4

RESULTS AND DISCUSSION

Rotating cage is a simple, compact methodology to simulate pipeline flow conditions in the laboratory to evaluate the corrosion rate of metals. The corrosion rate depends on many factors like rotation speed, volume of liquid and hence the flow pattern. To ensure the reproducibility of the results from the rotating cage under atmospheric conditions, the corrosion rate of Carbon steel I was measured under the following conditions.

Testing Temperature	Room temperature
Gas composition	CO_2 (Oxygen content not exceeding 10ppm by volume)
Initial pH	8.2 (prior to presaturation with CO_2)
Testing Time	24h
Rotating speed	500rpm
Surface area of specimens	$34.14 cm^2$
Number of specimens	8 per test
Total number of tests	6
Test Solution	Substitute Ocean water as per ASTM D1141
Volume of solution	4 Litres

The data (Run I, IV, V and VI) were utilized for the global level **Inter laboratory study to Establish Precision statements for ASTM G 202, Standard Test Method Using Atmospheric Pressure Rotating Cage by ASTM Committee G-I on corrosion of metals, subcommittee G 01.05 on Laboratory Corrosion Tests** wherein Dr.R.Shyamala, Professor and Head, Department of Chemistry, Avinashilingam University, Coimbatore was one of the participants.

The average corrosion rates (25.97mpy) is in close agreement with the standard corrosion rate established by ASTM for rotating cage method (23 +/- 2 mpy)) under the experimental conditions.

4.1 Theoretical background of CO_2 corrosion

4.1.1 Wet CO_2 corrosion

One of the major concerns in the capture and transport of CO_2 is corrosion. Dry CO_2 is inert to commonly used pipeline materials such as carbon steel. However, CO_2 is an acid gas and will react with water to form carbonic acid. Carbonic acid corrosion of carbon steels has been known for years as a major source of damage in oil and gas pipelines referred to as "sweet gas corrosion".CO_2 corrosion of carbon steel is an electrochemical process which involves the evolution of H_2.The major chemical reactions include CO_2 dissolution and hydration to form carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The electrochemical reaction at the steel surface includes the anodic dissolution of iron and cathodic evolution of H_2.

Anodic Reaction

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathodic Reaction

The cathodic reactions are the direct reduction of carbonic acid as well as reduction of hydrogen ions.

$$2H_2CO_3 + 2e^- \longrightarrow H_2 + 2HCO_3^-$$

$$2H^+ + 2e \longrightarrow H_2$$

Over all Reaction

$$Fe + CO_2 + H_2O \longrightarrow FeCO_3 + H_2$$

Thus, CO_2 corrosion leads to the formation of a corrosion product, $FeCO_3$, which when precipitated could form a protective or a non - protective scale depending on the environmental conditions.

CO_2 corrosion is a complicated process and is affected by many different parameters such as temperature, pH, CO_2 partial pressure etc. Much research work has been conducted in this field for the past three decades. In 1975, **de Waard and Milliams** identified the combined effect of CO_2 partial pressure and temperature as key parameters on the corrosion rates. Since then, many other parameters (pH, velocity etc.) have been discussed. However, research work related to CO_2 corrosion in solutions with high salt concentrations is scarce. **Sun et al. (2003)** investigated the effect of Cl^- ion on localized corrosion in wet gas pipelines. **Ma et al. (2003)** have also studied the influence of Cl^- ion on localized corrosion of iron.

Effect of NaCl concentration on the corrosion of pipeline materials is an important parameter in CCS because captured CO_2 is injected in deep saline aquifers (18% NaCl). **Haitao Fang et al. (2010)** have reported that the salt content of water in Texas gas well was found to be about 23% by weight. Therefore, it is necessary to know the effect of high content of salt on CO_2 corrosion of pipeline materials. Hence, mass loss studies with varying concentration of NaCl viz 1, 5, 15,and 30% in CO_2 atmosphere under simulated flow condition of 500rpm at atmospheric pressure were carried out.

Sequestered CO_2 is stored into saline underground water by injecting through downhole tubular consisting of cemented case pipes which causes turbulent flow conditions creating **flow-induced localized corrosion (FILC).**

According to **Long et al**. **(2005)** flow velocity increases the corrosion rate due to the shear force and accelerates mass transfer of ion reactant and also the flow velocity would destroy corrosion scale and change the compactness of the scale, which may likely induce localized corrosion. Also, the continuous flow of CO_2 for a longer time may affect the stability of the corrosion product $FeCO_3$. Hence, It becomes important to analyze the effect of period of rotation on the pipeline material and hence mass loss studies were carried out at different periods of rotation (24, 48, 72 and 96h) under a simulated normal pipe line flow velocity of 500rpm.

4.2 Corrosion behavior of Carbon steels

4.2.1 Effect of NaCl concentration

4.2.1.1 Carbon Steel I

In general, the corrosion rates of the carbon steels in NaCl solution varies with concentration. Initially the corrosion rate increases from 1% to 5% of NaCl. The dissolution of the metal is found to be maximum at 5% NaCl concentration for all periods of rotation. Molar conductance of an electrolyte is more in dilute solutions which is attributed to the increase in the degree of dissociation of the electrolyte. **(Puri, Sharma and Pathania 2008-09).** At higher concentrations, the conductivity of NaCl gets decreased since the solution reaches saturation and hence a decreased corrosion rate at 15% and 30%.

4.2.1.2 Carbon Steel 5LX42

NaCl concentration influences the corrosion to a greater extent. As in CS I the corrosion rate is maximum at 5% concentration except for 96h (maximum at 15%). However, the corrosion rate is minimum at 30% concentration for all periods of rotation.

4.2.1.3 Carbon Steel 5LX60

The high salt concentration decreases the general corrosion rate significantly and nonlinearly which is in good agreement with the results obtained by **Haitao Fang et al. (2010).** In general the corrosion rate was found to be maximum at 5% NaCl concentration due to the high conductance of NaCl similar to the previous two cases.

4.2.2 Effect of period of rotation

4.2.2.1 Carbon Steel I

In general the corrosion rate decreases with increase in period of rotation for all the concentrations of NaCl solution. This may be attributed to the formation of passive corrosion product $FeCO_3$ as a protective layer at the steel surface. According to **Wei Liu et al. (2012)** the corrosion scale on the surface gradually gets accumulated with time and becomes interconnected and more compact, which would provide strong protection to the steel substrate by a blocking effect.

But under the continuous flow condition there is a possibility of the removal of the corrosion products formed on the surface layer leading to localized corrosion. Hence, a slightly increased corrosion rate at longer period of rotation has been observed.

4.2.2.2 Carbon Steel 5LX 42

It is obvious that the corrosion rate decreases with period of rotation. This kind of protection has been arrived due to the corrosion product formation as a protective layer. These results are in good agreement with corrosion studies of metals in CO_2 by **Suhor et al. (2012).** But, the minor deviation in this trend at 48h and 96h in 15% NaCl concentration revealed the possibility of flow effects challenging the protectiveness of any corrosion product films formed.

4.2.2.3 Carbon Steel 5LX60

The corrosion behavior of the metal depends on the formation and retainment of a protective iron carbonate layer on the surface. It was found that as the period of rotation increases, the corrosion rate decreases following the same trend as that of other two carbon steels studied.(CS I and CS 5LX42). This behavior in the CS 5LX60 is related to the formation of $FeCO_3$ which is the corrosion product in CO_2 environment **(De Waard et al., 1991).**

4.2.2.4 Change in pH

pH represents the H^+ ion concentration in aqueous solutions. H^+ is one of the main species involved in the cathodic reaction of CO_2 corrosion process. The pH of the test media for the carbon steels studied before and after each run with different concentrations of NaCl and the change in pH towards the acidic region in all the experiments confirms the carbonic acid corrosion of selected carbon steels.

4.3 Corrosion behavior of Stainless Steel

Stainless steel is not a single alloy, but it constitutes a large family of alloys with different properties for each member. They find their application due to their excellent resistance to corrosion. Chromium is the main component that transforms iron into stainless steel. Stainless steel must contain at least 10.5% chromium to provide adequate resistance to rusting, and if it contains more chromium the corrosion resistance becomes better. Stainless steels are not susceptible to uniform CO_2 corrosion as carbon steels. Stainless steel resists corrosion mainly through the formation of a passive film. However, CO_2 can indirectly affect the performance of stainless steel by dissociation of carbonic acid, which leads to a lowering of pH.

$$CO_2 + H_2O \longrightarrow H_2CO_3^- \longrightarrow H^+ + HCO_3^-$$

The corrosion behavior of stainless steel is mainly influenced by the environmental factors like chloride ion concentration and pH of the solution. Hence, the effects of NaCl concentration, effect of period of rotation on the corrosion behavior of 304 and 316 stainless steels are carried out.

4.3.1 Effect of NaCl concentration on stainless steel

4.3.1.1 304 SS

Classical pitting corrosion is possible by the breakdown of passive film in the presence of aggressive anionic species like chloride ions. Chloride ion is a relatively small anion with a high diffusivity which interferes with passivation. The severity of pitting tends to vary with the logarithm of the bulk chloride concentration.

The dissolution of the metal was found to be maximum at 15% and remains almost same at 30% NaCl concentration for all period of rotation. This may be due to increased amount of chloride ion which may cause pitting or localized attack thereby increasing the corrosion rate of 304 SS.

4.3.1.2 316 SS

The corrosion rate increases with increase in chloride ion concentration. When the concentration of NaCl increases, the increased chloride ion leads to increase in aggressiveness of the medium and as a result the corrosion rate increases.

4.3.2 Effect of period of rotation

4.3.2.1 304 SS

For a given concentration of NaCl, the corrosion rate increases with increase in the period of rotation. A sudden increase in the corrosion rate at 72 and 96 h of exposure indicates the occurrence of localized corrosion.

As discussed earlier this may be due to the breakdown of the passive film formation with time and also because of the penetration of the smaller and negatively charged chloride ion through the passive layer to the positively charged metal cation destroying the protective function of the passive film **Ibrahim et al. (2009)**. The results obtained shows that there is a continuous increase in the corrosion rate with period of rotation due to the presence of aggressive ions in the test medium under the continuous flow condition.

4.3.2.2 316 SS

The corrosion rate increases with increase in time for all the concentrations of NaCl. This constant increase in the corrosion rate with period of rotation may be due to the aggressive chloride ions causing localized pits on the surface. According to **Uhlig and Revie (1984)**, once a pit is initiated, a passive - active cell is set up of large potential difference. The resultant high current density accompanies a high corrosion rate of anode (pit) and at the same time, polarizing the surface immediately surrounding the pit to a value below the critical potential. Through flow of current, chloride ions transfer into the pit forming concentrated solutions of Fe^{+2}, Ni^{+2}, Cr^{+3} chlorides, which account for an acid solution.

4.3.2.3 Change in pH

Passivation film on the stainless steel surface gets away in low pH condition such as acidizing environment and corrosion occurs. The high Cl^- concentration and lowering of pH ensures that the pit surface remains active.

4.4 Statistical analysis

The results of the corrosion rates were subjected to three way ANOVA between the type of metals, concentration of NaCl and period of rotation under CO_2, at atmospheric pressure. The mean corrosion rate of the selected carbon steels and stainless steels in NaCl concentration for various periods of rotation and allows us to calculate the most repeated trend of various metals in the test medium.

Following the most repeated trend, the corrosion behavior of metals found to follow the order

CS 5LX 60 > CS 5LX 42 > CS I> 304 SS > 316 SS

4.5 Surface Analysis

4.5.1 Optical microscopy

The surface morphology of the metal samples subjected to mass loss studies were examined by metallurgical microscope. The optical micrographs of the polished metals coupons and the samples exposed to 1% and 30% NaCl solutions for a 96h of rotation are presented in the **Figure 23** respectively.

The polished samples seldom show damage to coupon surfaces other than occasional pitting likely attributed to abrasion during polishing. The coupons subjected to NaCl atmosphere was covered by a dark layer of corrosion products which is more prominent in ferrous samples and pits formation in SS samples.

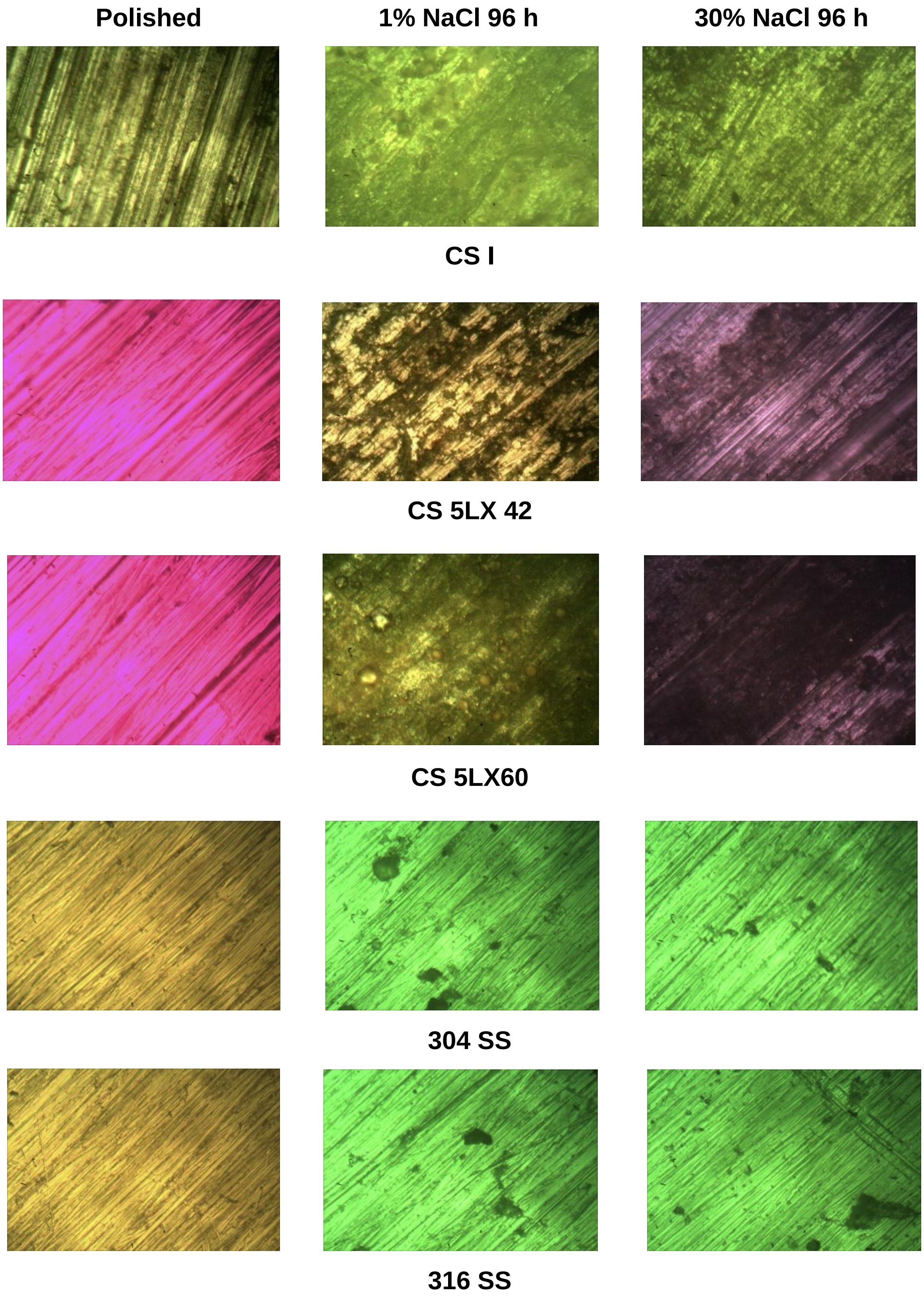


Figure 23 : Optical micrographs (40x) of the selected samples

4.5.2 SEM and EDS

The SEM micrographs of the sample CS 5LX 42 and CS 5LX 60 exposed to 1% and 30% of NaCl in CO_2 atmosphere in absence of oxygen for 96 h are shown in the **Figures** and the corresponding energy dispersive X-ray spectra (EDS) in the **Figures.** From the SEM images it is clear that the surface of the carbon steel is covered by the corrosion product. The EDS spectra show a very high amount of carbon and oxygen which is mainly due to Iron carbonate ($FeCO_3$) and iron carbide (Fe_3C) along with the constituents of some alloying elements present in the carbon steel. In the absence of O_2 the surface is covered by dense, crystalline $FeCO_3$.

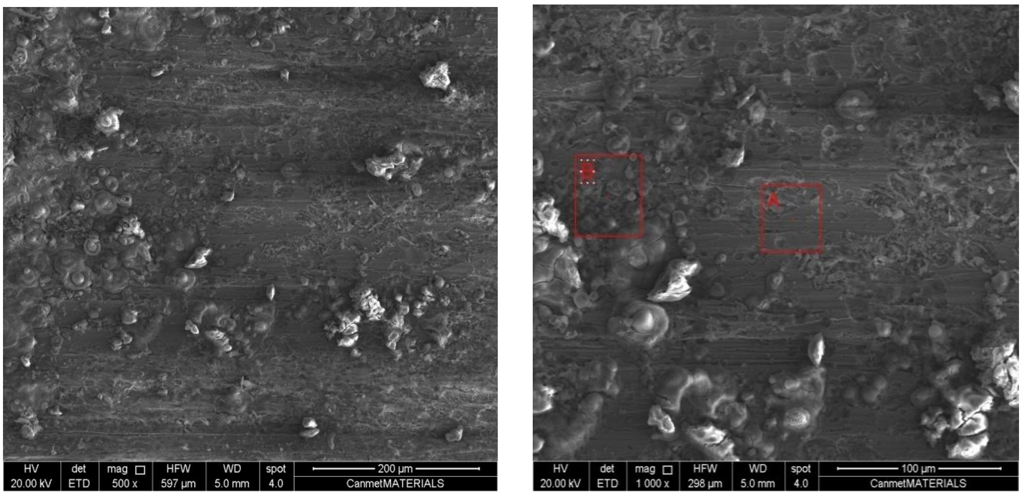


Figure .SEM images of CS 5LX 42 in 30% NaCl at 96h

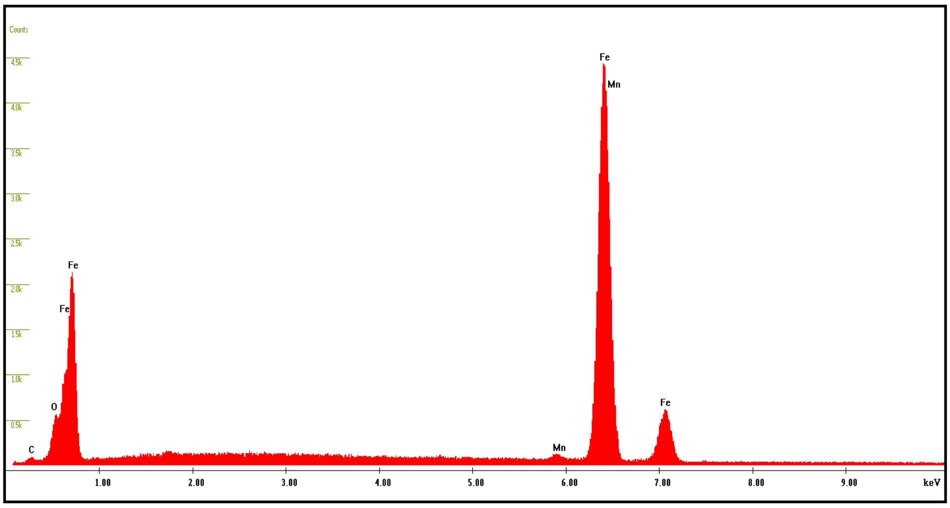


Figure 27a. EDS spectra of corroded surface of CS 5LX 42 in 30% NaCl at 96h

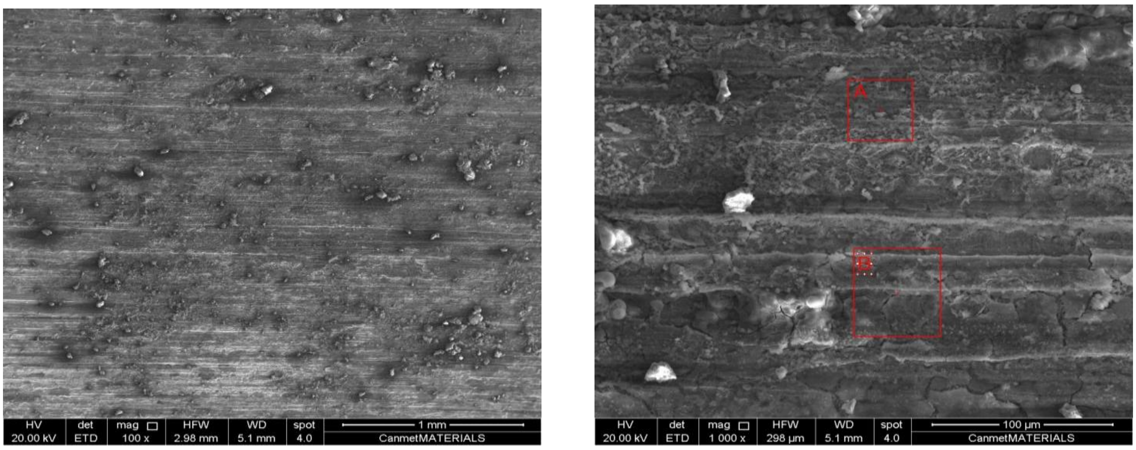


Figure. SEM images of CS LX 60 in 30% NaCl at 96h

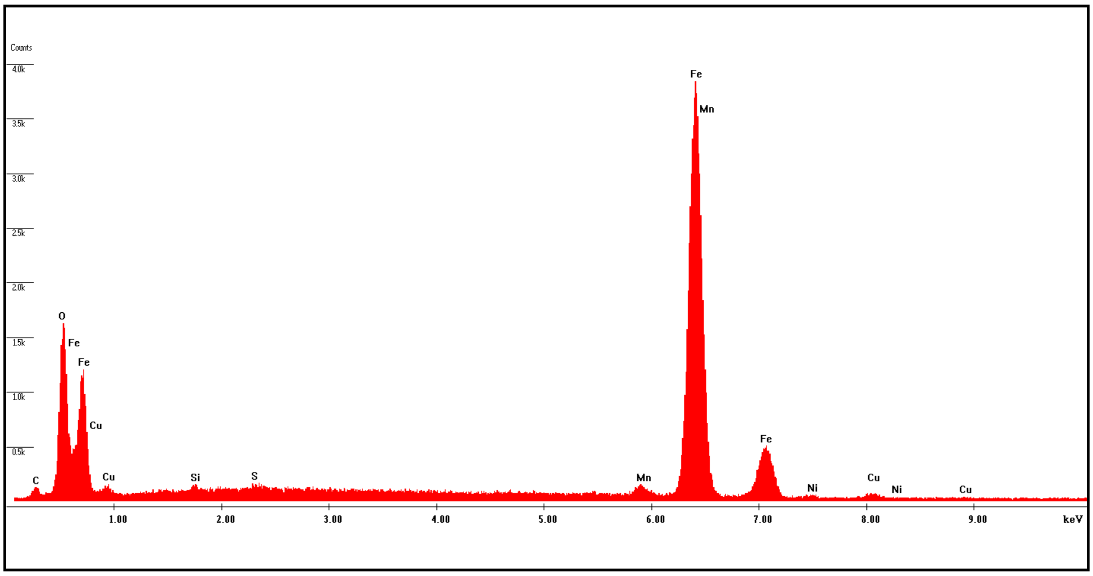


Figure. EDS spectra of corroded surface of CS 5LX 60 in 30% NaCl at 96h

SEM image of stainless steel in 1% and 30% NaCl showed the clear surface with no surface coverage except small pits. This is evident from the EDS in which apart from the metal peaks of the alloy, peaks of carbon and silicon are also seen. The presence of Si show the initiation of the pit formation and attack by the chloride ions will be predominant.

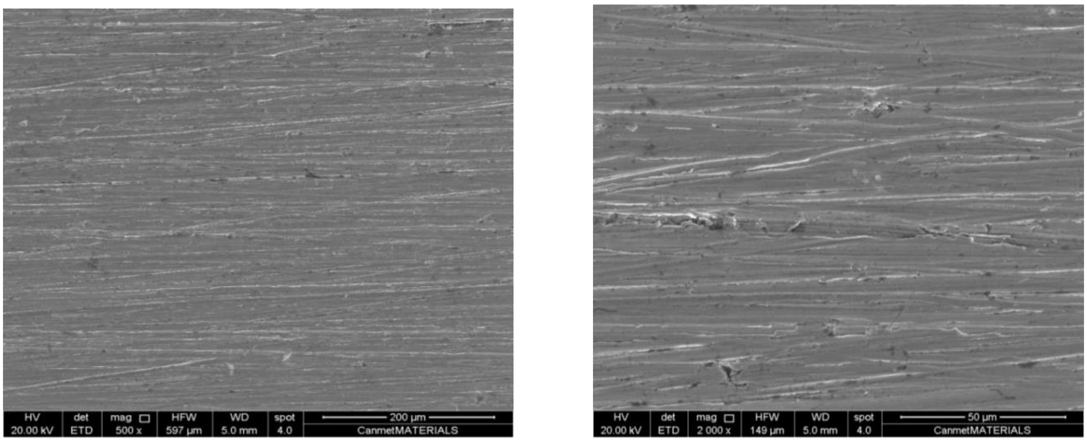


Figure 32. SEM images of 304 SS in 1% NaCl at 96h

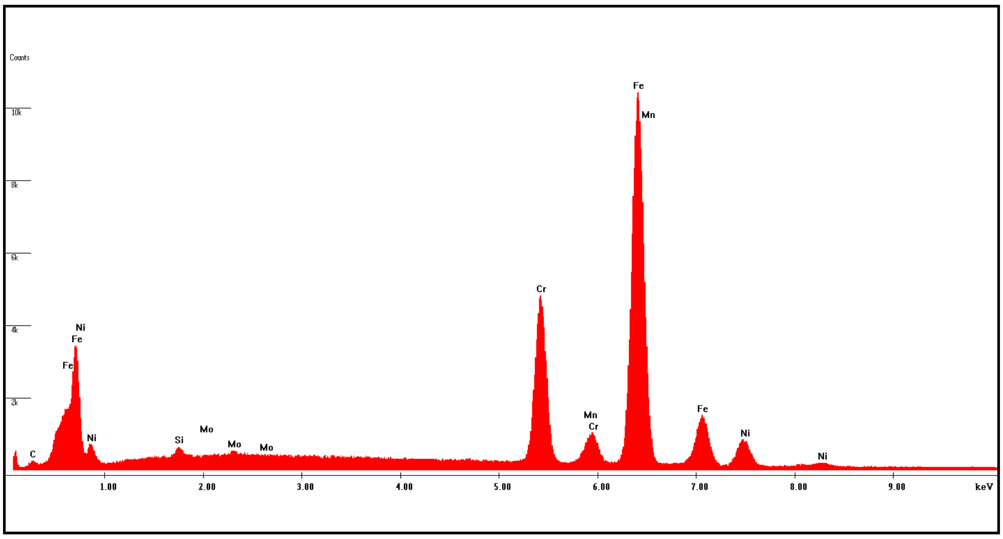


Figure. EDS spectra of corroded surface of 304 SS in 1% NaCl at 96h

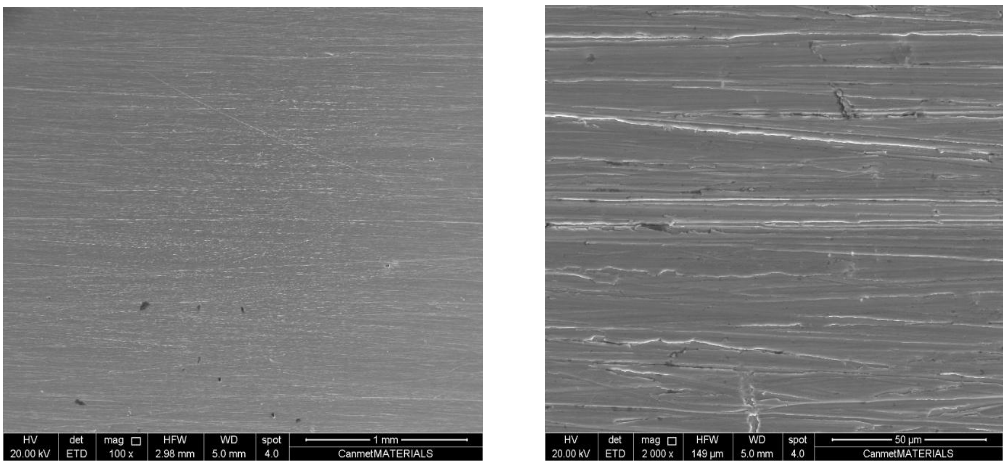


Figure . SEM images of 316 SS in 30% NaCl at 96h

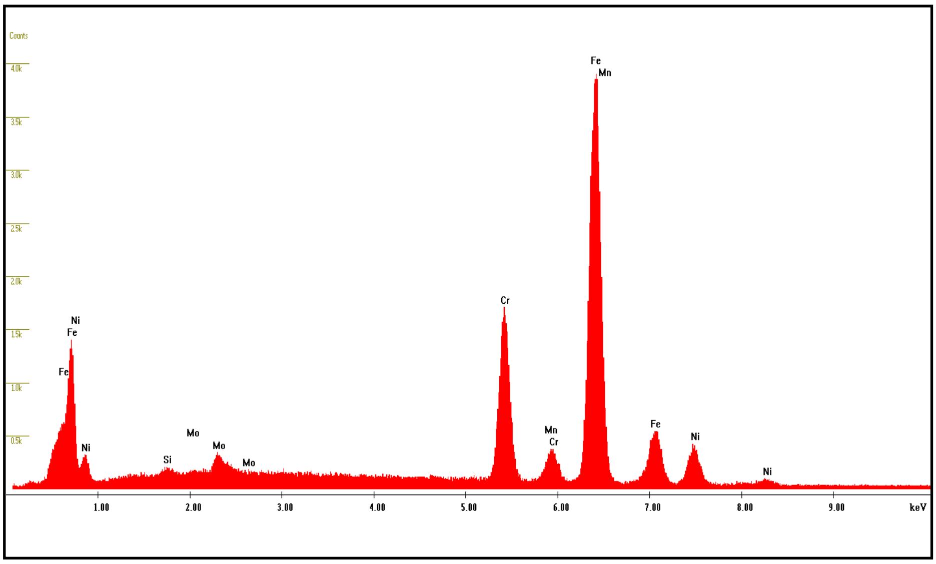


Figure. EDS spectra of corroded surface of 316 SS in 30% NaCl at 96h

4.6 Effect of impurity on CO_2 corrosion

4.6.1 Effect of MEA

Chemical absorption processes are widely used in industries for the treatment and purification of flue gas using MEA - the most commonly used alkanolamines. It is soluble in water at all concentrations thus eliminating the solubility issues observed by amine solvents. The solubility of MEA ensures that the solution can have a high capacity to carry CO_2.Typically it is expected that during the CCS process the impurities transported along with the CO_2 may have an effect on the integrity of the pipelines. Furthermore, CO_2 stream may also contain small amounts of residual impurities related to capture media (amine based solvents, catalyst, etc) used in the post-combustion capture process **(Ramgopal Thodla et al. (2009)**. Therefore during the scrubbing processes there is a possibility for MEA (solvent) to get into the CO_2 transportation pipeline along with CO_2 as an impurity. The effect of such impurities has not been adequately studied. According to **Mark A. Moore et al. (2008),** the majority of the piping and vessels in the gas plants are fabricated from carbon steel and the amines are in aqueous solution and there would be a high potential for corrosion.

4.6.1.1 Reaction between aqueous MEA – CO_2

According to **Danckwerts (1979),** CO_2 reacts with aqueous MEA mainly by the formation of an intermediate Zwitterion.

$$RNH_2 + CO_2 \longrightarrow RNH_2^+COO^-$$

The formed intermediate zwitterion then reacts with another mole of MEA to form stable complexes, ie., protonated MEA and MEA carbamate.

$$RNH_2^+COO^- + RNH_2 \longrightarrow RNH_3^+ + RNH\ COO^-$$

$$RNH_2^+COO^- + H_2O \longrightarrow RNH_3^+ + HCO_3^-$$

Carbamate formation is possible with MEA (primary amine) and it reacts with iron to form $FeCO_3$ passive layer but it will not be uniform. The formed $FeCO_3$ is less tenacious and is not considered to be protective. Moreover, pure amines and water-amine solution are not corrosive since they have low conductivity and high pH. But when they mix with natural gas or CO_2 the pH of the solution decreases and thus becomes corrosive **(Mahdi Nouri et al., 2008).**

In order to have a clear idea on the corrosion behavior of carbon steel and stainless steel in NaCl solution under CO_2 environment along with MEA as an impurity at atmospheric pressure condition, mass loss studies were carried out at different period of rotation (24, 48, 72 and 96h) under simulated flow condition of 500rpm.

4.6.1.2 Corrosion behavior of carbon steels in MEA

4.6.1.4 Effect of NaCl with 4M MEA on Stainless Steel

Both the type of SS shows negligible mass loss in NaCl with MEA for all rotation periods and at all concentrations. This makes use of SS in CO_2 pipelines.

4.6.1.5 Change in pH

The most supporting factor for the decrease in the corrosion of all the carbon steels and for stainless steels in Nacl solution with MEA than in the absence of MEA is due to the high pH value of the test media. The measured pH value of the test media ranges from of 7.48-10.65, which is high enough to behave as an alkaline solution.

4.6.1.6 Surface Analysis

4.6.1.7 SEM and EDS

Carbon steels (CS I,CS 5LX 42 and CS 5LX 60) exposed to 1% and 30% NaCl with 4M MEA for 96 h showed less corrosion rate than in NaCl. Minor local deposits and pitting was also observed. The corrosion products mainly formed in these pits are mainly carbonates and carbides of iron. In addition to carbonates and carbides the chloride also contributes to the pitting of the carbon steel which is observed from the EDS.

The surface morphology of 304 and 316 SS samples exposed to 1% and 30% NaCl for a period of 96h, shows the inner layer of the SS consists of iron, molybdenum, chromium and nickel whereas it contain iron, carbon and oxygen in the outer layer indicating the localized attack due to the chloride ions.

4.6.1.8 Statistical analysis

The results of analysis of variance for the carbon steels and stainless steels studied in NaCl + MEA with varying time intervals under CO_2, at atmospheric pressure gives significantly higher values for the corrosion rate of carbon steels The mean corrosion rate of carbon steels was found to be significantly high at 5% level.

The mean corrosion rate of the selected carbon steels and stainless steels in NaCl with MEA for various periods of rotation allow us to calculate the most repeated trend of various metals in the test medium. Following the most repeated trend, the corrosion behavior of metals found to follow the order

CS 5LX 42 ~ CS I ~ CS 5LX 60 > 304 SS ~ 316SS

4.7 Effect of MEG on CO_2 -Corrosion

MEG is mainly used in gas treating systems. According to **Jon Kvarekval et al. (2012)** Monoethylene glycol (MEG) is used to prevent the formation of solid gas-hydrates in wet natural gas pipelines operating at low temperatures. Glycols have slightly inhibiting effect on CO_2 corrosion. During handling and transportation, the glycol would be exposed to air and thus injection of oxygen-containing glycol might cause corrosion problems near the inlet of the pipeline.

Hence mass loss experiments were performed to study the effect of dissolved O_2 on CO_2 corrosion of carbon steel and stainless steels in CO_2-saturated MEG solutions.

4.7.1 Effect of NaCl with 4M MEG on carbon steels

4.7.1.1 Carbon Steel I

In general the corrosion rate increases with increase in the concentration of NaCl upto 15% where there is a decrease in the corrosion rate at 30%. This may be due to the initial dissociation of the electrolyte into Na^+ and Cl^- ions in the solution which in turn increases the conductivity to the sufficient level thereby the corrosion rate. At higher concentrations i.e., at 30%, the conductivity gets decreased since the solution reaches the saturation and hence a decreased corrosion rate.

4.7.1.2 Carbon Steel 5LX42

It shows that NaCl concentration influences the corrosion to a greater extent. As in CS I the corrosion rate is maximum at 5% concentration and minimum at 30% concentration for all periods of rotation. Corrosion rate decreases with high salinity.

4.7.1.3 Carbon Steel 5LX 60

It is evident from the figure that high salt concentration decreases the general corrosion rate significantly and nonlinearly. In general, the corrosion rate was found to be maximum at 5% NaCl concentration due to the high conductance of NaCl similar to the previous two cases.

4.7.2 Effect of period of rotation

4.7.2.1 Carbon Steel I

The decrease in corrosion rate with increase in period of rotation for 15 and 30% of NaCl with MEG solution is observed. This may be attributed to the formation of passive corrosion product ferrous carbonate and iron oxide as a protective layer at the steel surface. The corrosion product formed on the surface gradually gets accumulated with time and becomes adherent and more compact, which would provide strong protection to the steel substrate by a blocking effect. But under the continuous flow condition there is a possibility of the removal of the corrosion products formed on the surface layer leading to localized corrosion. Hence, a slightly increased corrosion rate at longer period of rotation has been observed for 1% and 5% NaCl solutions.

4.7.2.2 Carbon Steel 5LX 42 , Carbon Steel 5LX 60

The corrosion rate decreased with increase in period of rotation except for 5% NaCl with MEG. This may be due to the localized attack of chloride ions on the protective layer.

According to **Makarenko et al. (2000),** a dense crystalline $FeCO_3$ would be formed on the surface. But, when O_2 is added, it retards the formation of dense $FeCO_3$, where as it forms less protective iron oxides. Hence, an increase in the corrosion rate is observed at a maximum of 96h.

4.7.3 Effect of NaCl with MEG on stainless steel

4.7.3.1 Change in pH

The most supporting factor for the decrease in the corrosion of all the carbon steels and for stainless steels in Nacl solution with MEG than in the absence of MEG is due to the high pH value of the test media. The measured pH value of the test media is in the range of 9.5 -10.8 which is high enough to behave as an alkaline solution.

4.7.3.2 Statistical analysis

The results of analysis of variance (Three way ANOVA) for the carbon steels and stainless steels studied in NaCl along with MEG at various time under CO_2, at atmospheric pressure gives significantly higher values for the corrosion rate of carbon steels.The mean corrosion rate of carbon steels was found to be significantly high at 5% level.

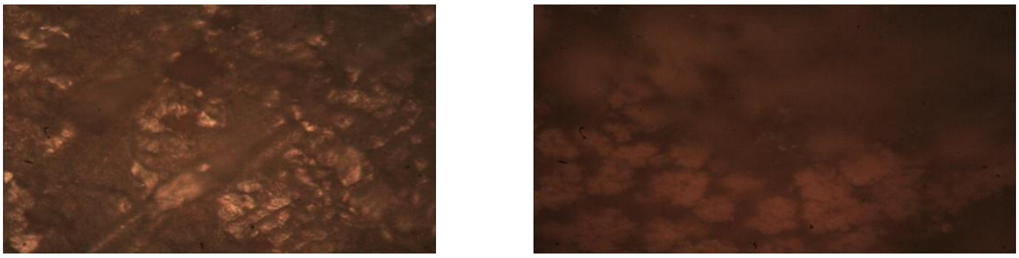
The mean corrosion rate of the selected carbon steels and stainless steels in NaCl along with MEG concentration for various periods of rotation allow us to calculate the most repeated trend of various metals in the test medium. Following the most repeated trend, the corrosion behavior of metals found to follow the order

CS I ~CS 5LX 60 ~ CS 5LX 42 ~ 304 SS > 316 SS

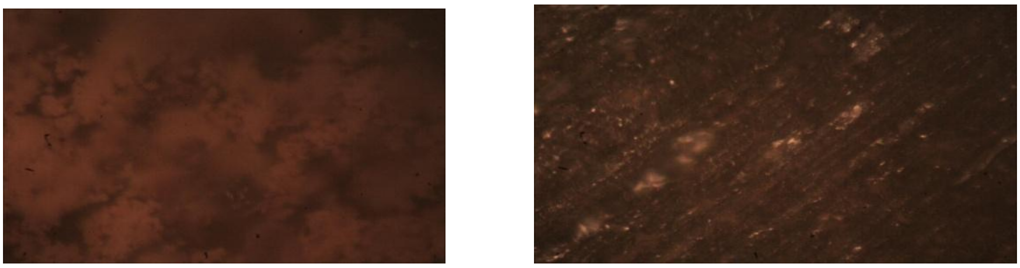
4.7.3.3 Surface Analysis

The optical micrographs of the five different metal samples exposed to NaCl with 4M MEG are presented in the **Figure.**

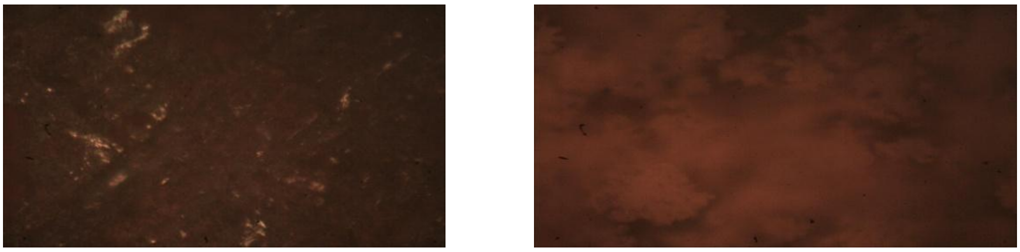
1% NaCl 96 h **30% NaCl 96 h**



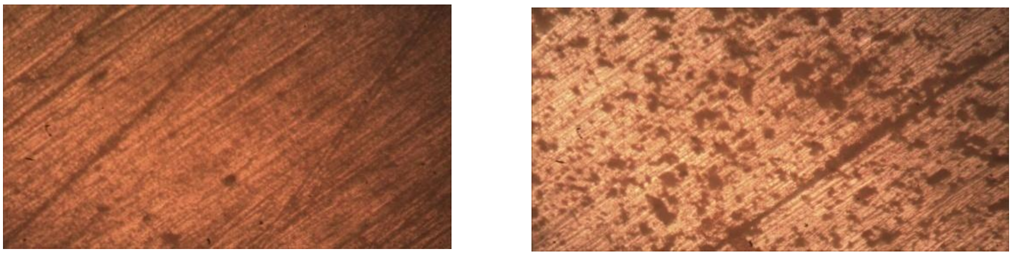
CS I



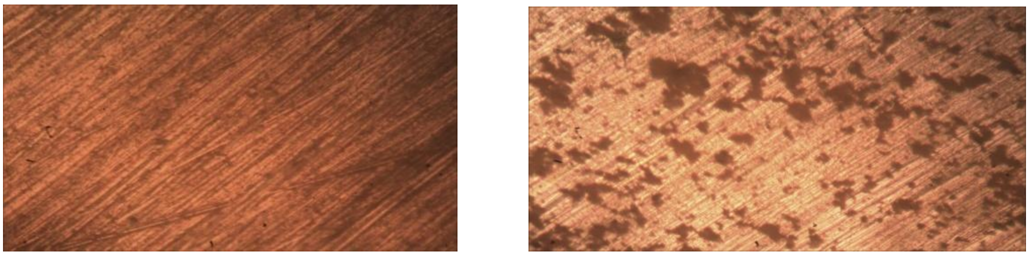
CS 5LX 42



CS 5LX 60



304 SS



316 SS

Figure . Optical micrographs (40x) of the selected samples at 96h

4.7.3.4 SEM and EDS

Carbon steels (CS I,CS 5LX 42 and CS 5LX 60) exposed to 1% and 30% NaCl with 4M MEG for 96 h showed higher corrosion rate than in NaCl. The sample surface was completely covered by corrosion products and minor pitting was also observed. The corrosion products mainly formed in these pits are mainly carbonates and oxides of iron.

Stainless steels (304 and 316) exposed to 1% and 30% NaCl with 4M MEG for 96 h was found to have negligible mass loss. The sample surface was completely covered by corrosion products and minor pitting was also observed. The corrosion products mainly formed in these pits are mainly carbonates and oxides of iron. In addition to oxides and carbonates the chloride also contribute to the bitting of the stainless steel which is observed from the EDS.