Corrosion Studies of Metal Alloys in Carbonated Ionic Liquid Solution

Amita Chaudhary and Ankur Dwivedi*

Abstract— **Low pH of saturated carbonated solvent in carbon capture plants causes serious corrosion to metal surfaces in direct contact. Material corrosion can affect the integrity of a plant since it lowers productivity and raises maintenance costs dramatically. The main regions for metal corrosion in the acid-gas loading sections are the CO2 absorbent storage, absorption unit, lean-rich exchanger, and regenerator unit. Weight loss and electrochemical techniques are used to calculate the corrosion rates of carbon steel, aluminium, copper, and stainless steel in the aqueous solution of 0.1M TETAL solution with 0.5 mol/mol CO2 loading. The corrosion current densities were determined by extrapolating from Tafel plots and using polarization-resistance measurements. A scanning electron microscope (SEM) analysis is also done to observe the change in surface morphology of different metal surfaces. The stainless steel shows minimum change in comparison to carbon steel and aluminium. The measurement findings show that TETAL acts as a corrosion inhibitor in carbonated solutions. On analysing the different metal surfaces, it was found that stainless steel exhibited better resistance in both CO2-rich and lean TETAL. Corrosion rates are also calculated at different temperatures (30, 60, and 90 C). It is observed that increasing the temperature increases the rate of corrosion on metal surfaces. The corrosion rate is calculated using both experimental approaches; the corrosion rate was found to be nearly the same.**

Index Terms— **CO_2 Loading; Tafel plot; Linear Polarization; Corrosion Rate; Ionic liquid; Absorption.**

I. INTRODUCTION

An important environmental issue is global warming, which is a result of excessive CO_2 emissions from the burning of fossil fuels, which average 2.73 million tons per hour due to fossil fuel combustion and the construction sector[1]. Again, after the COVID-19 pandemic, the CO_2 emission rate further increased to 423 ppm at the atmospheric level. In each and every field of R&D, new policies on environment, health, and safety work towards minimising carbon dioxide in the environment. The existing commercial CO_2 capture facilities use aqueous amines and alkanol amines for carbon dioxide absorption at 30% w/w. These solvents face problems like solvent loss, degradation or decomposition of solvents, VOC generation, and causing corrosion to equipment.

The corrosion of equipment material in the working solvent is an area of growing interest. The corrosion of carbon steel, aluminium, nickel, and magnesium alloys depends on the nature of the cation, anion, and experimental conditions, i.e.,
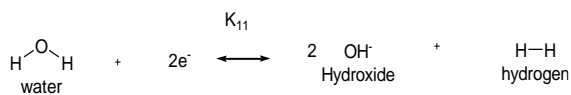
temperature, applied potential, and the concentration of CO_2 in the carbonated solution. Several studies were conducted to determine the corrosion rate of the metal alloys in the CO_2-saturated solution. Pauline et al. used electrochemical techniques to investigate the influence of amines on the corrosion behaviour of CO_2 capture plants[2]. Howlett et al. reveal that the ionic liquid composed of trihexyltetradecylphosphonium and bis(trifluoromethanesulfonyl)amide or bis(2,4,4-trimethylpentylphosphinate) forms the protective layer on the surface of metal alloys, which protects them from corrosion[3]. Another study was done in a pilot plant using a proprietary solvent specified by Toshiba. It was found that the corrosion rate in this solvent was due to the high content of amine[4]. The corrosion behaviour of different metal alloys in seven ILs with different chemical structures was investigated by Uerdingen et al. under flow conditions at high temperatures up to 90 C [5]. They found that ionic liquids act as corrosion inhibitors and protect metals from corrosion[6].

Using combinations of MDEA and piperazine solutions, Zhao et al. investigated the corrosion process in the CO_2 chemical absorption process[7]. Wattanaphan et al. looked at the corrosion of carbon steel in relation to MEA-based CO_2 capture systems[8]. Reddy et al. used electrochemical methods to investigate the corrosivity of several ILs against 1018 carbon steel and 316 stainless steels at normal temperatures [9]. The presence of harmful chloride ions caused them to discover localised corrosion in 1-butyl-3-methylimidazolium chloride. By using electrochemical and weight-loss methods, Perissi et al. determined the corrosion rate in several metals and metal alloys (copper, nickel, brass, Inconel 600, AISI 1018 steel, and so on) in an ionic liquid made of 1-butyl-3-methyl-imidazolium bis-(tri-fluoromethanesulfonyl) imide ($[C_4mim]$ $[Tf_2N]$)[10]. They came to the conclusion that the tested solution's concentration of carbon dioxide rose along with the corrosion rate at high temperatures. As a result, solvents and corrosive-resistant materials are needed for effective CO_2 absorption. Ionic liquid has replaced most of the conventional organic solvents in many applications over the last few decades[11]. Organic salts that are non-volatile and have melting temperatures below 100 °C are known as ionic liquids. Their major constituents are bulky anions and small organic cations. They are chemically and thermally stable. Modifying their moiety or changing their composition helps in customising

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them for use in various applications.

The electrochemical and corrosion behaviour of metals and alloys in various CO_2-philic solvents has been the subject of numerous investigations[12]. Richard claims that redox reactions, ionic transport for the conductive medium, and electron transport between the anode and cathode sites are the four processes that cause corrosion to occur[13]. Research has shown that the presence of dissolved CO_2 in aqueous solutions can cause significant corrosion to the equipment used in the processing and transportation of natural gas and crude oil. Due to the high concentration of absorbed CO_2 and temperature, the absorption column, the lean-rich solvent exchanger, the desorption column, and the overhead condenser are the parts of the carbon dioxide capture plant that are most likely to corrode. On the other hand, a more contemporary model that relies on chemical and electrochemical reactions between tested metal specimens and associated chemical solutions is based on mechanistic descriptions of CO_2 corrosion mechanisms discussed in the reactions involved.

II. EXPERIMENTAL

A. Synthesis of Ionic Liquid Triethylenetetrammonium Lactate (TETAL)

Initially, equal moles of TETA, LA, and water are added in a round bottom flask fitted with a reflux condenser, a pressure funnel, and a mechanical stirrer. Firstly, TETA is taken in a batch reaction flask, and then LA is added to it dropwise using a pressure funnel. During the process, constant stirring is a must at uniform RPM without any vortex formation. In the reaction of acid and base, a lot of heat is produced. So, to reduce the effect of this heat, the reaction flask should be set in an ice bath. The reaction mixture is stirred for 4-5 hours at room temperature. The completion of the reaction can be checked using thin-layer chromatography. The final product is a pale yellow liquid with a viscosity higher than water. Afterwards, the final product was washed 2-3 times with dichloromethane to remove unreacted reactants, followed by vacuum heating at $80\ ^0C$ overnight.

The chemical reaction involved in the preparation of ionic liquid TETAL (Triethylenetetrammonium Lactate) is shown in Fig. 1 [11].

Fig. 1. Reaction involved in the synthesis of TETAL

IUPAC names of the reactants and products:
1. (2R)-2-hydroxy propanoic acid
2. (2-aminoethyl)({2-[(2-aminoethyl)amino]ethyl})amine
3. {2-[(2-aminoethyl)amino]ethyl}(2-azaniumylethyl)amine
4. (2S)-2-hydroxypropanoate

B. Reactions Involved in Corrosion

In an aqueous TETAL-H_2O-CO_2 environment, chemical and electrochemical reactions coexist at the metal-solution interface. There are seven chemical reactions and four electrochemical reactions [12]. The goal of this research is to identify the oxidising agents responsible for corrosion in the H_2O-TETAL-CO_2 system at a fixed temperature and 0.5 moles /mole CO_2 loading. From this determination, we could identify and control the parameters in the system that play a significant role in the corrosion process.

1. De protonation of ionic liquid in the presence of a base, here it is a water molecule, H_2O

2. Regeneration of TETAL carbamate

3. Hydrolysis of carbon dioxide

4. Dissociation of water

5. Dissociation of bicarbonate ion

6. Formation of $M_x(OH)_y$ (Fe, Cu, Al, Ni, Mn)

7. Formation of MCO_3 (Fe, Cu, Al, Ni, Mn)

8. Metal dissolution (Fe, Cu, Al, Ni, Mg)

9. Reduction of hydronium ion

10. Reduction of bicarbonate ion

11. Reduction of water

$$K_{11}$$

H–O–H (water) + 2e⁻ ⟷ 2 OH⁻ (Hydroxide) + H–H (hydrogen)

C. Experimental Procedure

The study setup contains an electrochemical cell containing an aqueous solution of ionic liquid (30%v/v). A three-electrode assembly is used to study the corrosion behaviour of the aqueous solution of TETAL, as shown in Fig. 2. A silver chloride electrode is used as a reference electrode via the bridge tube kept in a test solution. A 2mm distance is maintained between the reference electrode and the working electrode (different metals and metal alloys undergo corrosion studies. The third electrode is the counter electrode; Pt wire is used as the counter electrode in the three-electrode assembly.
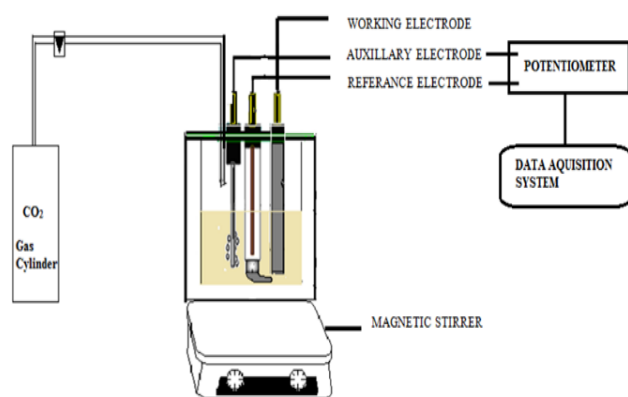
Fig. 2. Schematic diagram of experimental setup

The temperature of the solutions was maintained constant using a water bath with accuracy ±0.1 ºC. A digital MFC is used to check the flow rate of CO_2 gas in the aqueous solution of TETAL. A computer-controlled potentiostat was used to measure corrosion. The experiments were conducted with **NOVA 1.8,** the electrochemistry software from Metrohm Autolab. The specimens of Carbon Steel, Aluminium, copper, and stainless steel were obtained from the central workshop of IIT Delhi in the form of 1.5 cm × 4 cm metal strips. Before testing, the metal specimens were rubbed with 600 and 2000-grit SiC paper, followed by washing with acetone and then with distilled water 2-3 times to remove impurities present at the metallic surface. Then, they dry in the oven at 110 C to remove moisture. The tests were conducted in an open system. All tests were performed at room temperature to determine the corrosion rate. Experiments are also conducted at three different temperatures, 30 ^{C}, 60 ^{C}, and 90 ^{C,} without CO_2 loading, and the results are illustrated in Fig.3. To study the corrosion rate of different metal species in a carbonated ionic liquid solution, Tafel plots are used obtained by autolab instrument using linear progression method at a scan rate of 0.1 mV/s. The resulting tafel plots for different metal specimens are shown in Fig. 4. The graphs are plotted with the applied potential to the measured current. By superimposing a straight line along the linear portion of the anodic or cathodic curve and by extrapolation it through corrosion potential (E_{CORR}), the corrosion current (I_{CORR}) can be calculated using tafel plots. The

point of intersection at E_{CORR} provides the corrosion potential. Tafel constants (β_A) from a fit of the anodic linear region and a cathodic Tafel constant (β_C) from a fit of the cathodic linear region are the slopes of the straight line fitted to the Tafel plot. Equation (2) was utilised to compute the corrosion rate of the alloy in the tested solutions, taking into account the Icorr values.

D. Methods Use for Determining Corrosion Rate

Corrosion Rate for different metals is calculated using two standard methods given by ASTM [13, 14]:

(i)   Weight loss method

$$Corrosion\ Rate(mm.y^{-1}) = \frac{Wt.Loss \times k}{Metal\ density(gcm^{-1}) \times exposed\ area(cm^2) \times exposure\ time(hr)} \quad \dots (1)$$

Where, $k = 8.75 \times 10^4\ cm^2$

(ii)   Electrochemical method using linear polarisation

$$Corrosion\ Rate = \frac{I_{corr} \times eq.wt \times 3.27 \times 10^{-3}}{\rho} \quad \dots (2)$$

I_{corr} = corrosion current density ($\mu A/cm^2$)
Eq.wt = Equivalent weight (g) of metal alloy
ρ = Density of material (g/cm^3)
Corrosion rate = mm year^{-1}

For alloys, their weight fractions can be calculated as:

$$Eqv.Wt = \frac{1}{\sum_{i=1}^{M} \frac{xiZi}{Mi}} \quad \dots (3)$$

Where xi= atomic mass fraction, Zi= electron exchanged and Mi= atomic weight of different constituent metals in the alloy.

3. RESULTS AND DISCUSSION

A. Corrosion Rate Using Electrochemical method

The first experiment was conducted at three different temperatures in an electrochemical cell. The effect of temperature on the polarisation curve of different metals was analysed using the linear polarisation method available in the software NOVA 1.8. the results are displayed in Fig.3 below.

Fig. 4 shows a standard cyclic polarization curve for each of the four metal specimens that were examined in an aqueous solution of 0.1M TETAL solution with 0.5 mol/mol CO_2 loading at ambient circumstances. As the system potential is raised, the curve illustrates the way the metal surface changes from an active to a passive condition.

The corrosion rate (empty) and Icorr (A/cm2) values of all four tested metal alloys are calculated using the electrochemical method also, and the results are tabulated in Table 1.
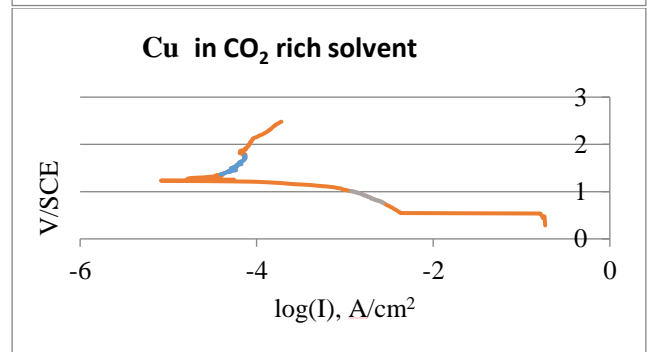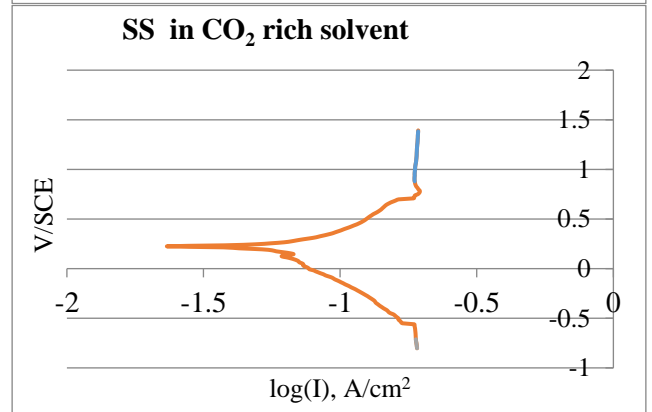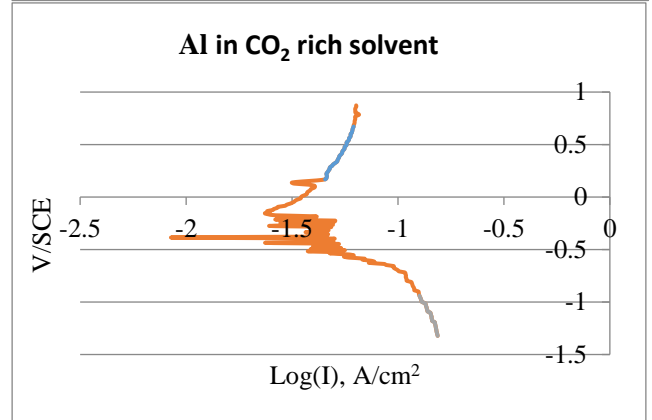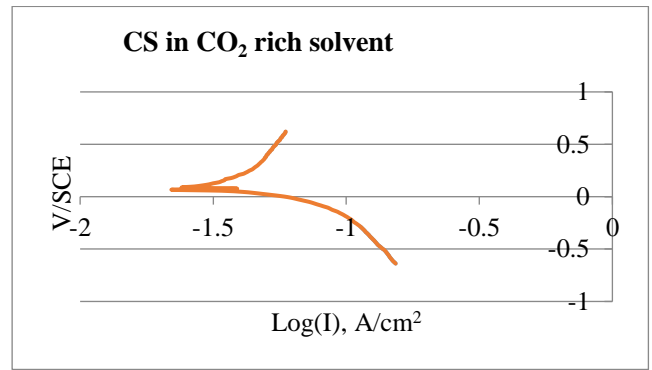
Fig. 3. Linear polarisation curves of different metals in 0.1M TETAL solution at different temperatures
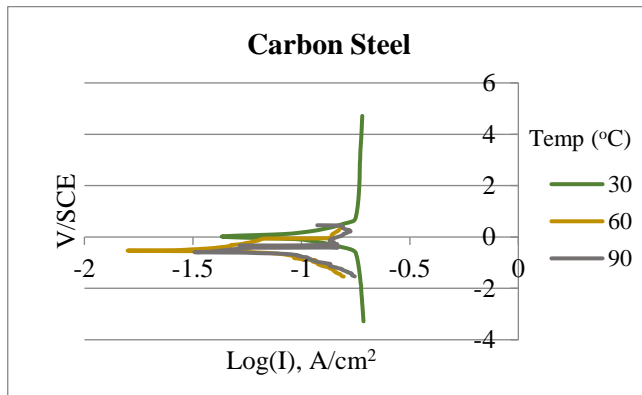

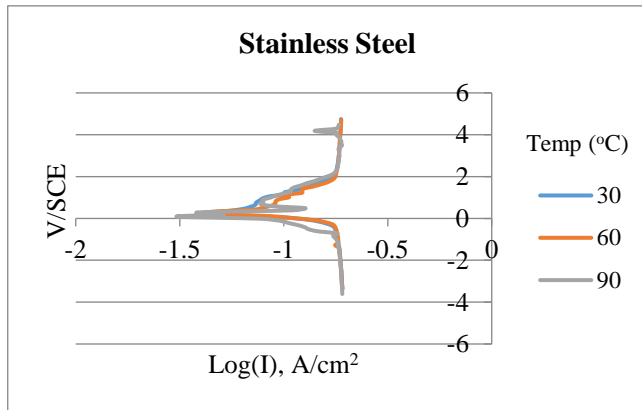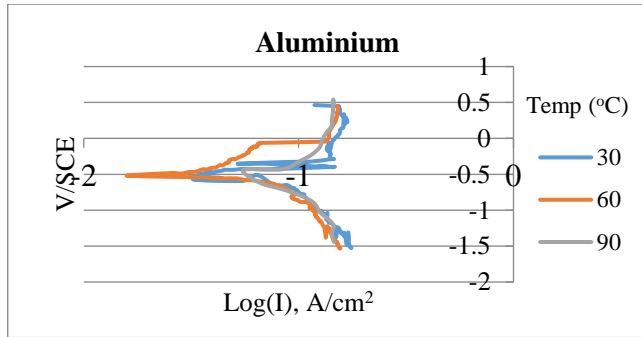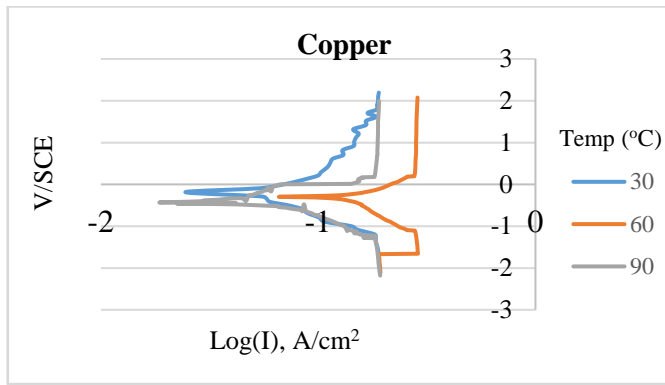**Fig. 4.** Linear polarisation curves of different metals in 0.5mole of CO_2 loading in 0.1M TETAL solution at room temperature.

TABLE I

CORROSION RATES IN DIFFERENT METAL ALLOYS AT AMBIENT CONDITIONS (ELECTROCHEMICAL METHOD)

S. No	Specimens	Eq. wt	Density (kg/m³)	I_{CORR} (A/cm²)	CR (mmpy)
1.	Copper (Cu)	31.7	8.96	3.73	0.043
2.	Aluminum (Al)	8.99	2.7	1.25	0.0136
3.	Carbon Steel (CS)	55.85	7.87	1.22	0.0283
4.	Stainless steel (SS)	56.3	7.89	0.25	0.0058

TABLE 2

CLEANING METHODS FOR DIFFERENT METAL SPECIMENS

S.No	Metal Specimens	Washing solution	Condition	Procedure
1	Steel and Carbon steel	50g $SnCl_2$ + 20g SbC_3	5 minutes at room temperature	Follow with light scrub using non-metallic brush
2	Aluminium	70% HNO_3	5 minutes at room temperature	Follow with light scrub using scrubbing pad
3	Copper	15-20% HCl	5 minutes at room temperature	Follow with light scrub using non-metallic brush

Clean strips are then rinsed in distilled water again and dried in a drying oven for 1 hour at 150 ^{0}C. Dried strips are allowed to cool for about 30 minutes and then weighed. Then, the strips are immersed in a test solution containing 0.5 moles of CO2 per mole of 0.1M TOTAL for 22 days, undisturbed. After the test period, strips are removed and rinsed with tap water to remove residual test solution, allowed to air dry in the oven for 1 hour, and then finally weighed. Then, the corrosion rate is calculated using the weight loss method, as shown in Table 3.

The SEM images are taken at 10x magnification and 20 kV and it is clearly shown in Fig.5, the surface roughness is increased in the order of Aluminum>Carbon Steel> Stainless Steel.

TABLE 3

CORROSION RATES IN DIFFERENT METAL ALLOYS AT AMBIENT CONDITIONS (WEIGHT LOSS METHOD)

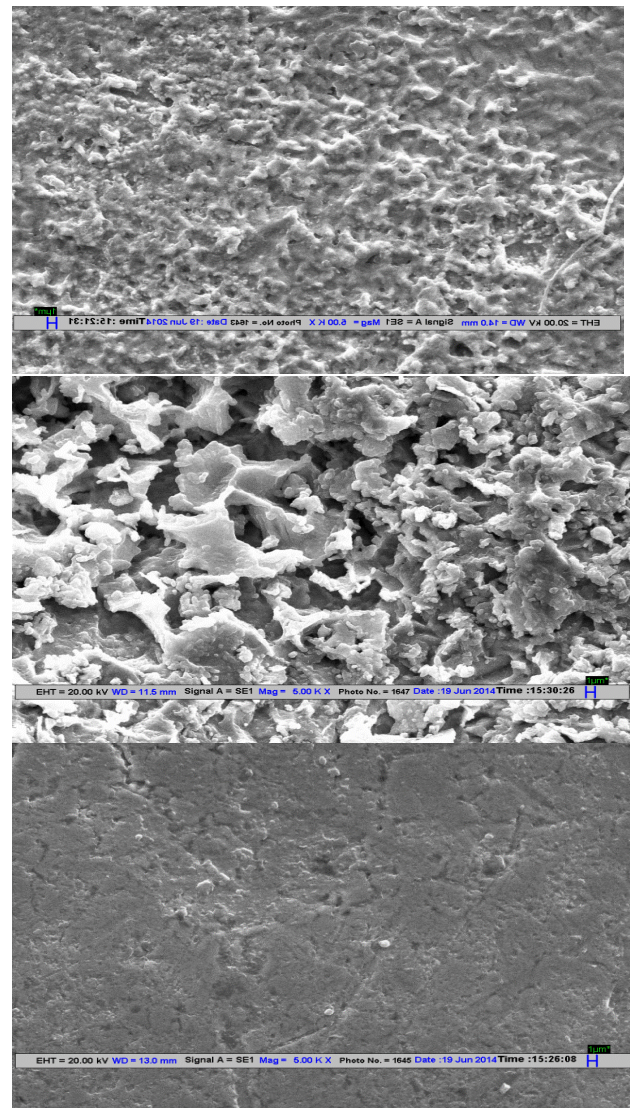| Material	Initial weight (g)	Final weight (g)	Weight loss (g)	Exposed hours (hr)	Exposed area (cm²)	Alloy density (kg/m³)	Corrosion Rate (mmpy)
SS	2.098	2.098	0.001	528	6.75	7.89	0.002
CS	17.027	16.974	0.053	528	12.4	7.87	0.091
Al	3.761	3.555	0.206	528	11.5	2.7	1.099

Fig. 5. SEM images of corroded material surface morphology (a) CS, (b) Al, (c) SS

IV. CONCLUSIONS

The corrosion process of different metal alloys was tested in this work using two standard methods, electrochemical and weight loss methods. The following conclusions are obtained:

I. On increasing the temperature from 303 to 363 K of carbonated TETAL solution, the corrosion rate increases due to the high transportation of ions.

II. The rate of reduction and oxidation is also increased at

the metal-liquid interface resultant in accelerating the corrosion rate.

III.   In the TETAL solution, the corrosion rate is found to be comparatively very low in comparison to amines <0.1 empty.

IV.   So, the studies concluded that TETAL act as corrosion inhibitor by producing a passive coating on metal surface.

It has been found that stainless steel 304 shows better resistance to uniformed corrosion in a carbonated ionic liquid solution at room temperature. So, by transforming the conventional amines into ionic liquids, the corrosion rate can decrease, as proved in these studies. Further studies can be done to prove the mechanism of corrosion resistance TETAL at high temperatures.

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