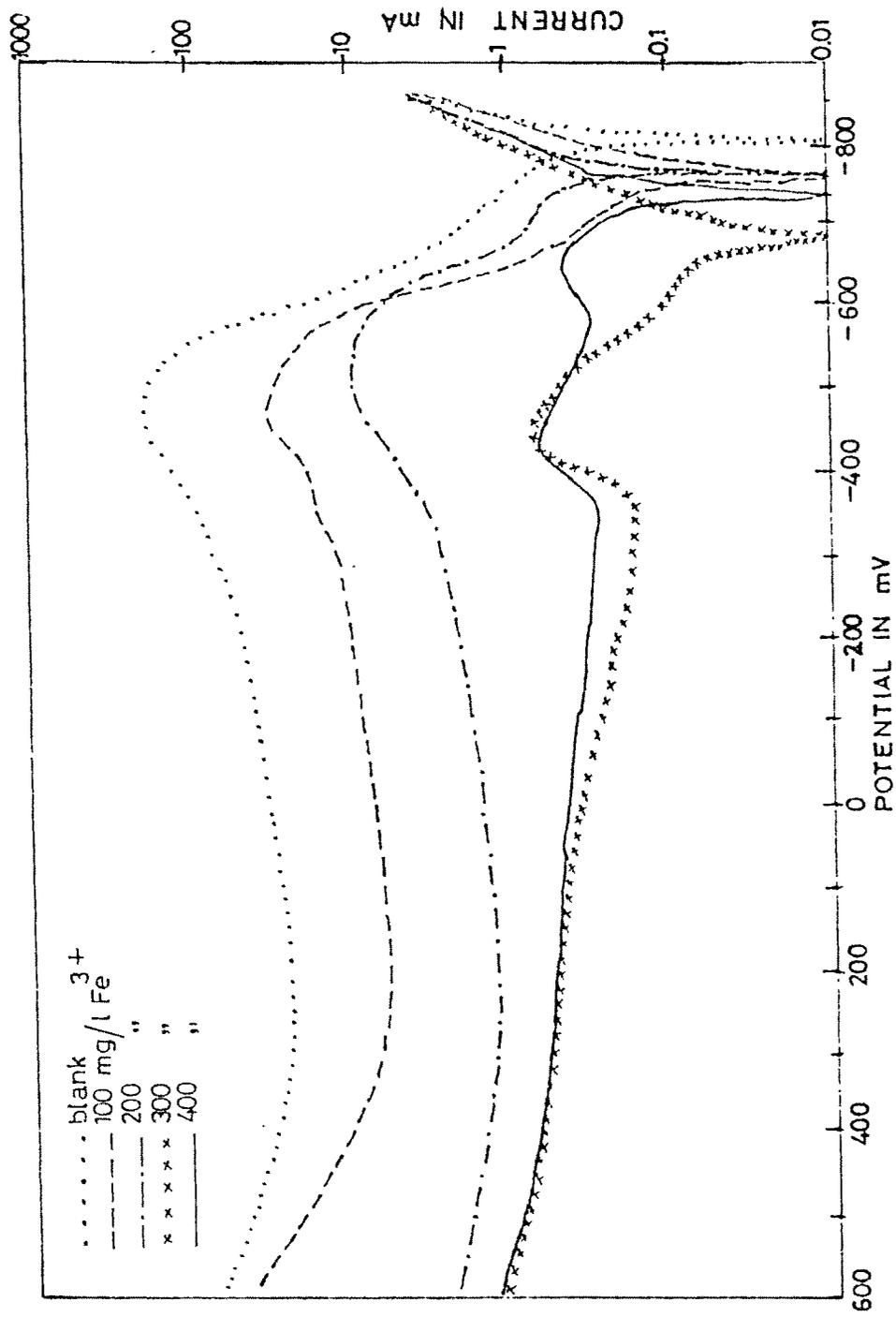


FIG.10 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.075% ANTIMONY TRIOXIDE

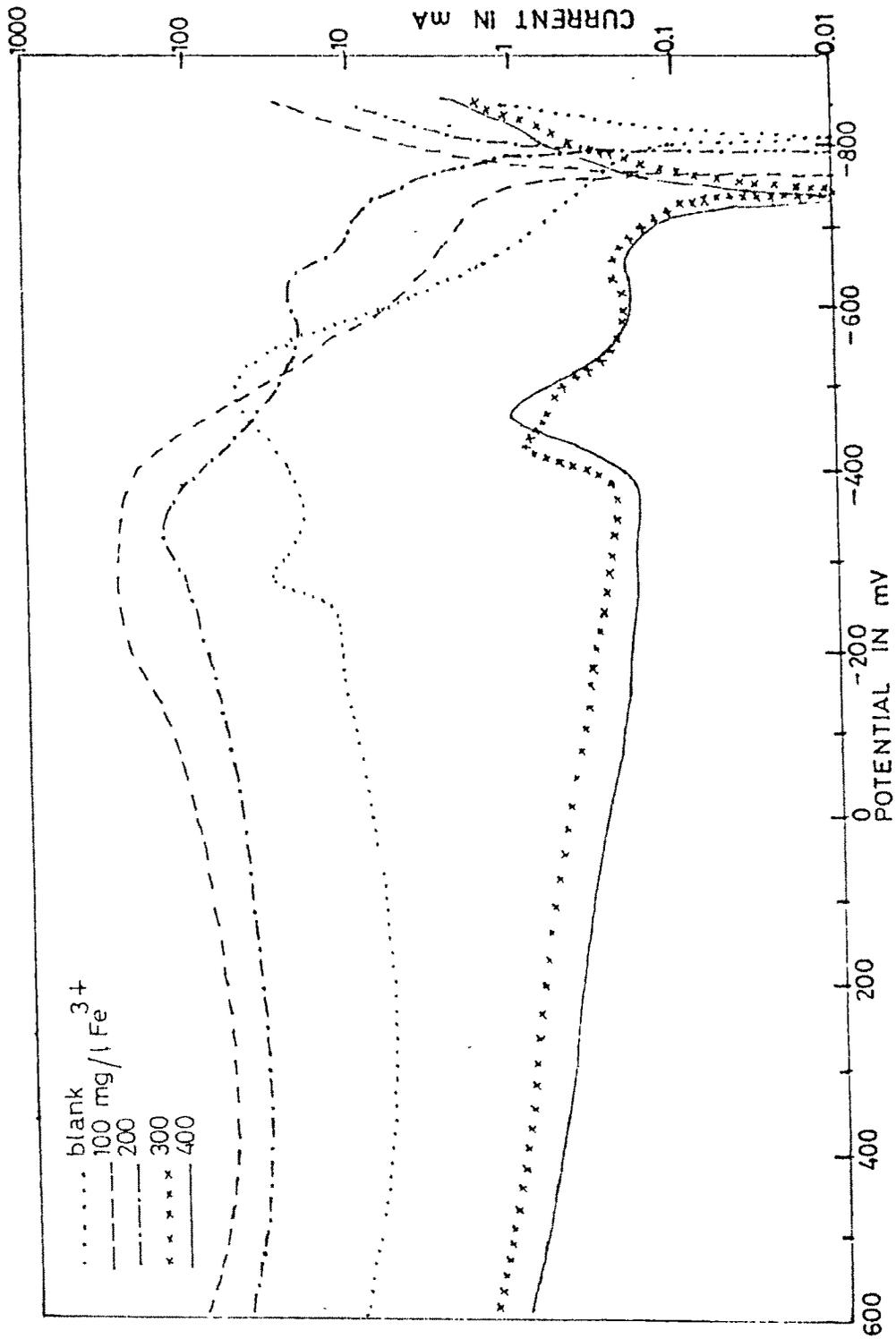


FIG.11 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.1% ANTIMONY  
 TRIOXIDE

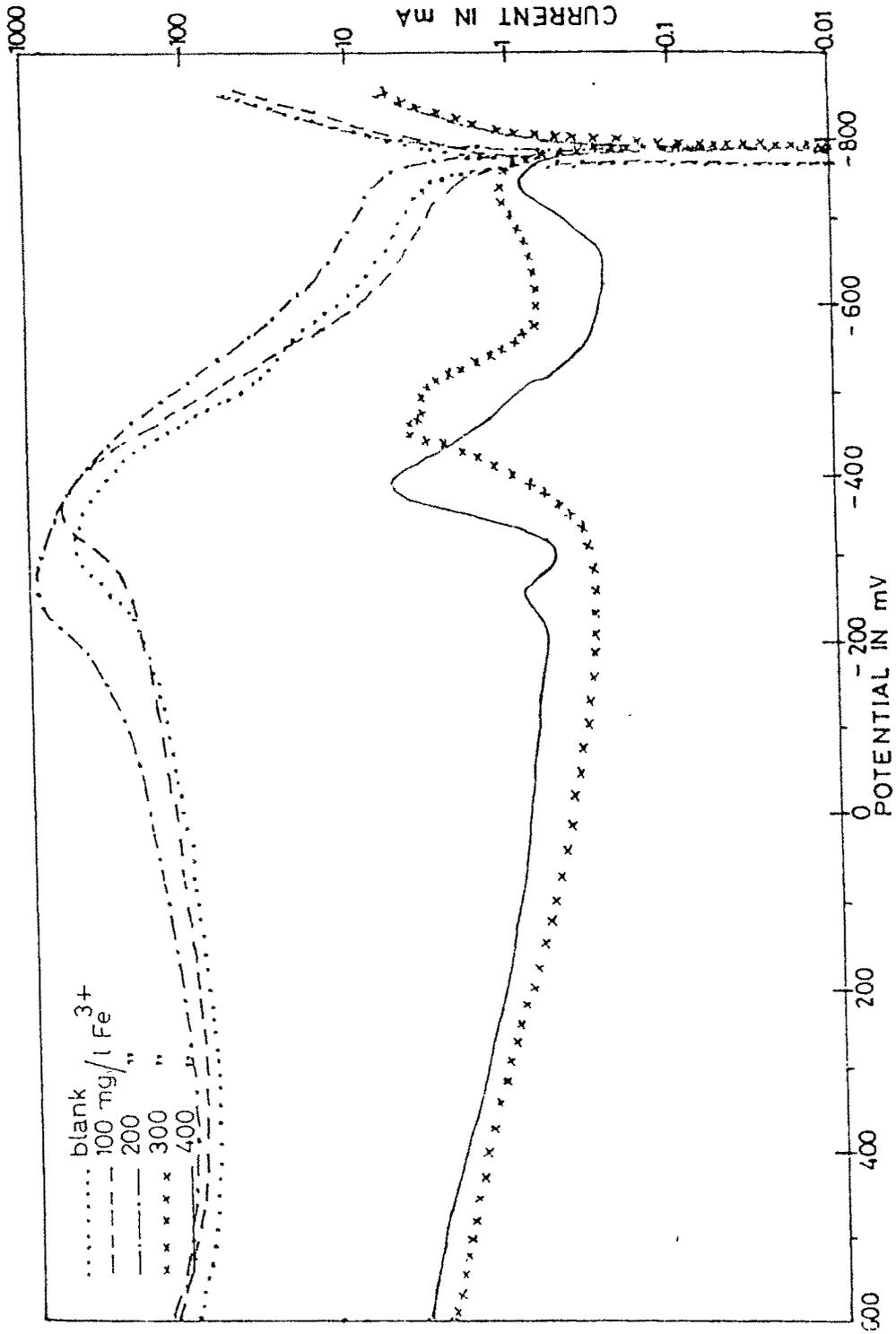


FIG.12 EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION SCANS  
 OF CS IN SYN. GVSL SOLUTION WITH 0.13% ANTIMONY TRIOXIDE

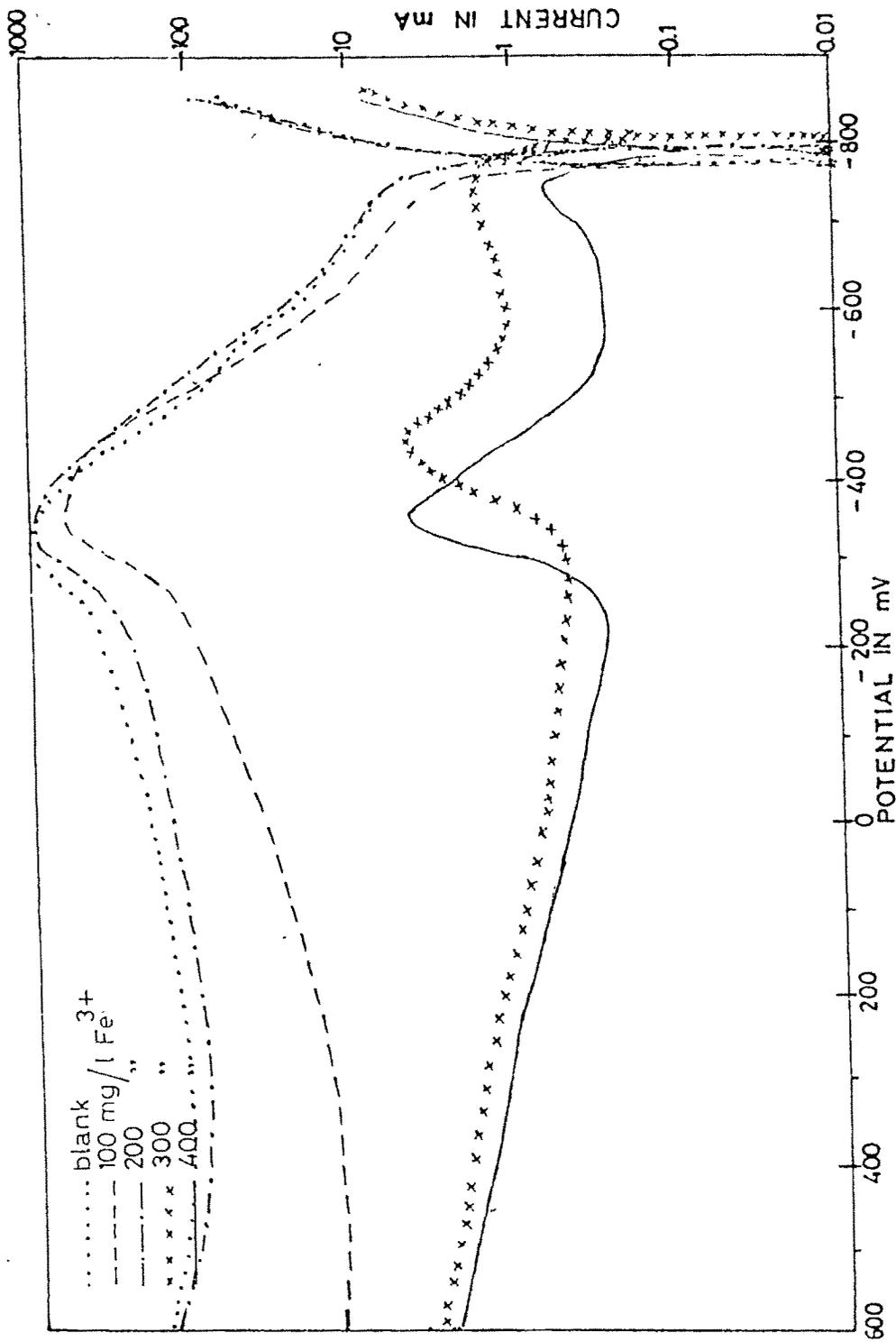


FIG. 13: EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.14% ANTIMONY  
 TRIOXIDE

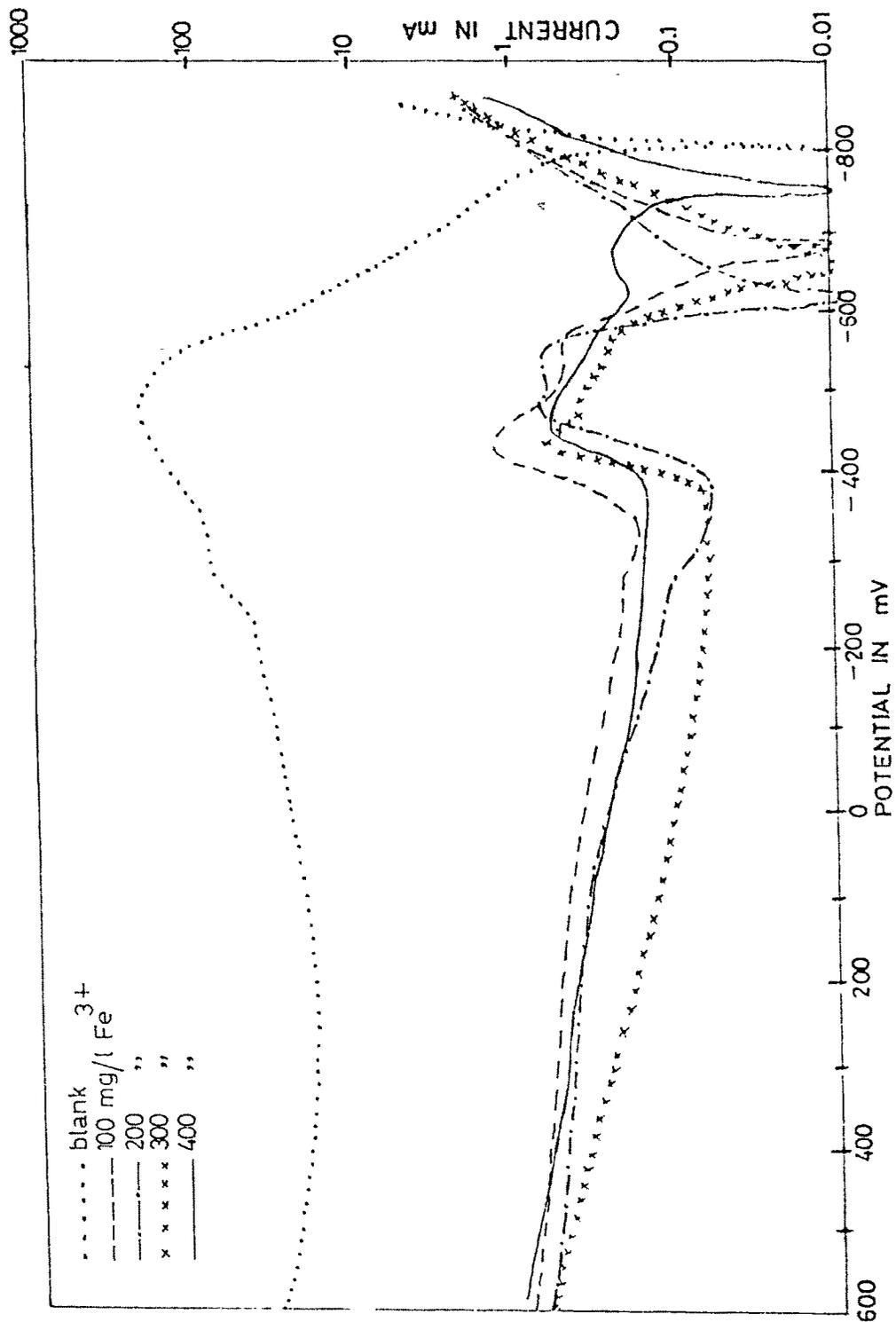
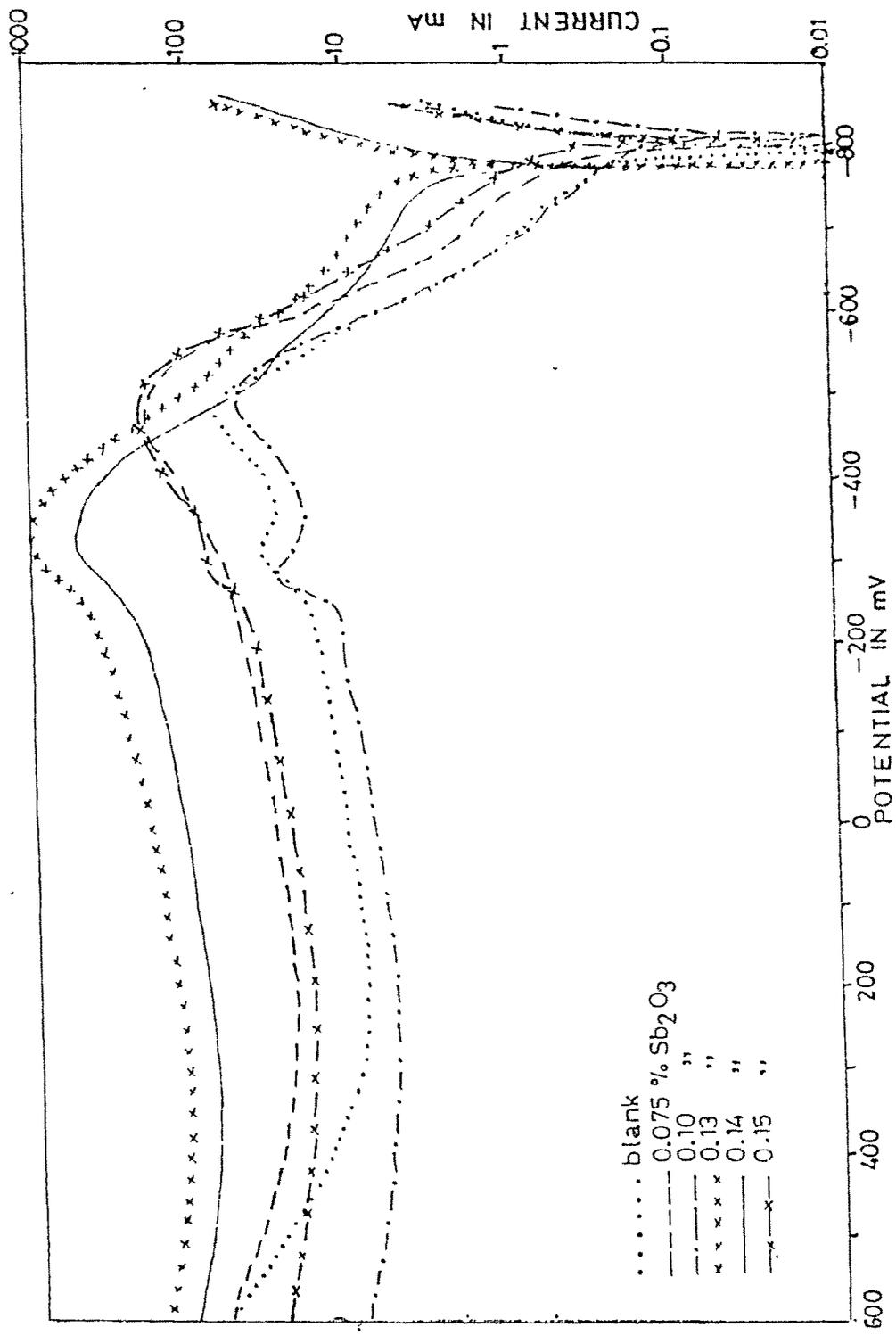


FIG.14 : EFFECT OF FERRIC IONS ON THE POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY  
 TRIOXIDE



**FIG. 15:** EFFECT OF ANTIMONY TRIOXIDE ON POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN 0.1N. GVSL SOLUTION WITHOUT FERRIC IONS

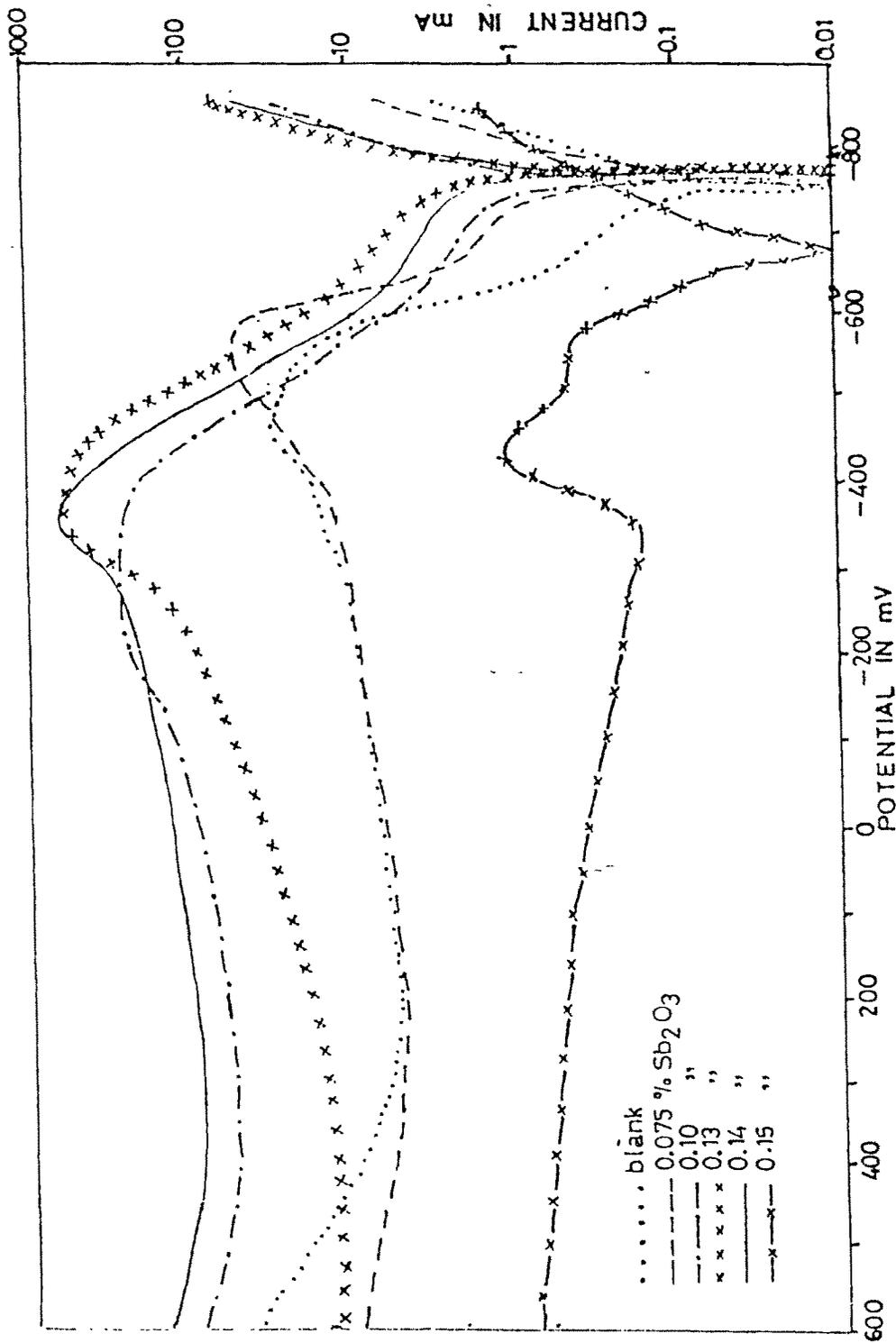


FIG.16: EFFECT OF ANTIMONY TRIOXIDE ON POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.01% FERRIC IONS

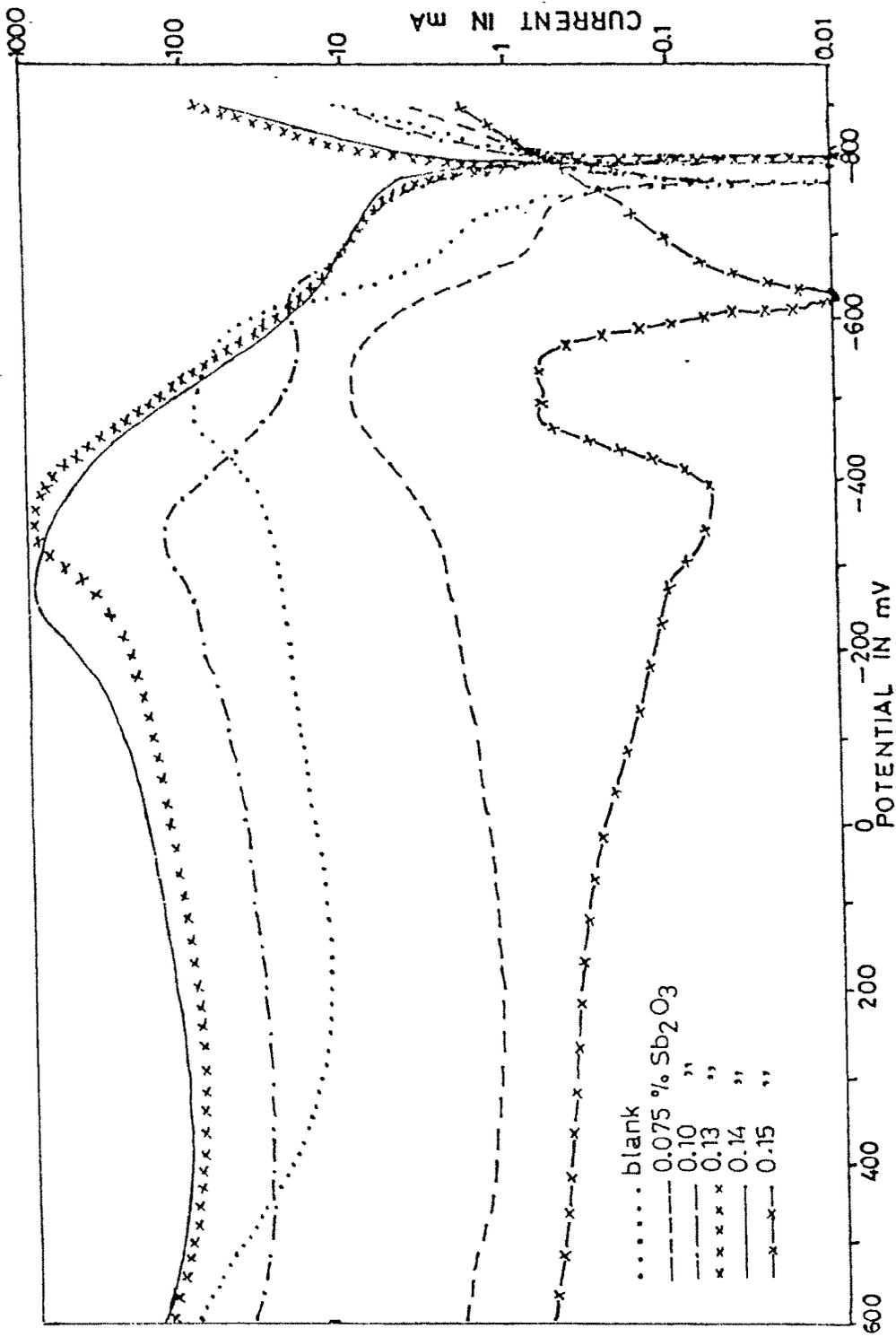


FIG.17: EFFECT OF ANTIMONY TRIOXIDE ON POTENTIODYNAMIC POLARIZATION SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.02% FERRIC IONS

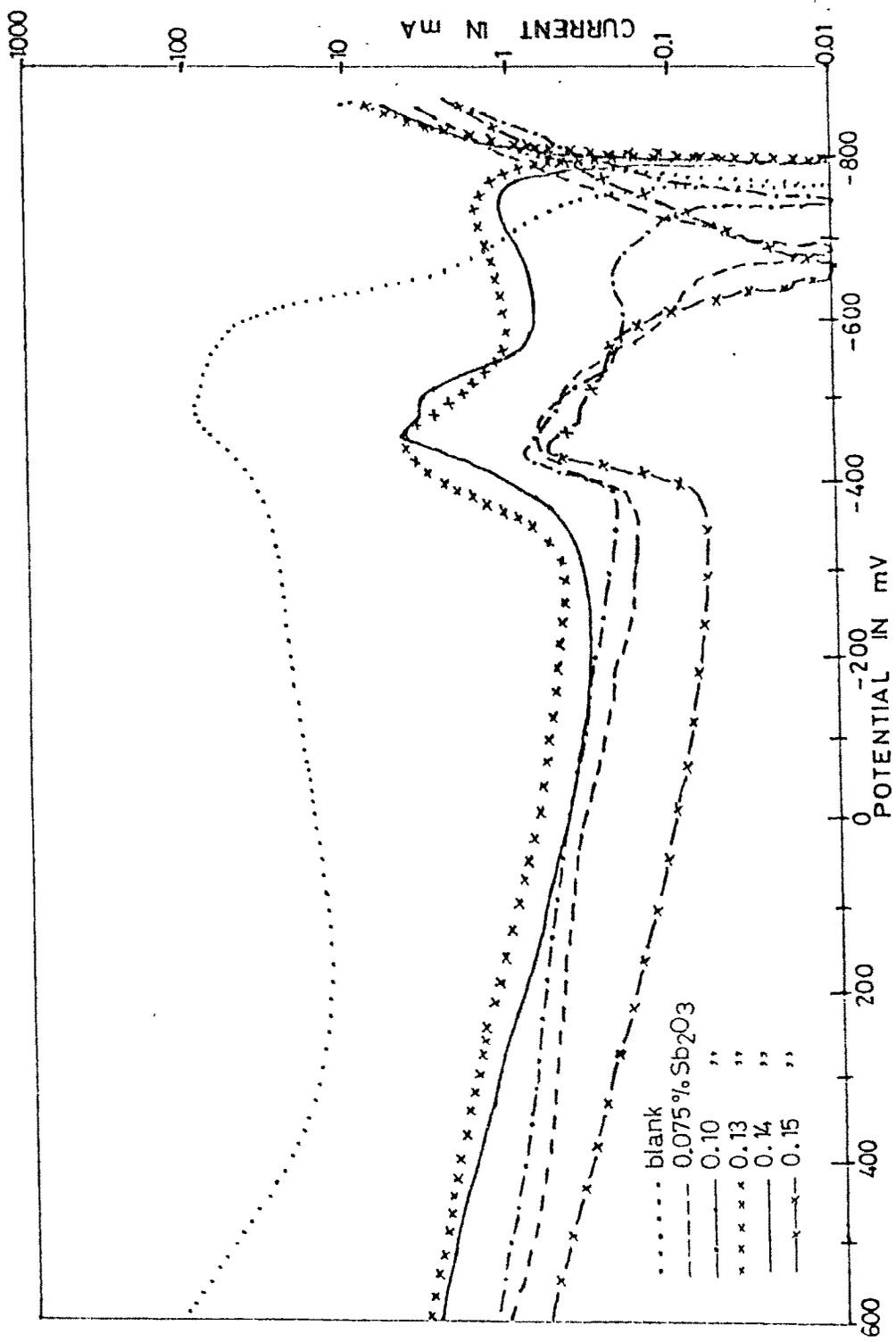


FIG. 18 : EFFECT OF ANTIMONY TRIOXIDE ON POTENTIODYNAMIC POLARIZATION  
SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.03% FERRIC IONS

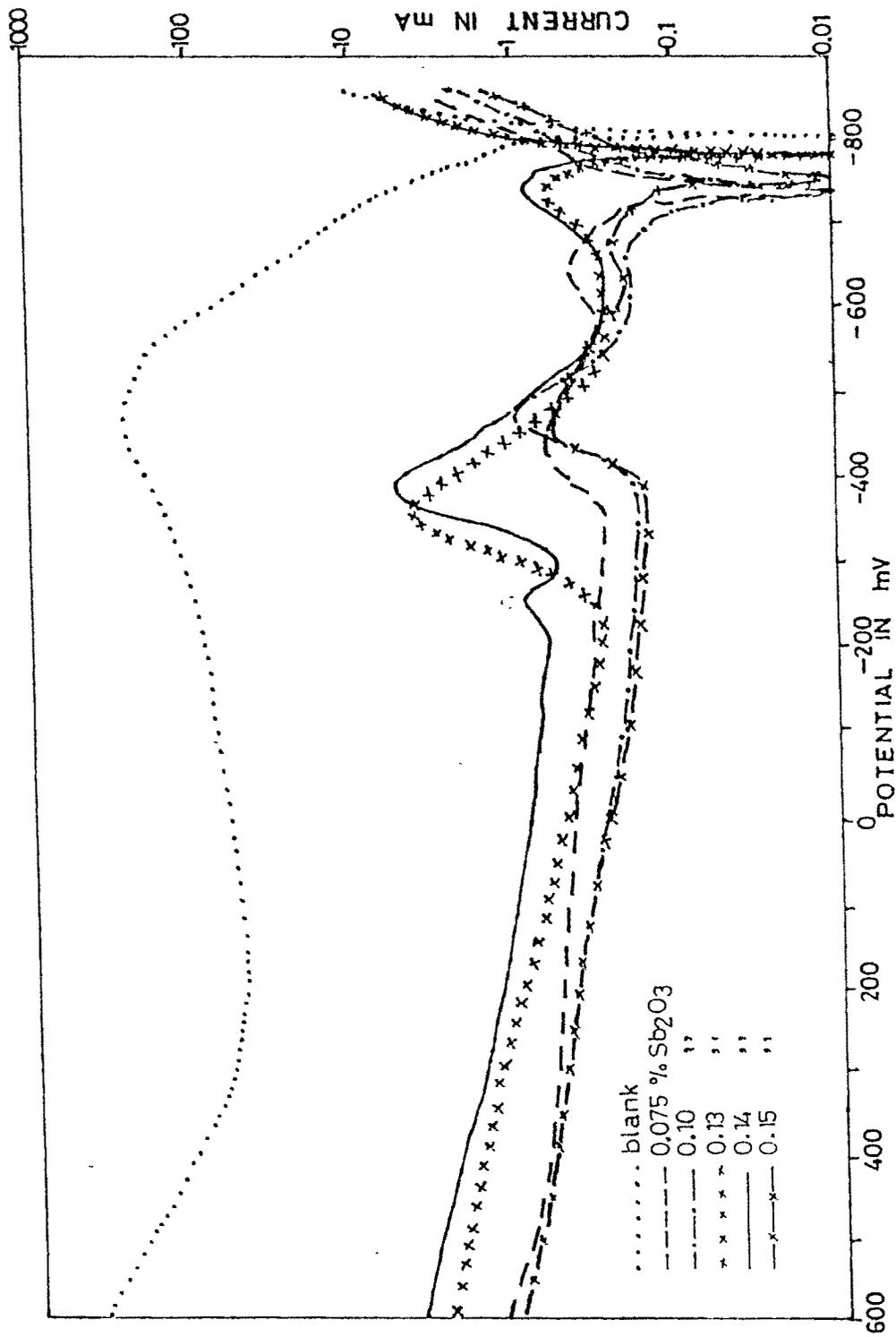
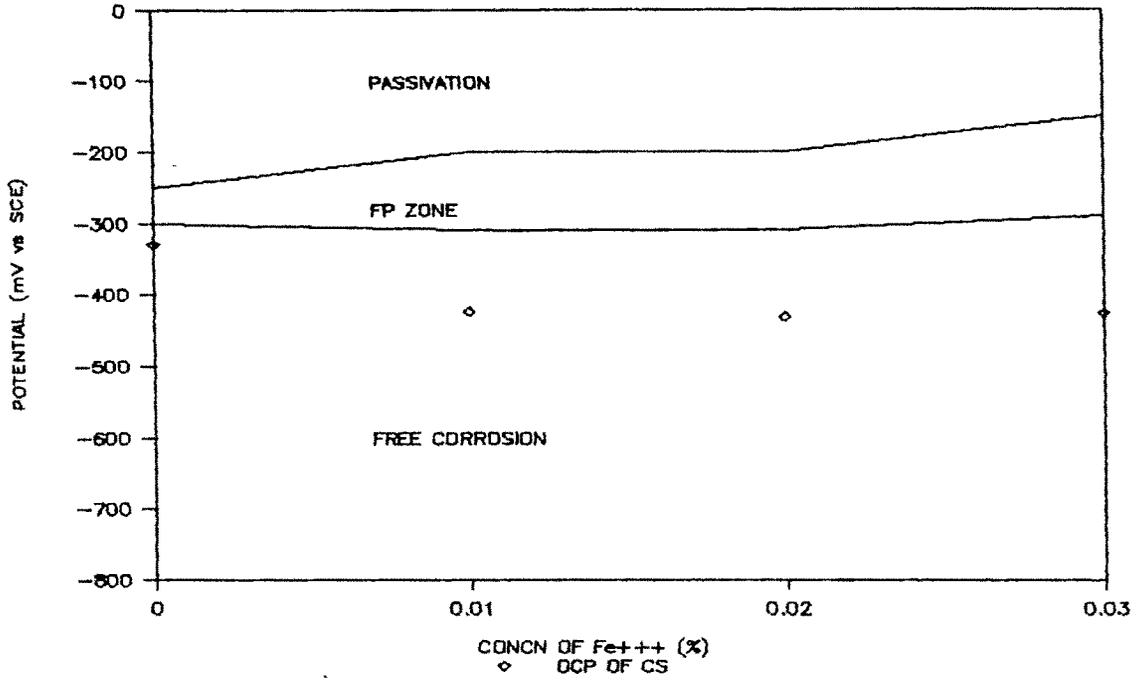


FIG.19 : EFFECT OF ANTIMONY TRIOXIDE ON POTENTIODYNAMIC POLARIZATION  
 SCANS OF CS IN SYN. GVSL SOLUTION WITH 0.04% FERRIC IONS

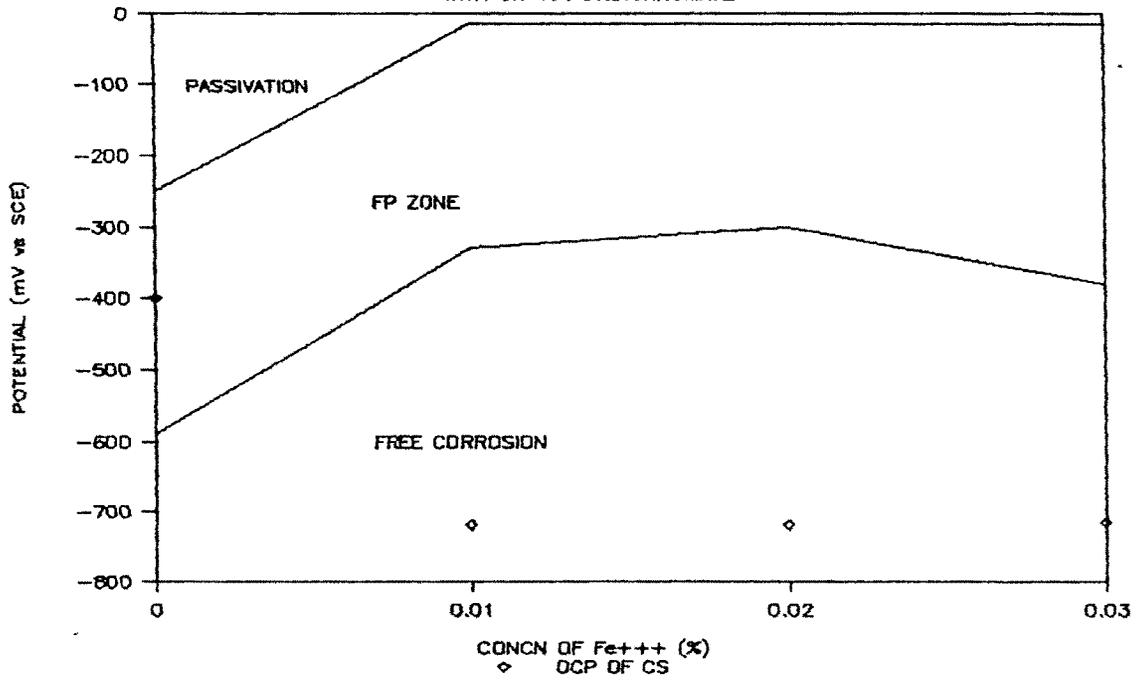
**FIG20: OCP OF CS IN GV SOLUTION**

WITH 0.1 % Vanadium Pentoxide



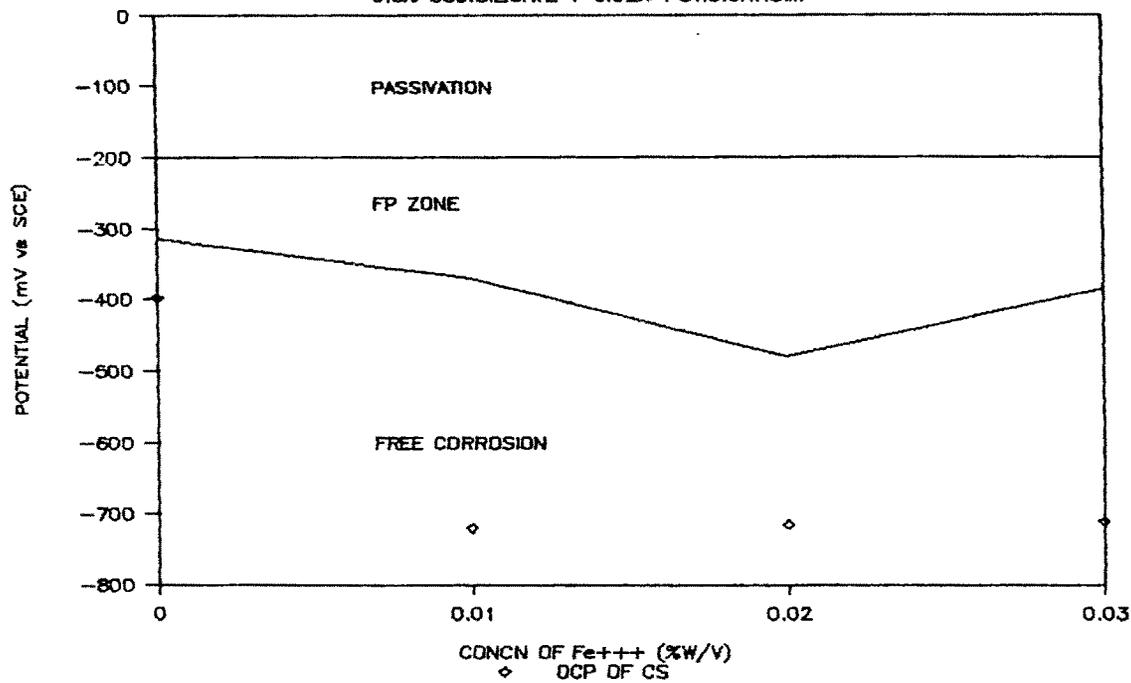
**FIG21: OCP OF CS IN GV SOLUTION**

WITH 0.7 % POT.DICHROMATE



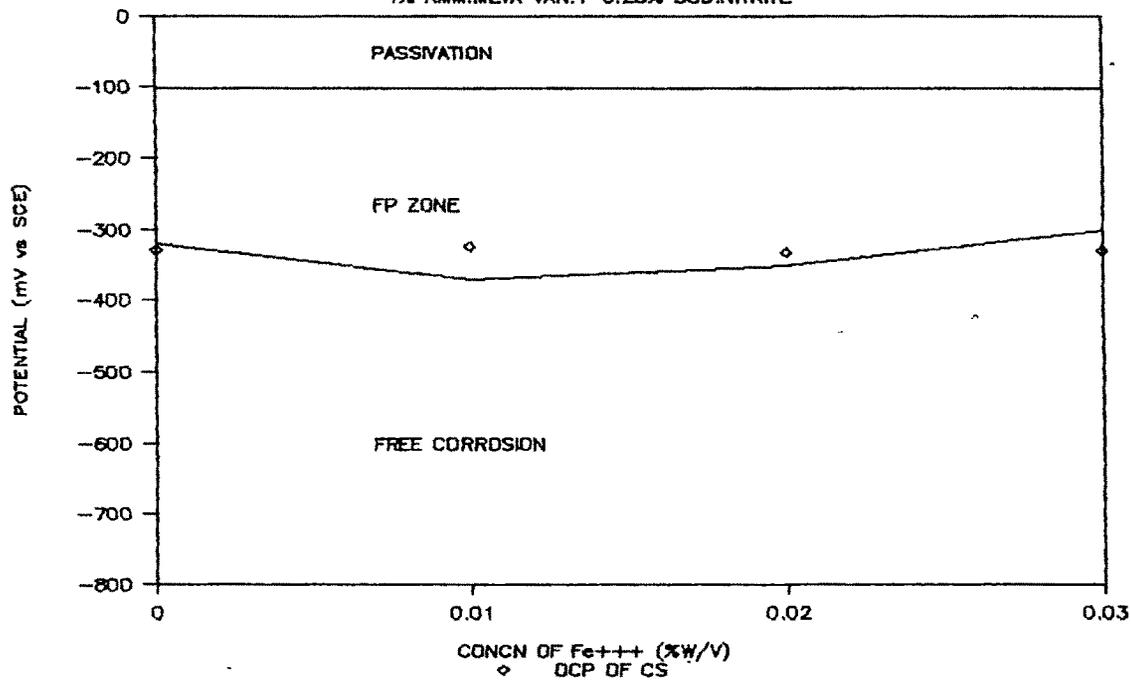
**FIG22:OCP OF CS IN GV SOLUTION WITH**

0.6% SOD.SILICATE + 0.02% POT.DICHROM.



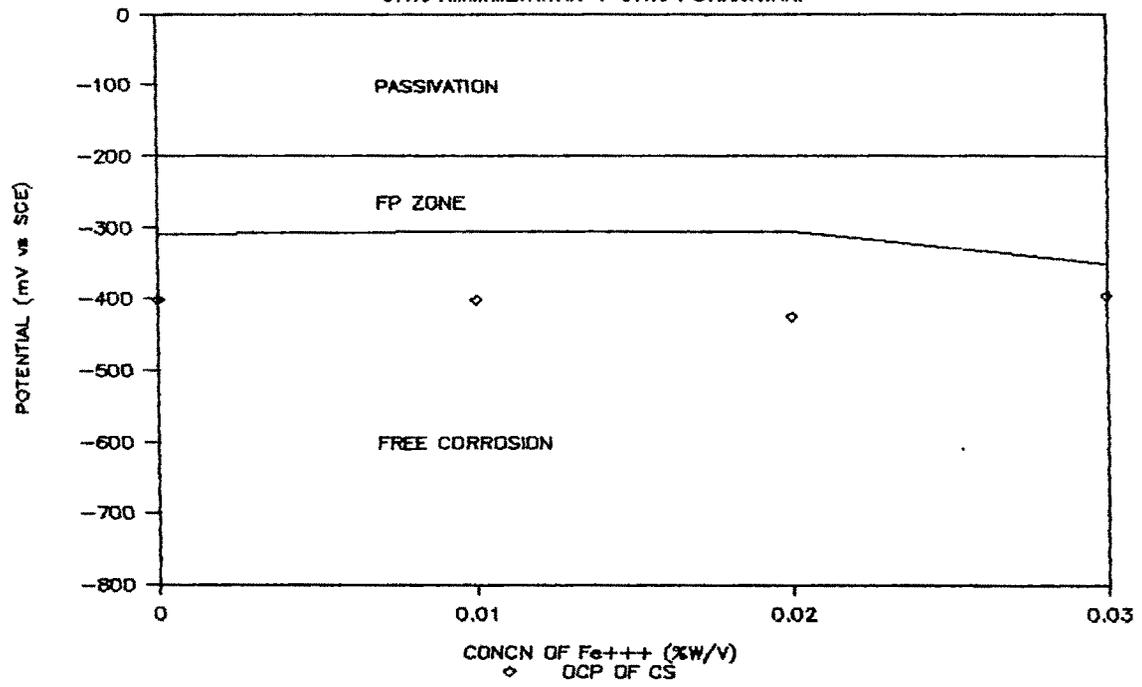
**FIG23:OCP OF CS IN GV SOLUTION WITH**

1% AMM.META VAN.+ 0.25% SOD.NITRITE



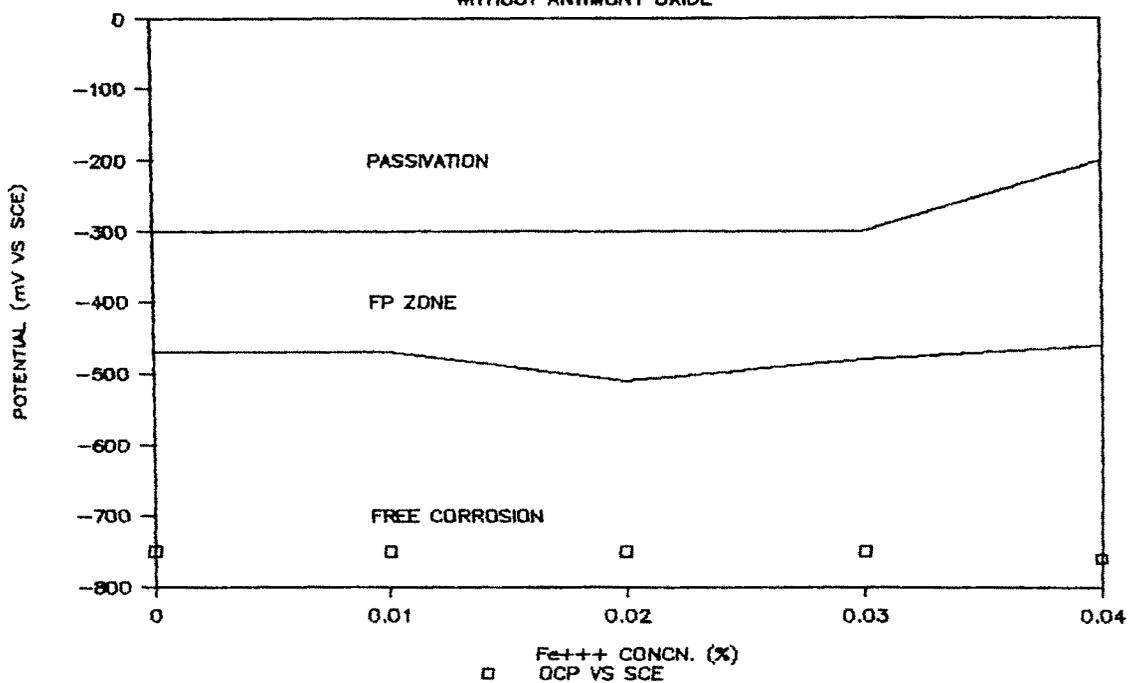
**FIG 24: OCP OF CS IN GV SOLUTION WITH**

0.1% AMM. META.VAN + 0.1% POT. ANT. TAR.



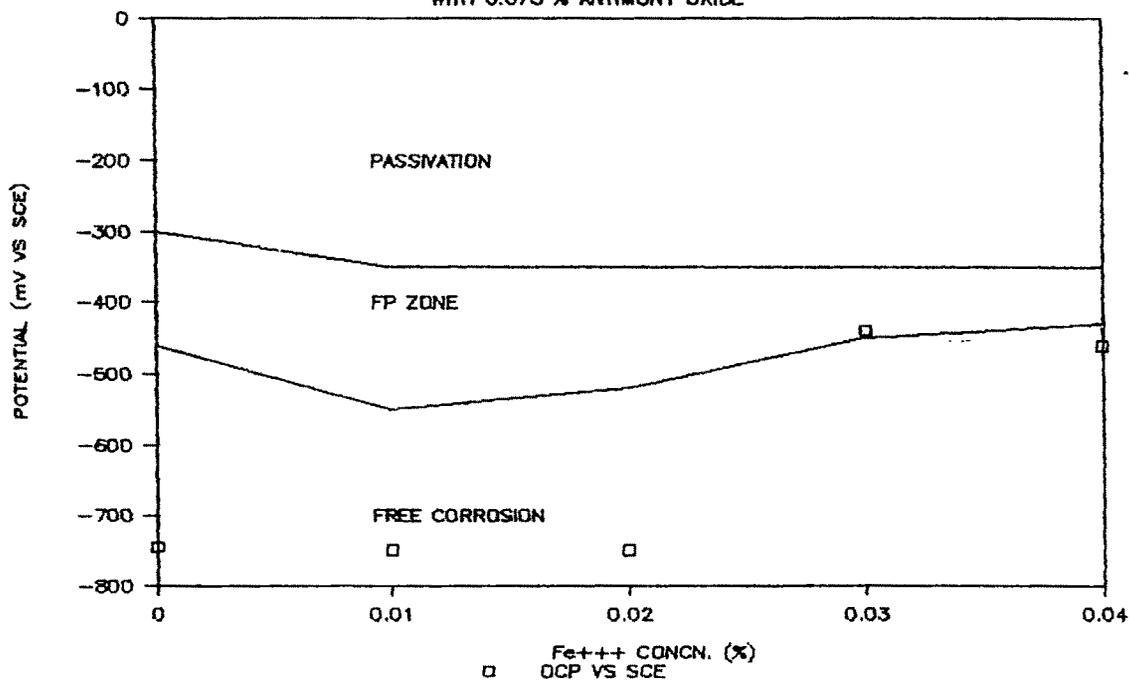
### FIG25: OCP OF CS IN GV SOLUTION

WITHOUT ANTIMONY OXIDE



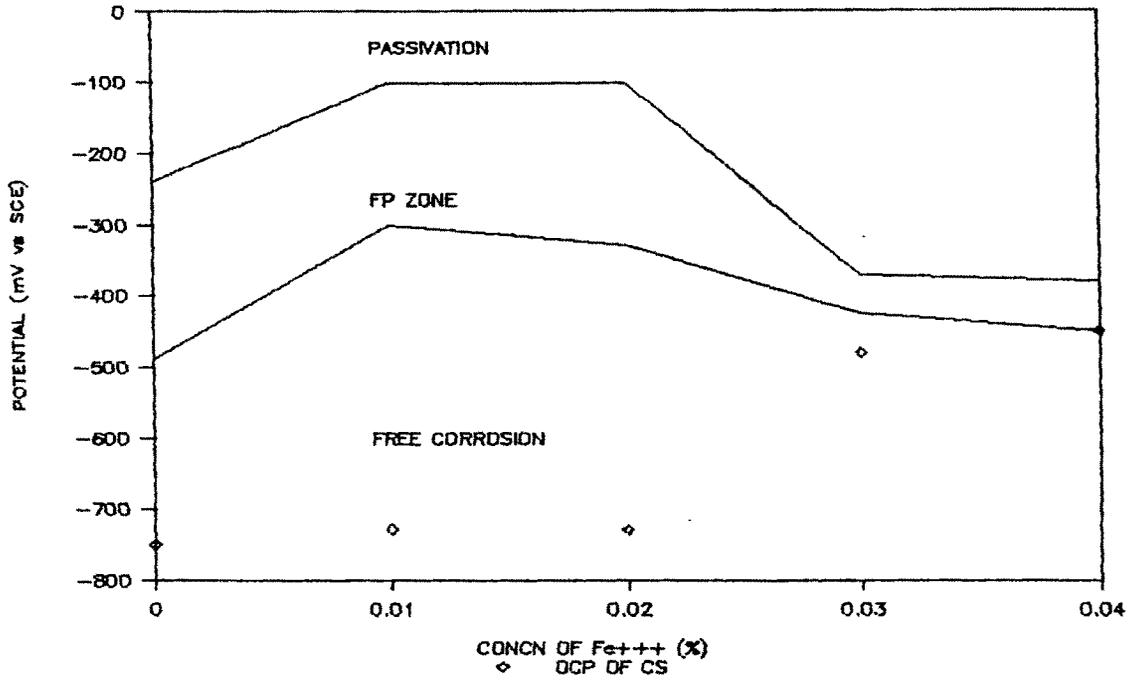
### FIG26: OCP OF CS IN GV SOLUTION

WITH 0.075 % ANTIMONY OXIDE



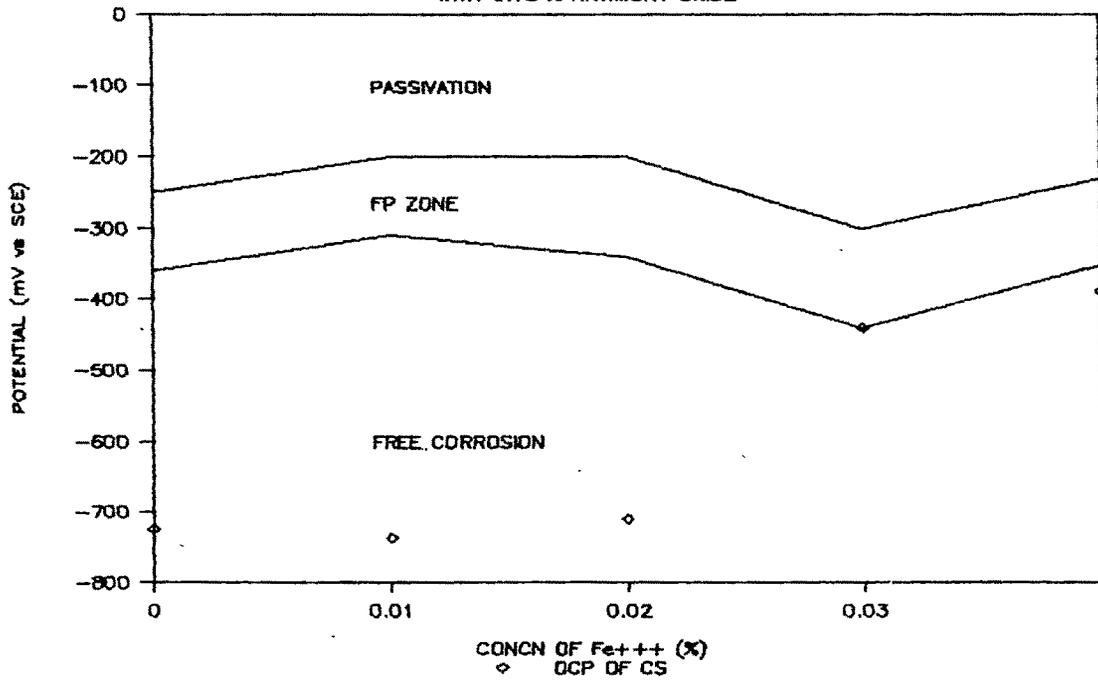
**FIG27: OCP OF CS IN GV SOLUTION**

WITH 0.1 % ANTIMONY OXIDE



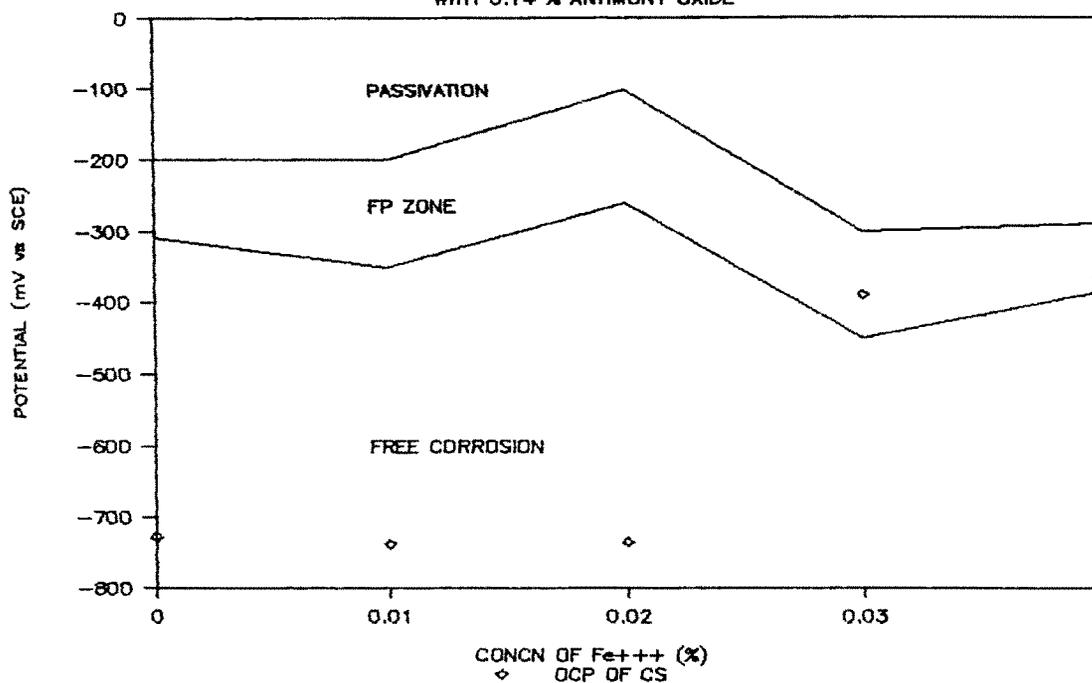
**FIG28: OCP OF CS IN GV SOLUTION**

WITH 0.13 % ANTIMONY OXIDE



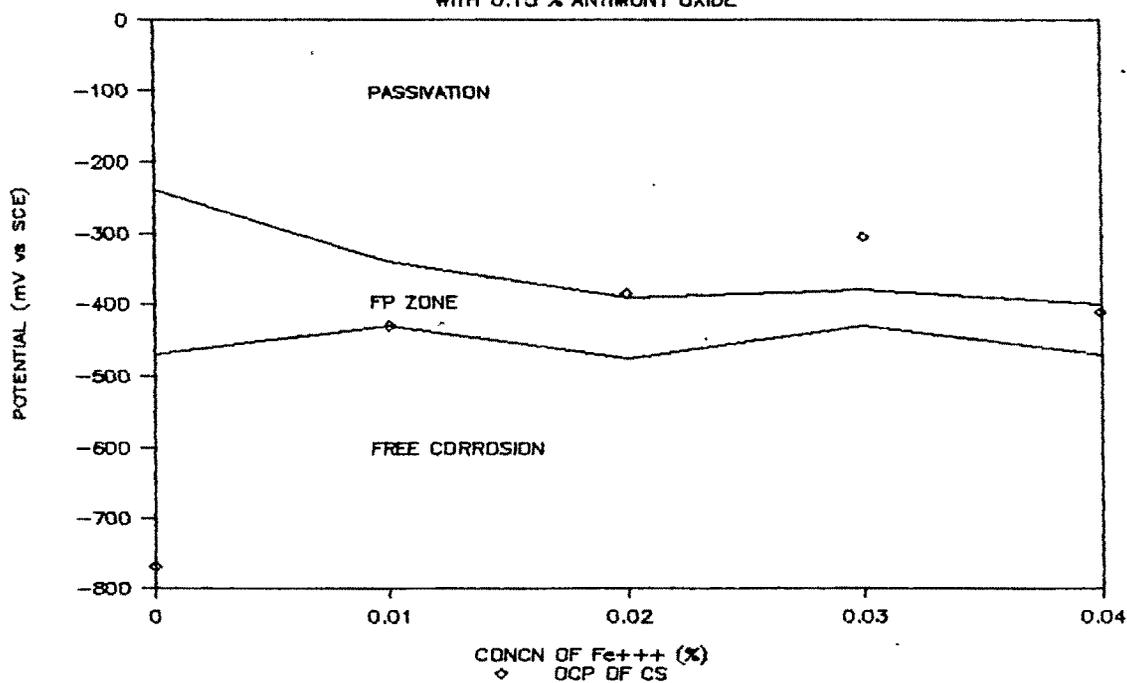
**FIG29:OCP OF CS IN GV SOLUTION**

WITH 0.14 % ANTIMONY OXIDE



**FIG30:OCP OF CS IN GV SOLUTION**

WITH 0.15 % ANTIMONY OXIDE



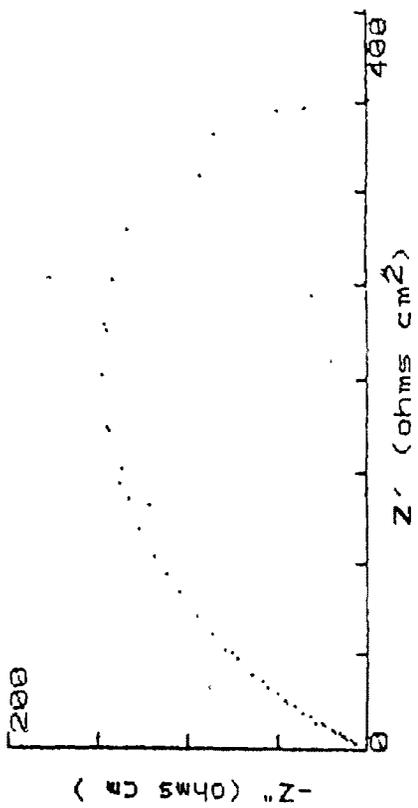
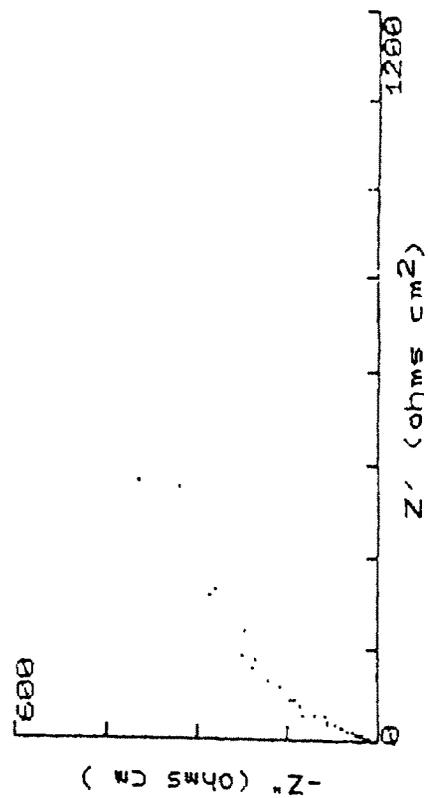
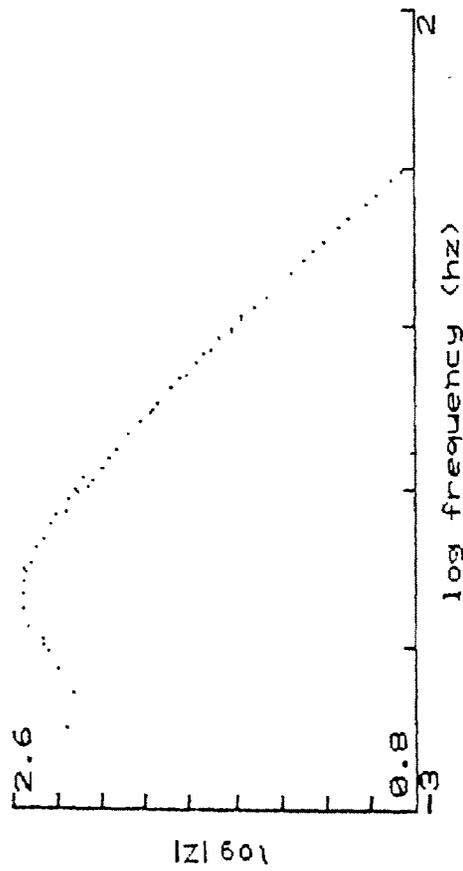
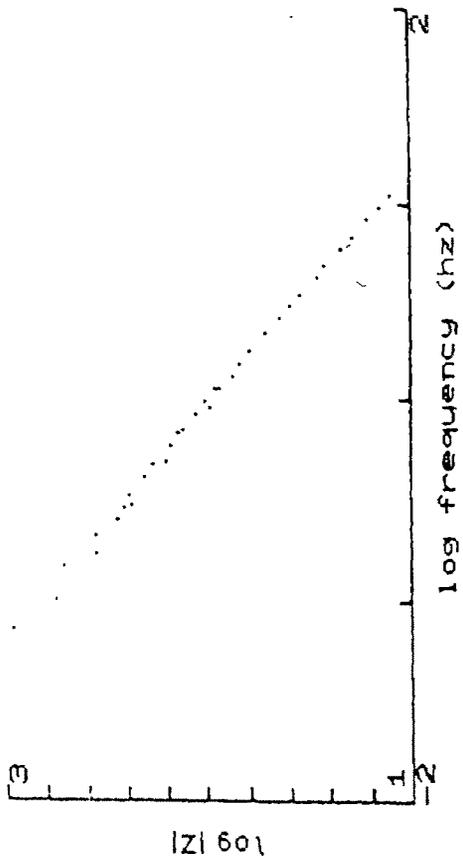


FIG.31 : BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITHOUT INHIBITORS

b) With aeration

a) Without aeration

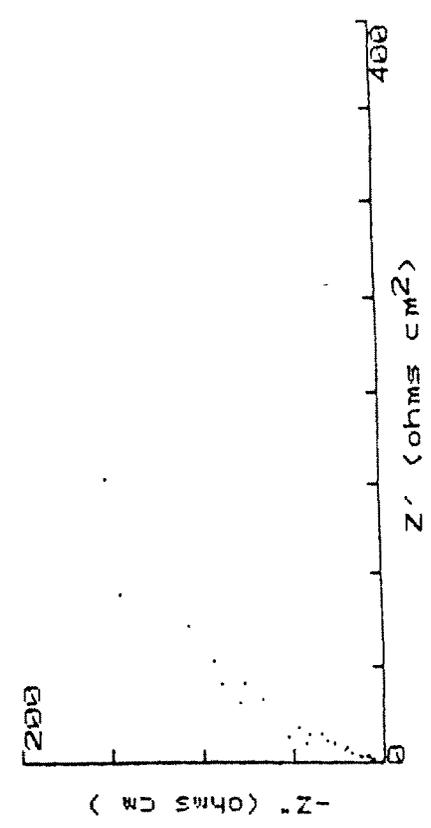
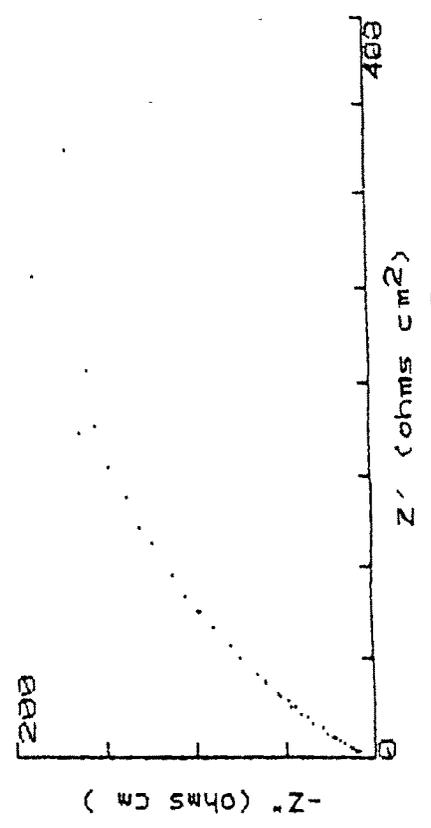
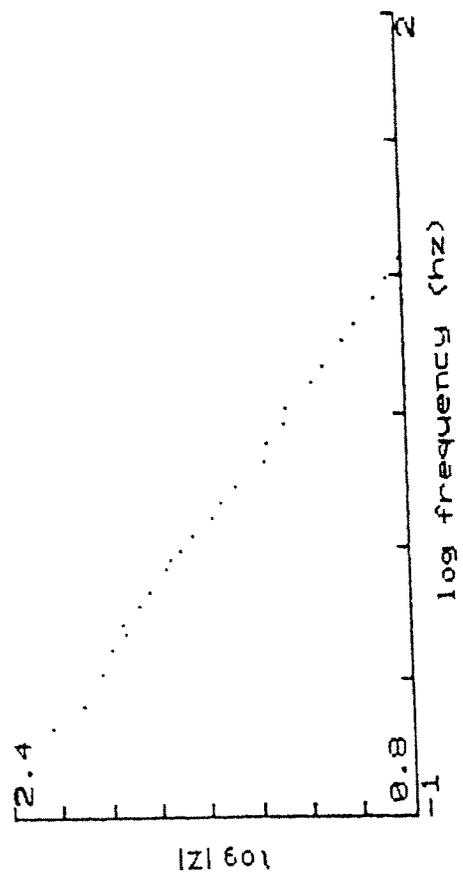
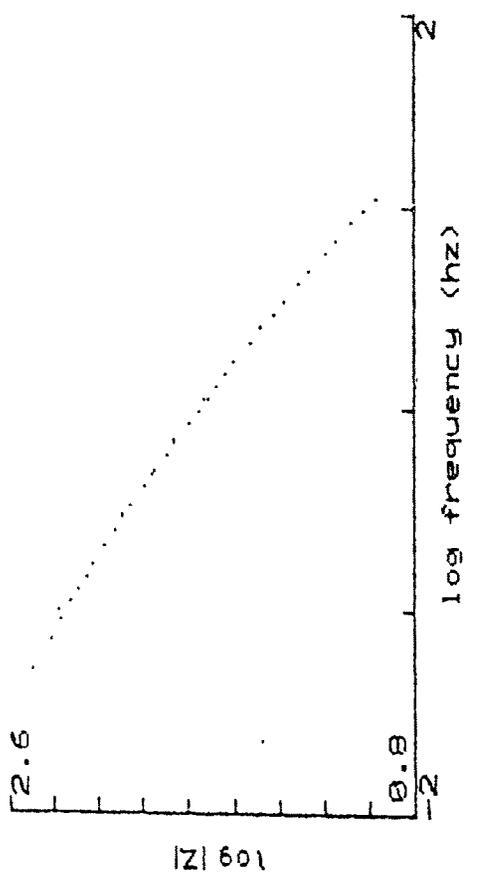


FIG.32: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY TRIOXIDE

b) With aeration

a) Without aeration

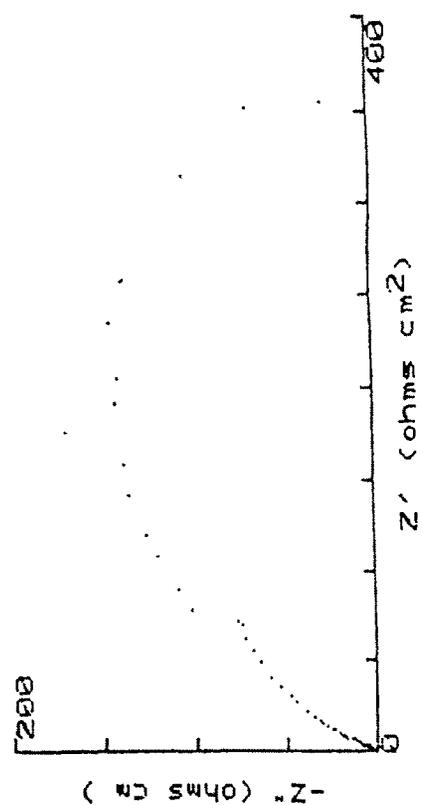
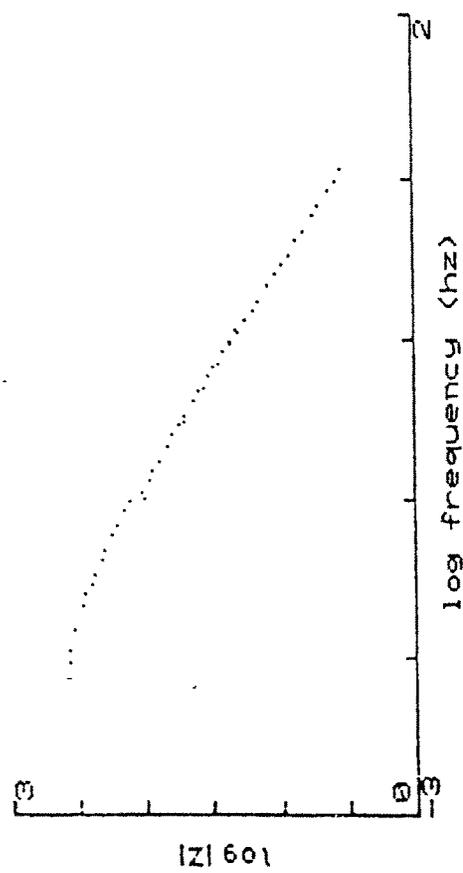
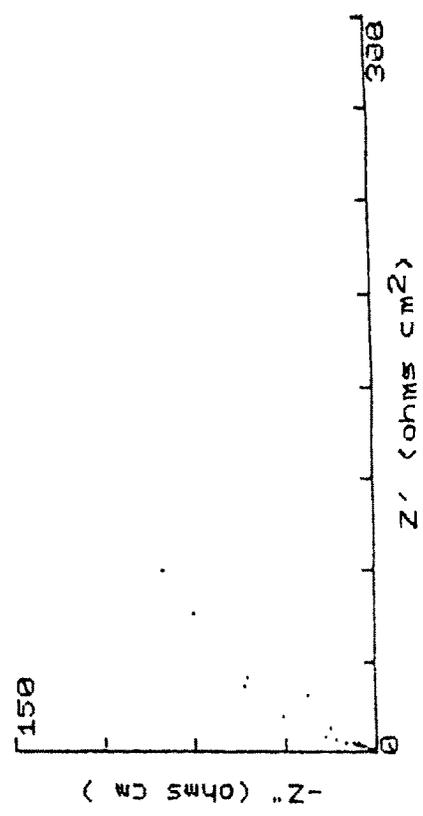
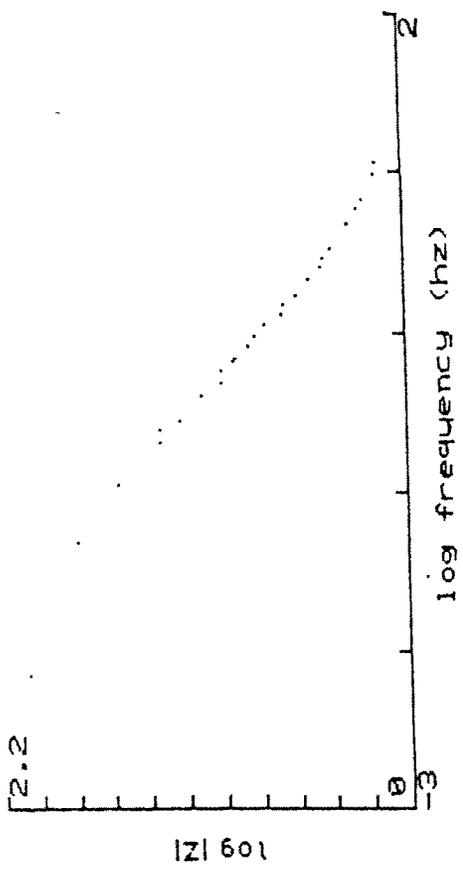


FIG.33: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.01% FERRIC IONS  
 a) Without aeration  
 b) With aeration

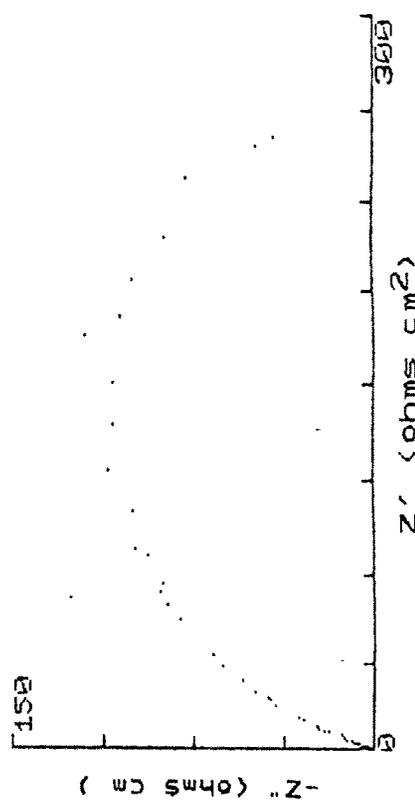
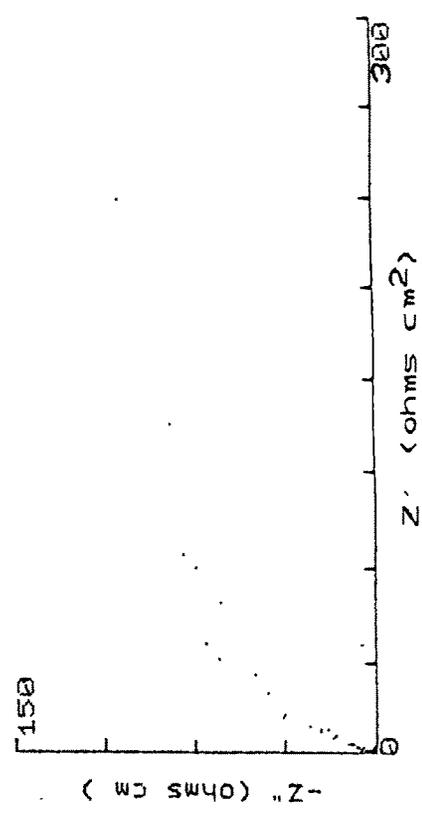
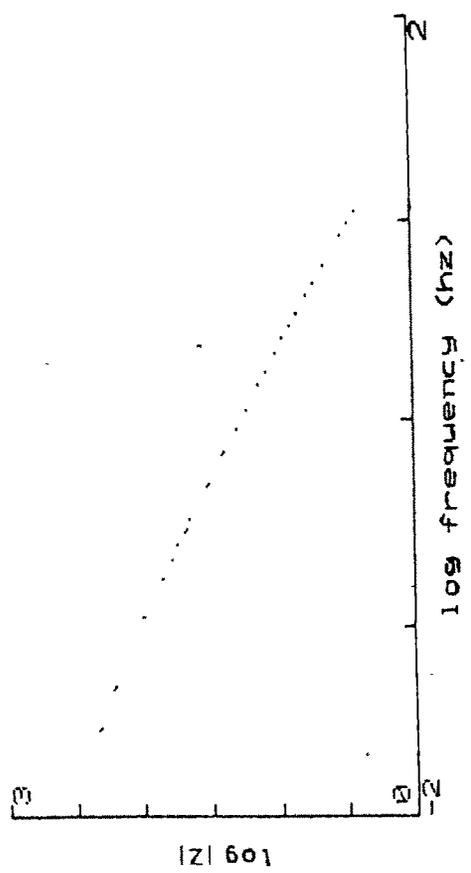
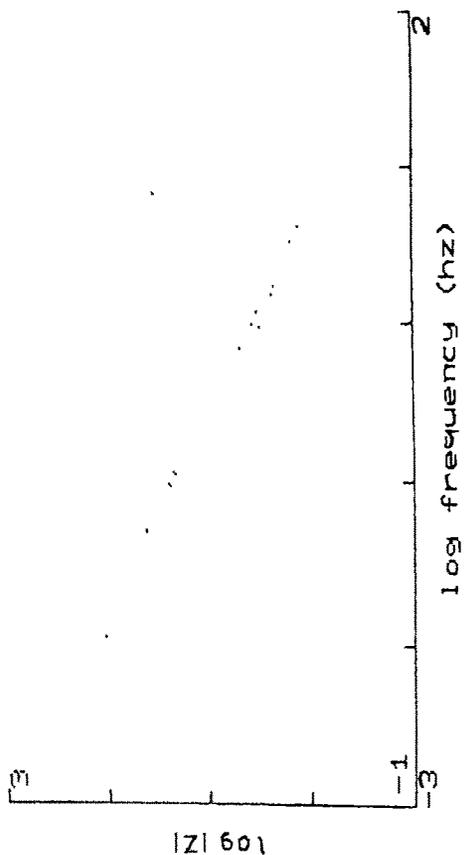


FIG-34: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY OXIDE AND 0.01% FERRIC IONS

a) Without aeration

b) With aeration

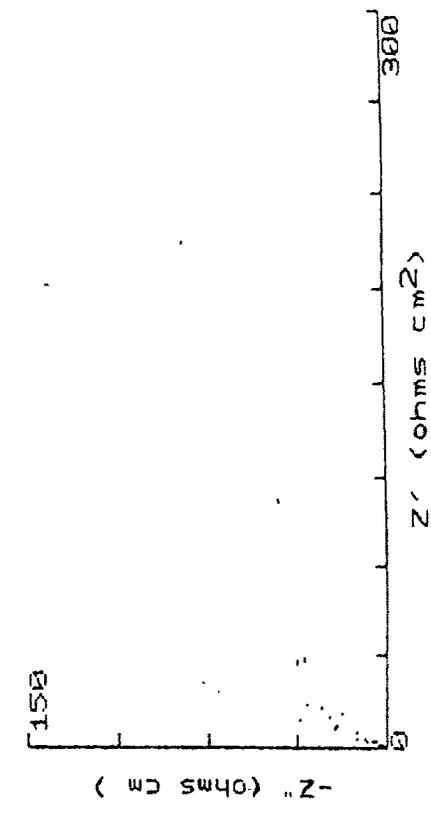
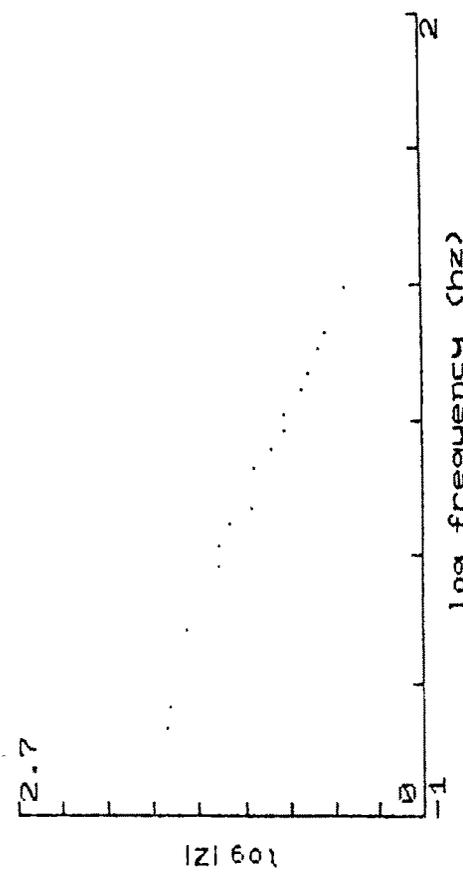
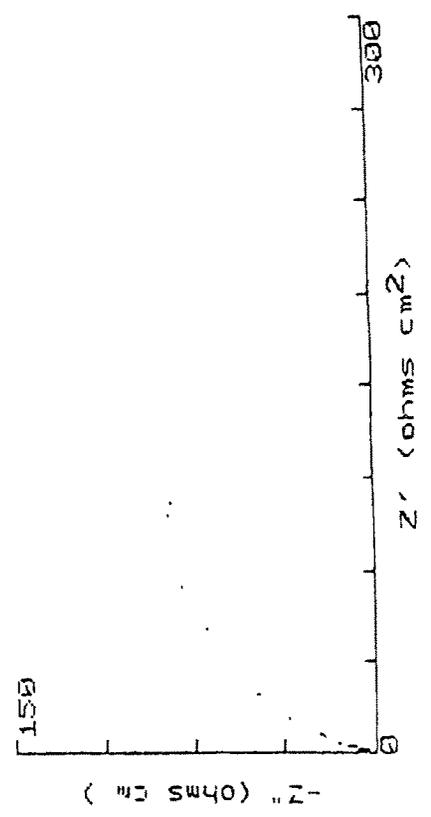
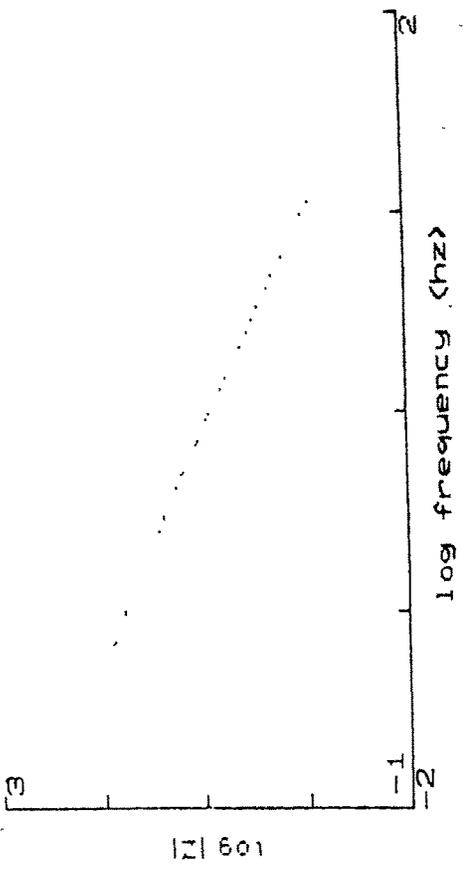


FIG.35: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.02% FERRIC IONS  
 a) Without aeration  
 b) With aeration

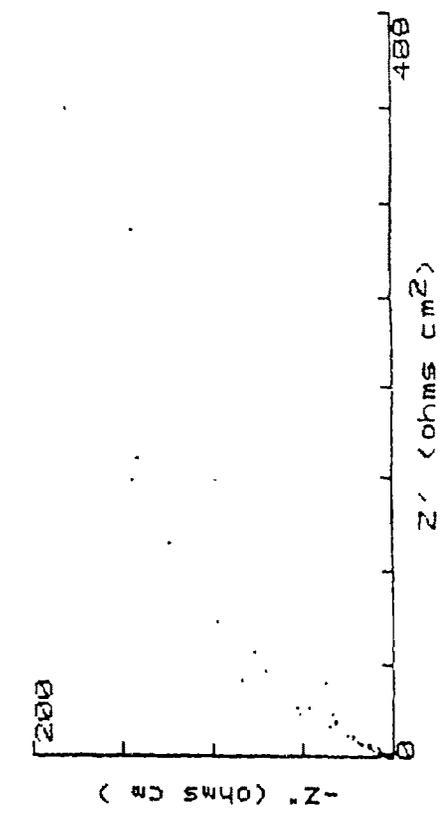
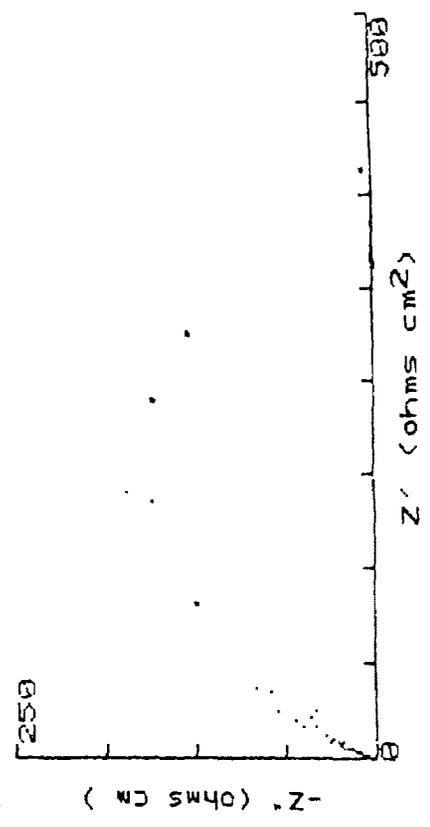
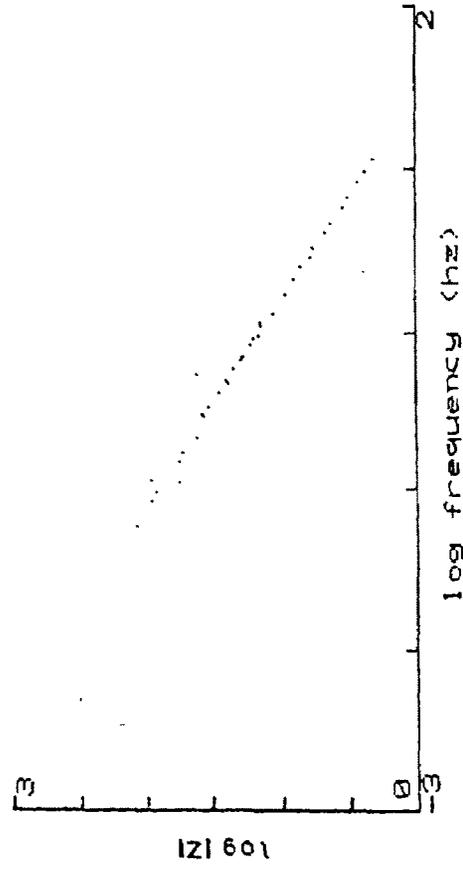
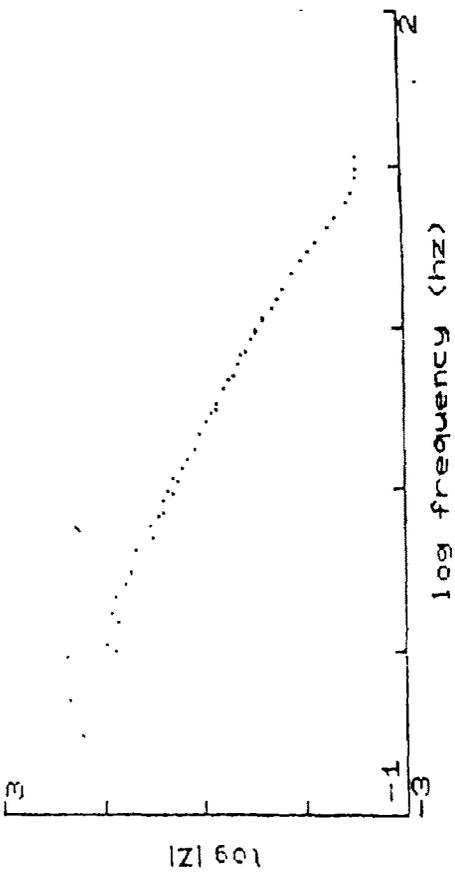


FIG. 36: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY OXIDE AND 0.02% FERRIC IONS

a) Without aeration

b) With aeration

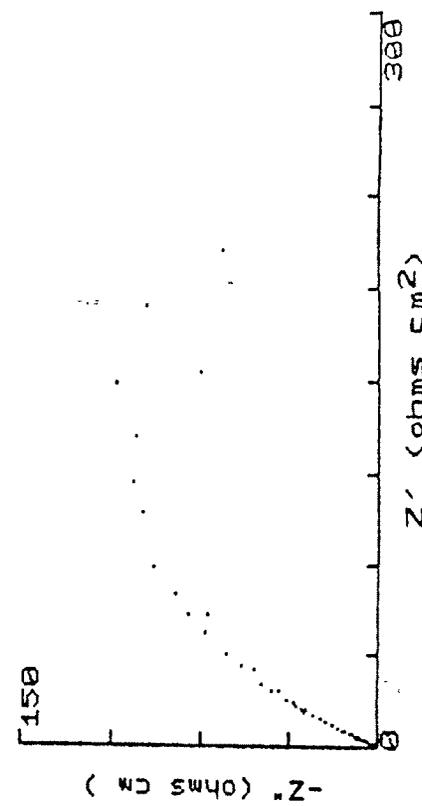
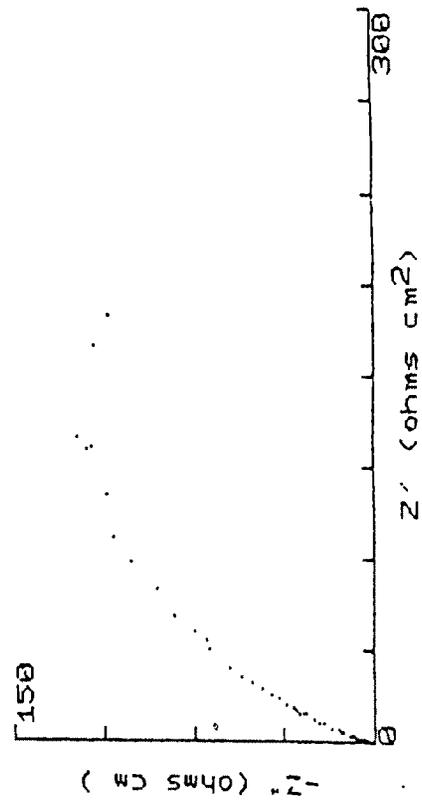
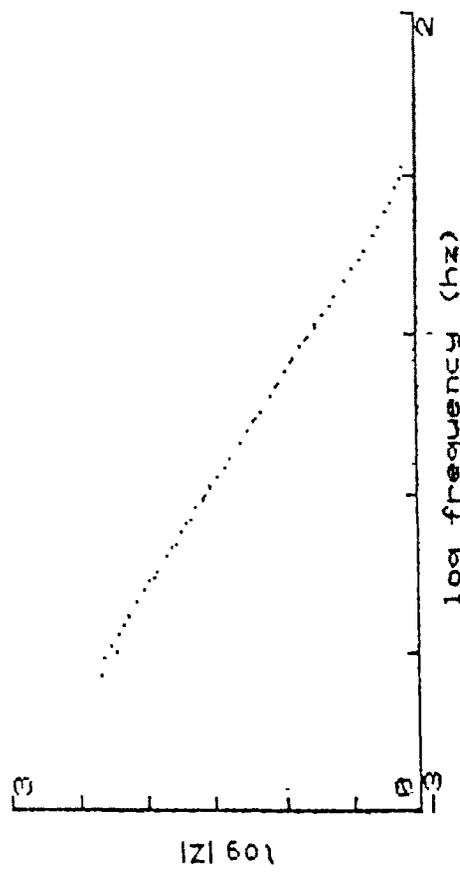
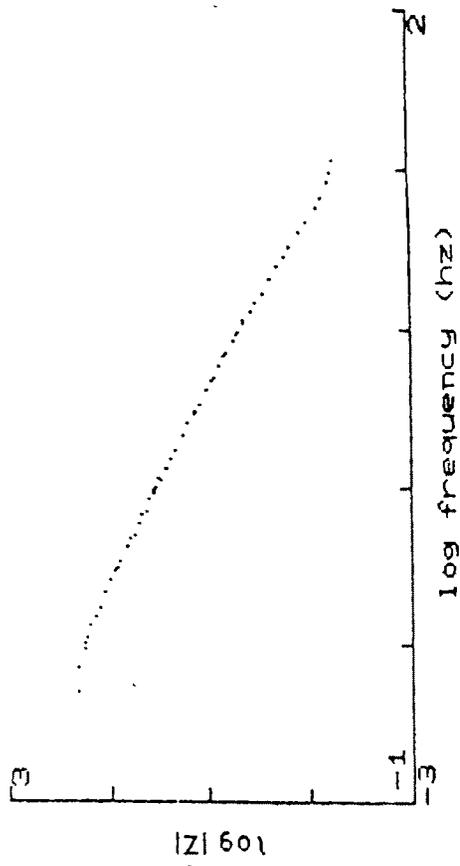


FIG.37: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.03% FERRIC IONS

b) With aeration

a) Without aeration

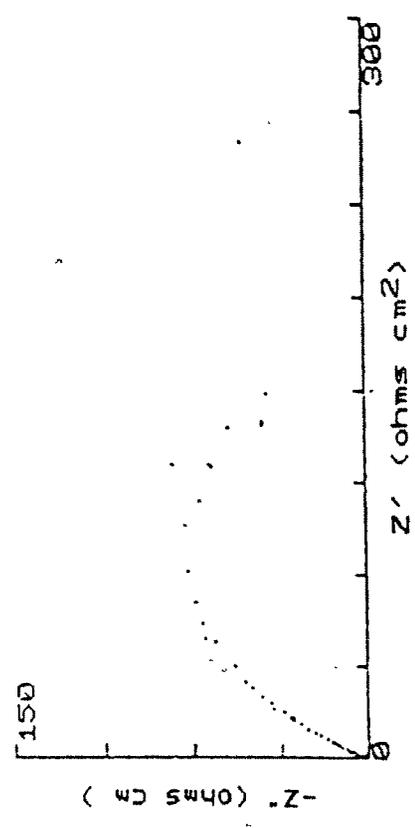
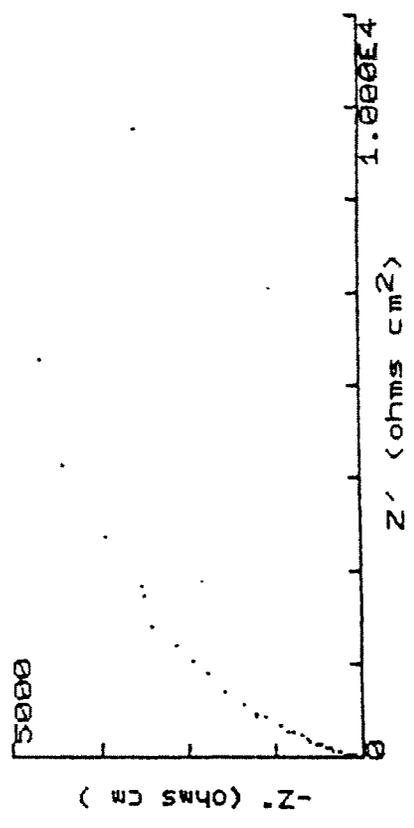
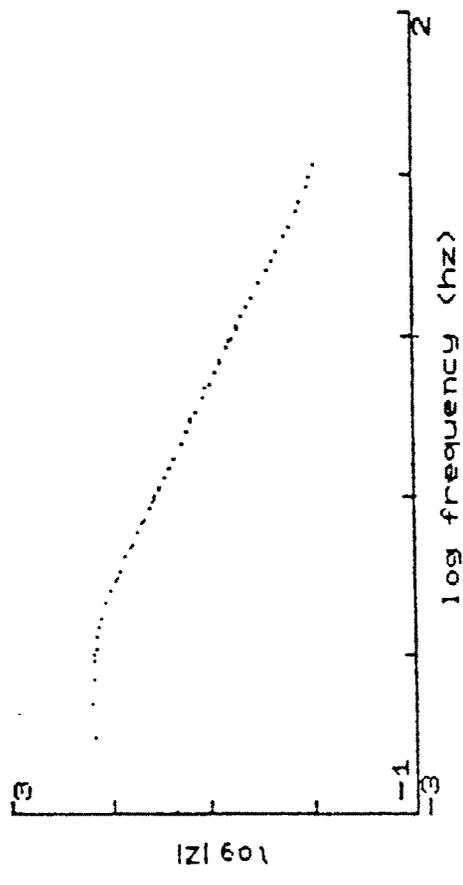
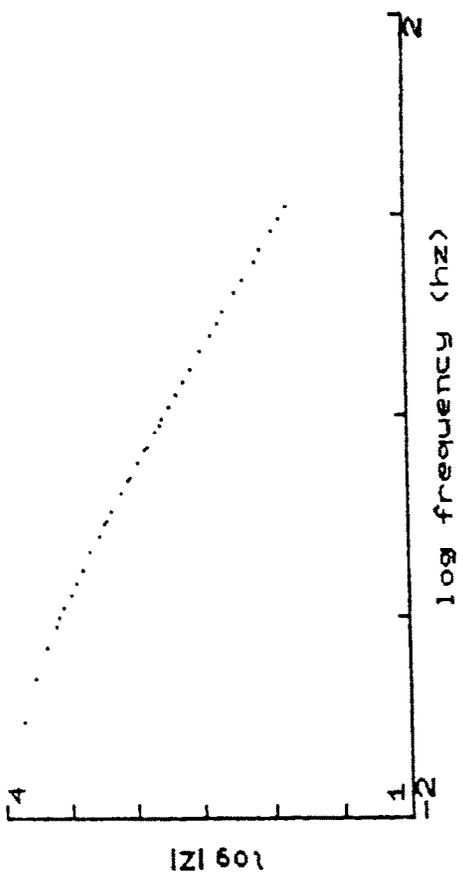


FIG.38: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY OXIDE AND 0.03% FERRIC IONS

a) Without aeration

b) With aeration

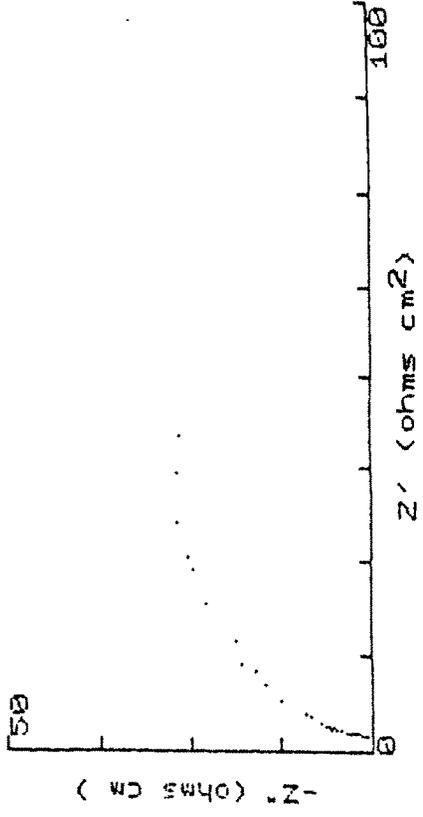
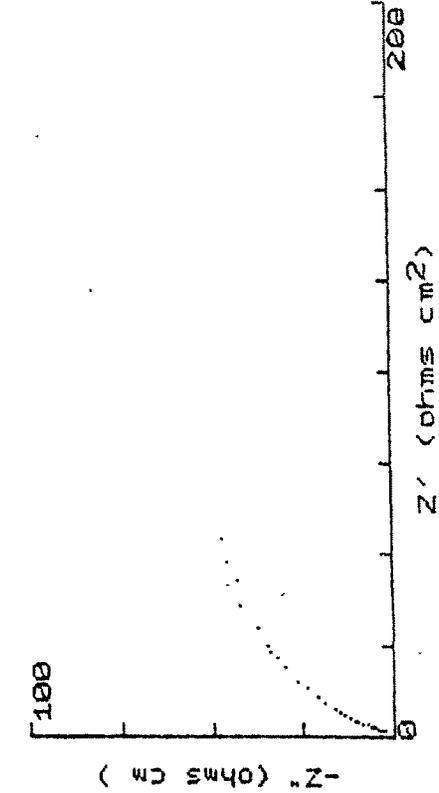
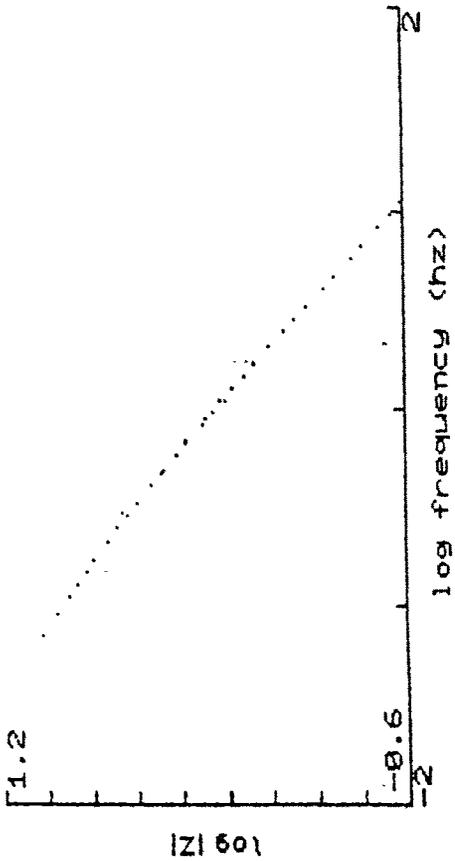
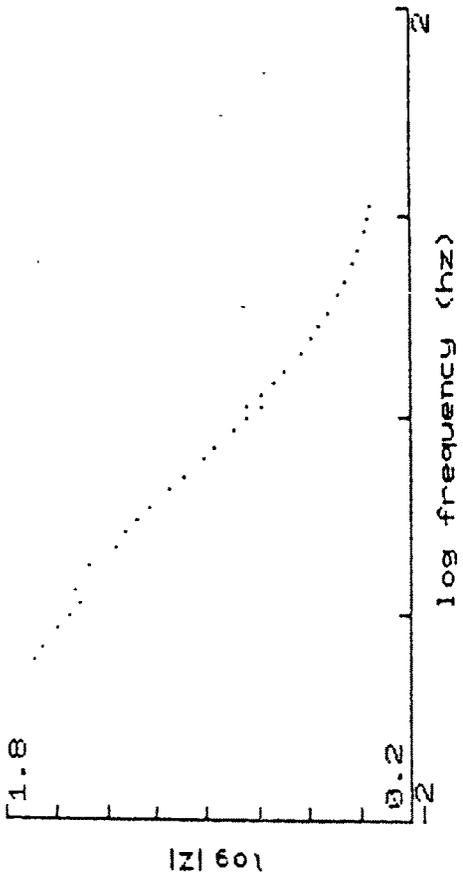


FIG.39: BODE AND NYQUIST PLOTS FOR CS IN SYNTHETIC GVSL SOLUTION WITH 0.04% FERRIC IONS

a) Without aeration

b) With aeration

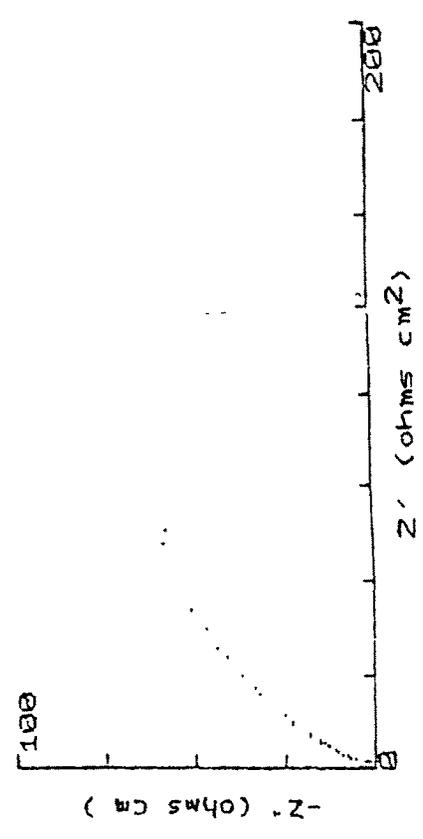
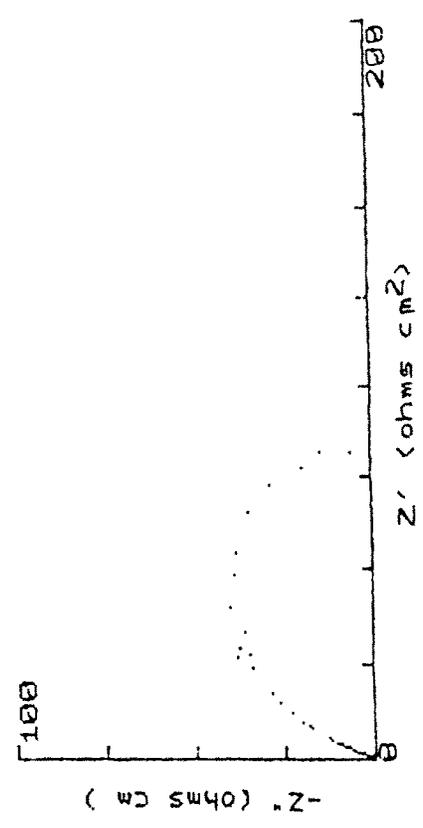
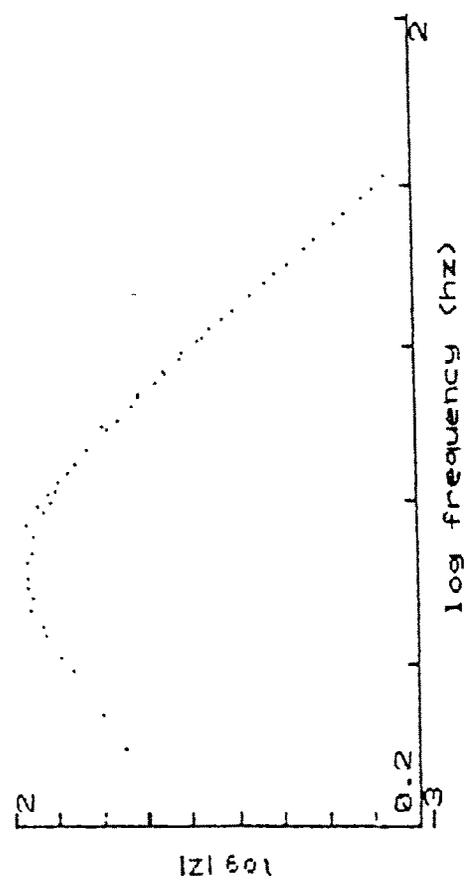
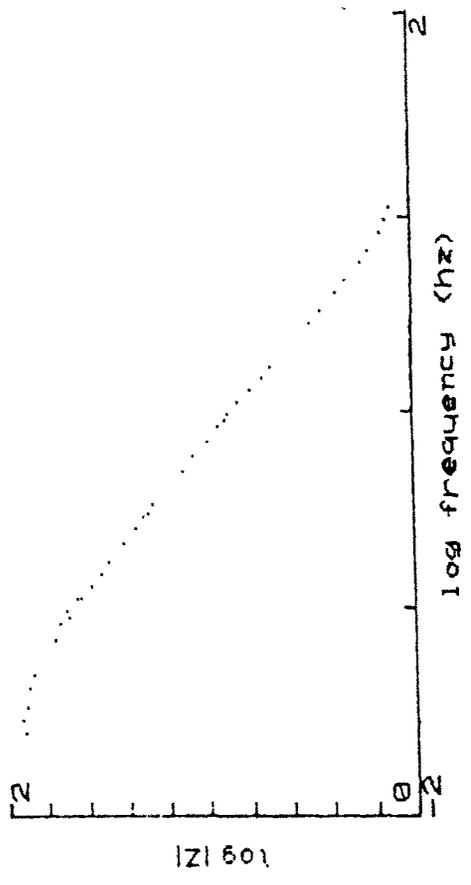


FIG.40: BODE AND NYQUIST PLOTS FOR CS IN SYN. GVSL SOLUTION WITH 0.15% ANTIMONY OXIDE AND 0.04% FERRIC IONS

a) Without aeration

b) with aeration

FIG 41 : EFFECT OF  $Fe^{+3}$  AND  $Sb_2O_3$  ON POLARIZATION RESISTANCE

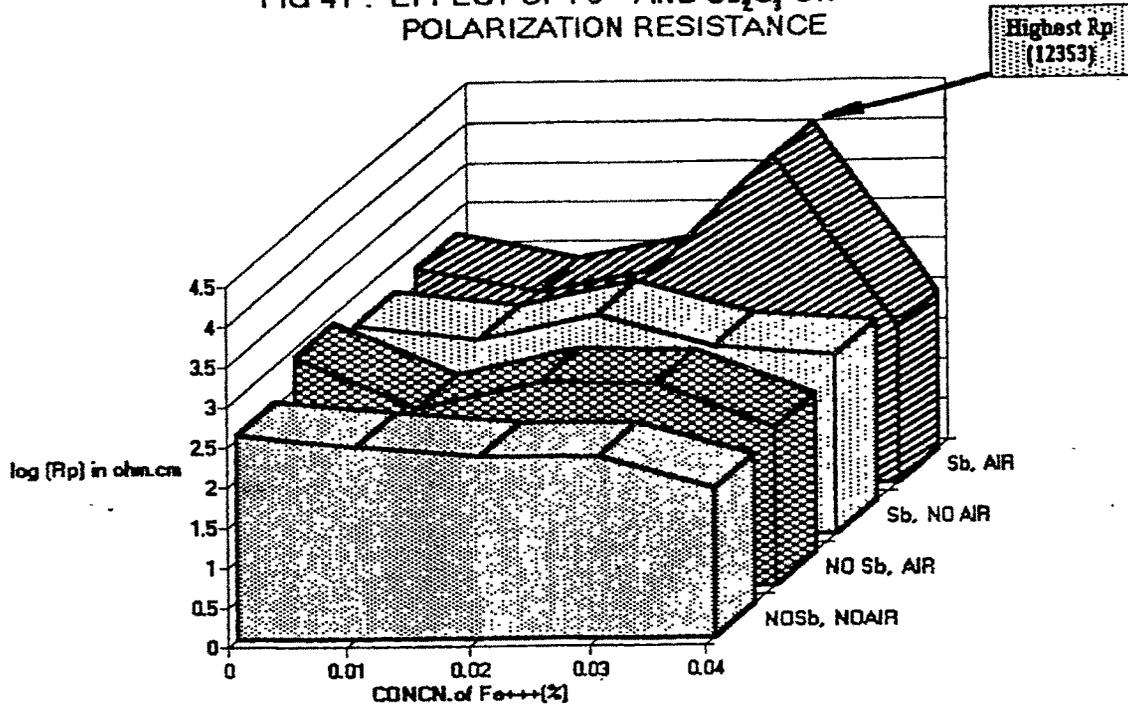
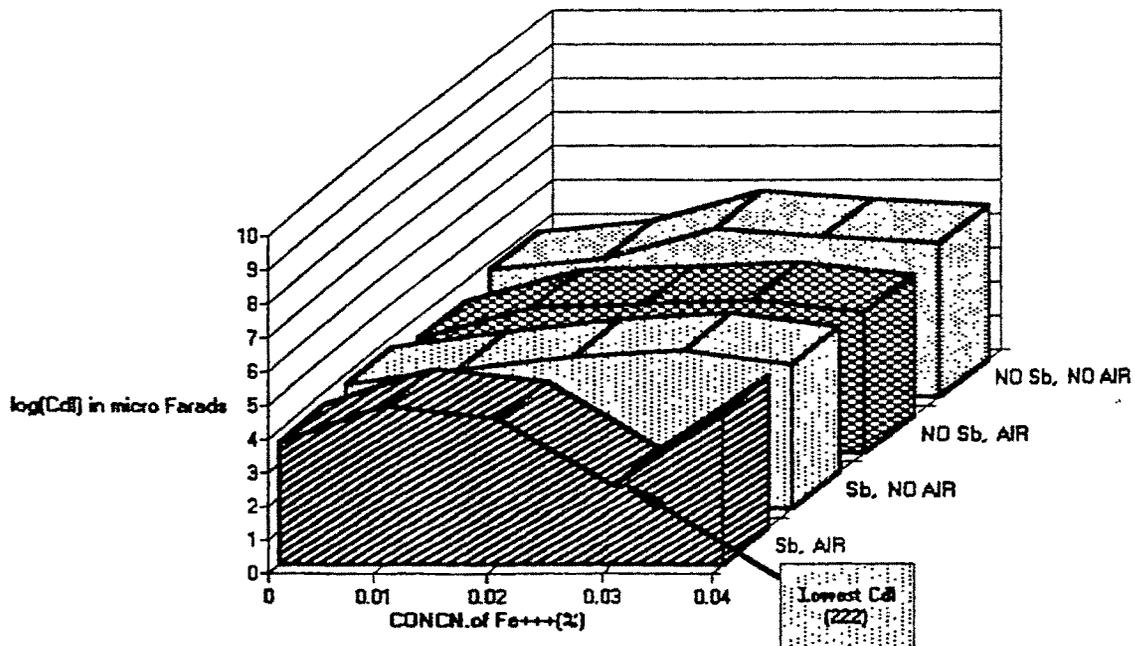


FIG 42 : EFFECT OF  $Fe^{+3}$  AND  $Sb_2O_3$  ON DOUBLE LAYER CAPACITANCE



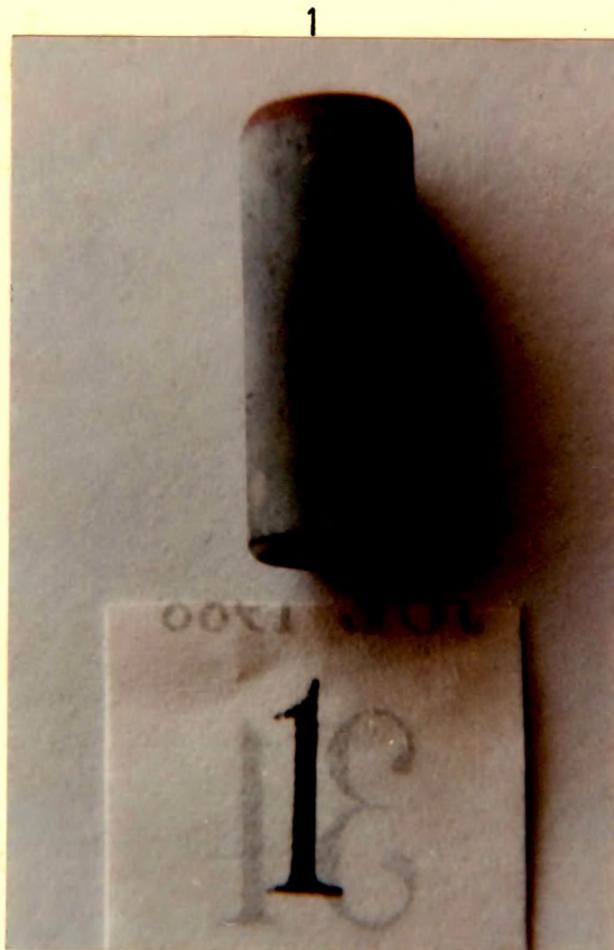


PLATE 1 : CYLINDRICAL CARBON STEEL SPECIMEN AFTER EXPOSURE TO SYN. GVSL SOLUTION WITHOUT INHIBITORS.

2

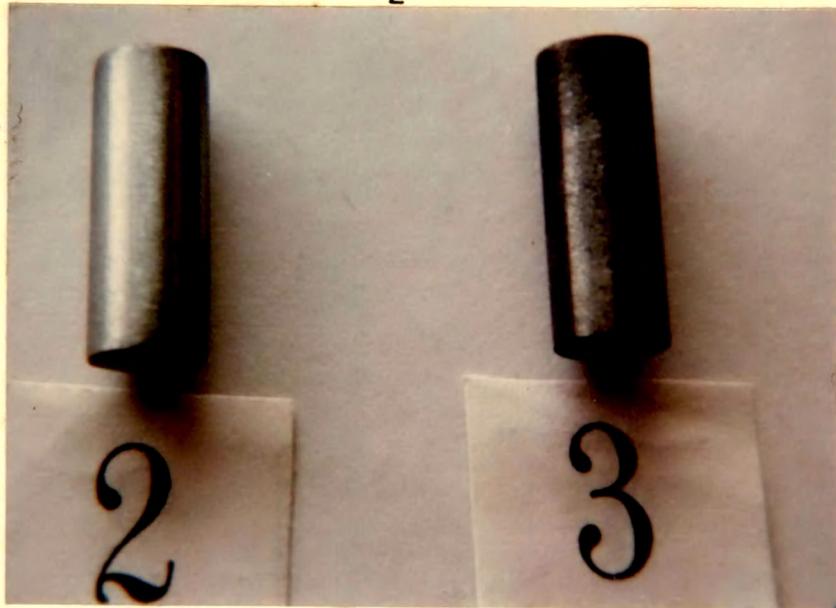


PLATE 2 : CYLINDRICAL CARBON STEEL SPECIMENS AFTER EXPOSURE TO (2) SYN. GVSL SOLUTION WITH 0.1% Sb2O3 AND 0.03% FERRIC IONS AND (3) WITH 0.03% FERRIC IONS ONLY

3

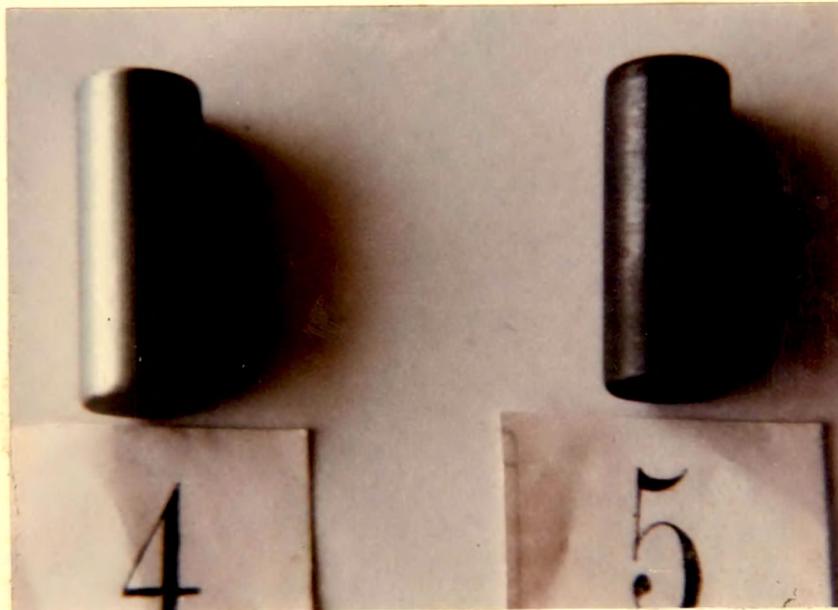
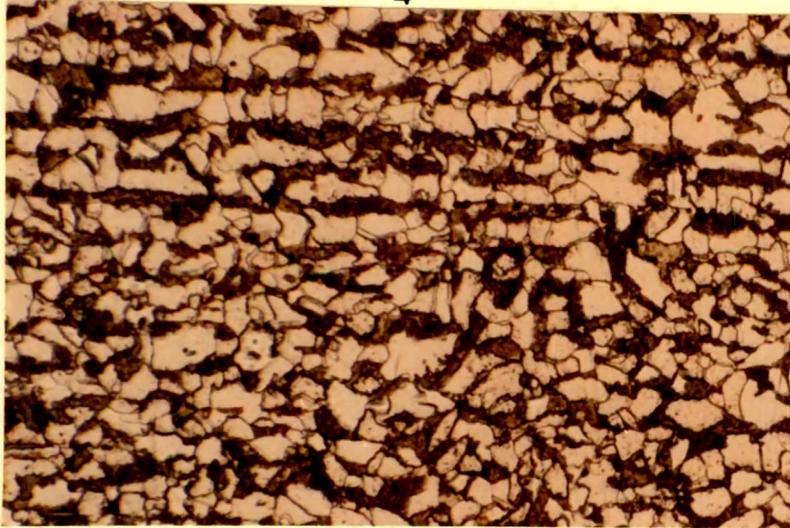


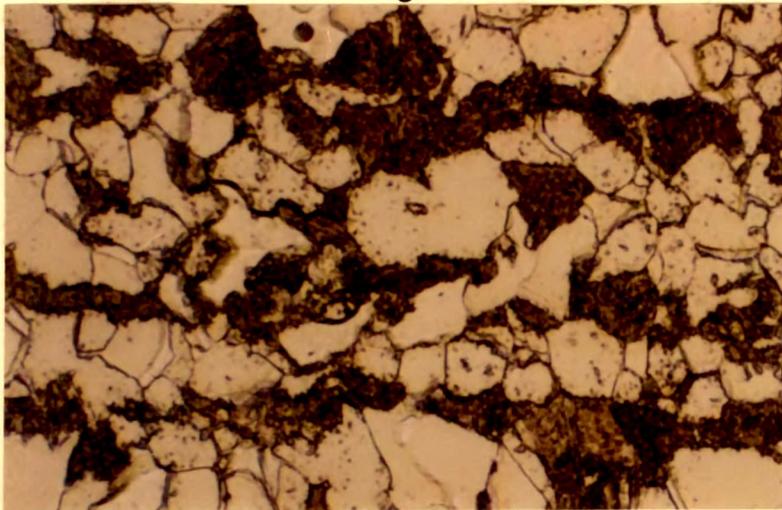
PLATE 3 : CYLINDRICAL CARBON STEEL SPECIMENS AFTER EXPOSURE TO (4) SYN. GVSL SOLUTION WITH 0.15% Sb2O3 AND 0.03% FERRIC IONS AND (5) WITH 0.03% FERRIC IONS ONLY

4



250 X

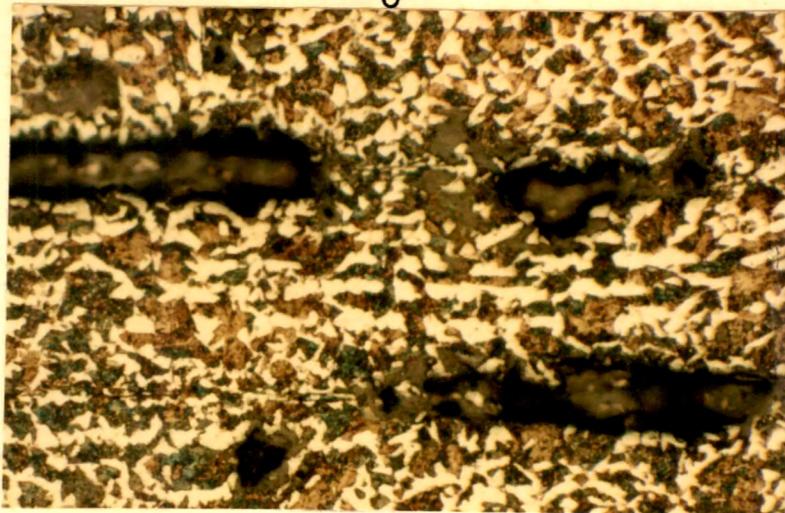
5



625 X

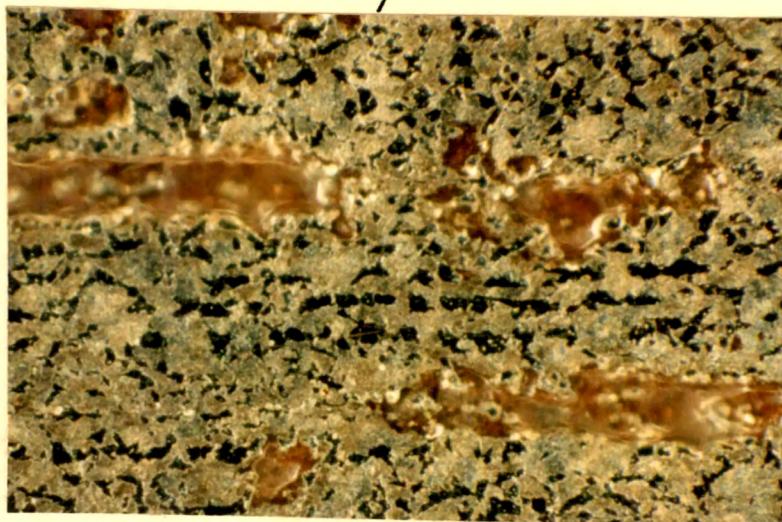
PLATES 4-5 : MICROSTRUCTURE OF THE UNEXPOSED CARBON STEEL SURFACE

6



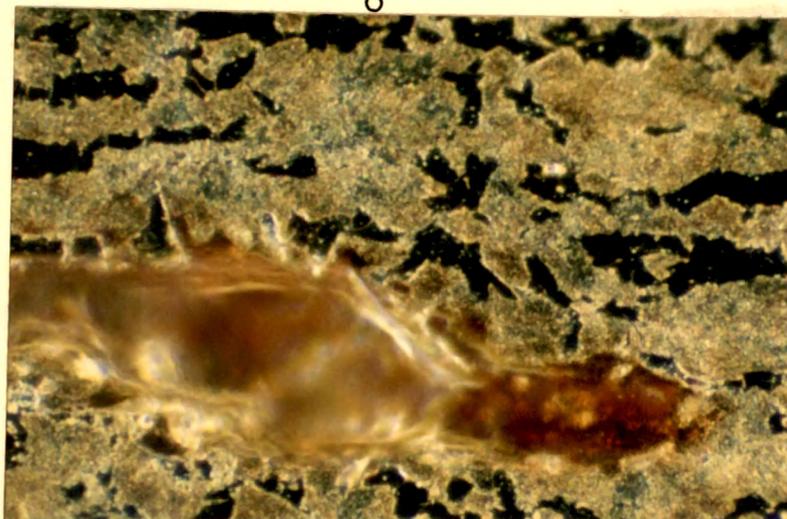
BRIGHT FIELD VIEW  
AT 250 X

7



DARK FIELD VIEW  
AT 250 X

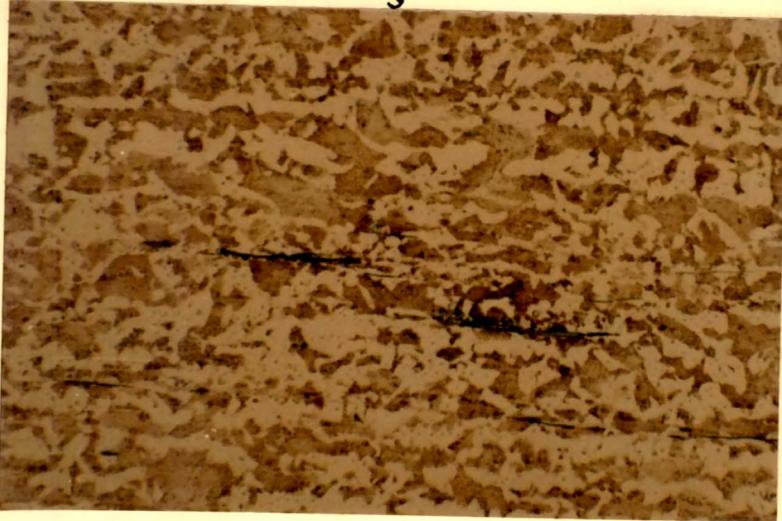
8



DARK FIELD VIEW  
AT 625 X

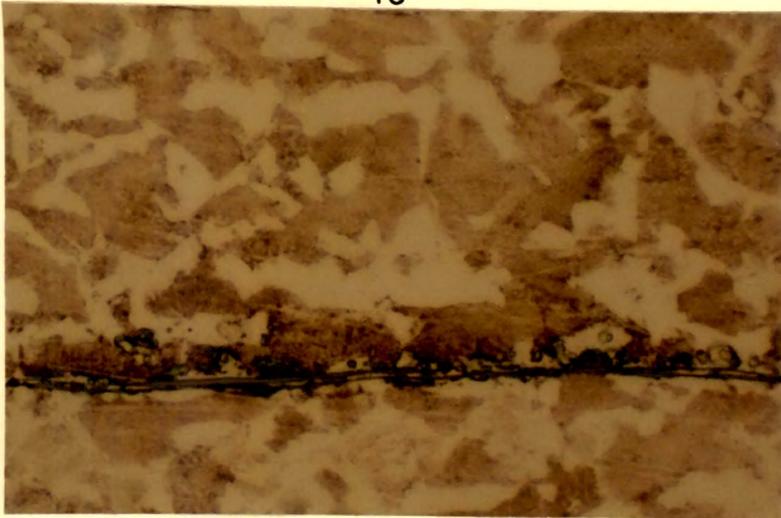
PLATES 6-8: MICROSCOPIC VIEW OF THE CARBON STEEL SURFACE  
EXPOSED TO UNINHIBITED SYN. GVSL SOLUTION.

9



BRIGHT FIELD VIEW  
AT 250 X

10



BRIGHT FIELD VIEW  
AT 625 X

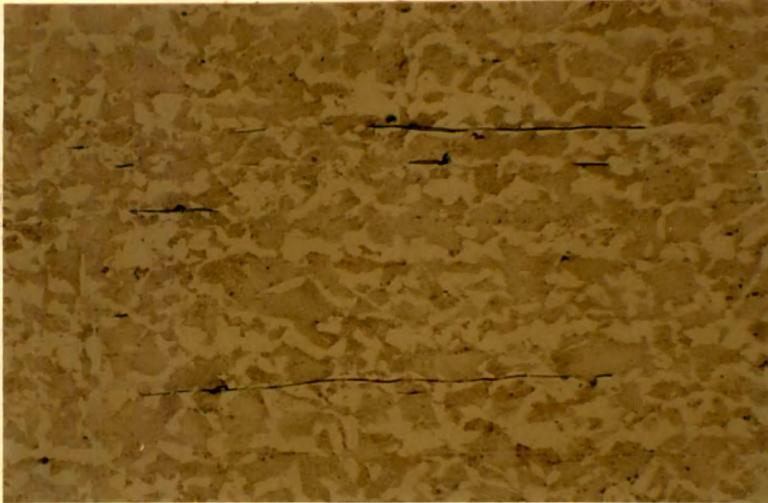
11



DARK FIELD VIEW  
AT 250 X

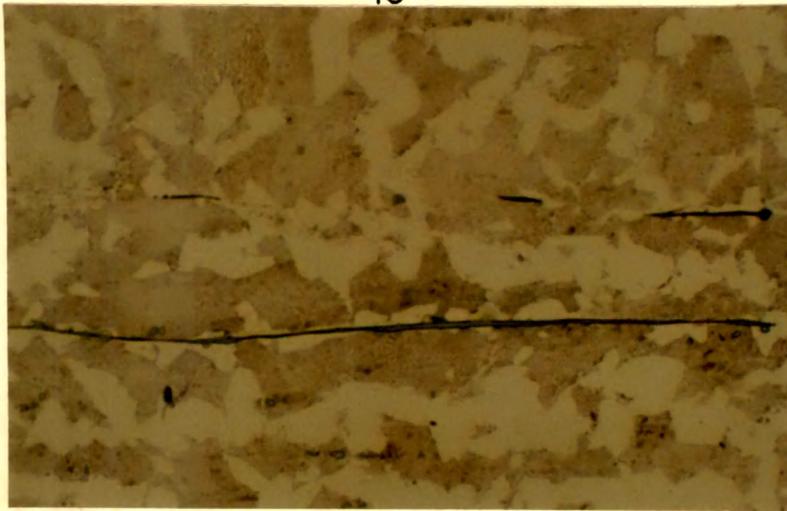
PLATES 9-11 : MICROSCOPIC VIEW OF THE CARBON STEEL SURFACE  
EXPOSED TO SYN. GVSL SOLUTION CONTAINING 0.1%  
Sb2O3 AND 0.03% FERRIC IONS

12



BRIGHT FIELD VIEW  
AT 250 X

13



BRIGHT FIELD VIEW  
AT 625 X

14



DARK FIELD VIEW  
AT 250 X

PLATES 12-14 : MICROSCOPIC VIEW OF THE CARBON STEEL SURFACE  
EXPOSED TO SYN. GVSL SOLUTION CONTAINING  
0.15% Sb2O3 AND 0.03% FERRIC IONS

## REFERENCES

1. Vetere, V. F., Electrochemical tests for control of characteristics of corrosion inhibitors, An. - CIDEPINT, 227 - 38, (1982)
2. JGC Corp. Jpn. Kokai, Corrosion control of CO<sub>2</sub> strippers, Tokyo Koho J.P. 6078, 616 May 4, (1985)
3. Mago, Blake F., Corrosion inhibition, Ger. Offen. 2,518,827, Oct. 30, (1975), US Appl. 464,858, April 29, (1974) 19
4. Mikhailovskii, Yu, N., Zashch. Met., 20 (2), (1984), 179-90
5. Fyfe, David, Separating an acid gas from a gas mixture, Ger. Offen. 2,421,572, November 14, (1974), Brit. Appl. 22, 356/73, May 10, (1975)
6. Turner, Mervyn E. D., Separation of acid gases from a gas mixture, Ger. Offen. 2,545,829, April 29, (1976), Brit. Appl. 74/46, 252
7. Atkins, K.T.G., Fyfe, D., Rankin, J.D., ICI, Ltd., London Safety in Ammonia Plants, AIChE Symposium, Vancouver, (1973)
8. Armstrong, R.D., Coates, A.C., Corrosion Science, 16, (1976), 423-33
9. ICI, London - Private Correspondence

10. Parkins, R.N., Forolius, Z.A., Mat. Perf., Jan. (1988), 19-29
11. Allemanno, I.V., Italy, Private Correspondence.
12. Parkins, R. L., Proc. of Conf. and fund. aspects of SCC, Ohio state Univer. (1967), 1-361
13. Staehle, R. W., Dissolution of iron - carbide in the pearlite matrix, Rapports Tech. Cebelcor, 114, RT. 177 (1970)
14. Staicopolus, D. N., The role of Cementite in the acidic corrosion of steel, J. Electrochem. Soc., 110, 1121 -1124 (1963)
15. Turner, Mervyn E.D., ICI Ltd., Agriculture Division, Billingham, U.K., Private Correspondence