3

MATERIALS AND METHODS

3.1 Selection of metals

Based on the literature survey carried out on the material composition for oil and gas industries, carbon steel and stainless steel have been selected as the materials for this study. Carbon steel is the primary material of choice in many capture plants and for gas piping mainly due to its cost effective factor especially when the pipeline transport distances are long. The redeeming factor for the use of carbon steel is that the exposed steel surface can become covered by a protective layer of corrosion products, mineral scale or inhibitors. Corrosion-resistant stainless steel is used mainly for the pipe line applications with high concentrations of carbonic acid, particularly in turbulent flow areas such as downstream of control valves or near pumps.

Coupons of three different carbon steels namely Carbon steel I, Carbon steel 5LX42, Carbon steel 5LX60 and two types of stainless steels (304 & 316 Stainless steels) of dimensions 7.5x1.9x0.3cm used in the present study were supplied by CANMET materials and Technology, Canada.

The as received metals were polished with fine quality silicon carbide (SiC) emery sheet (400 grits) prior to being tested. After polishing, specimens were washed with distilled water, dried and stored in a desiccator for use. The chemical composition and density of the materials used for this study are presented in Table 1.

Table 1. Composition and Density of the materials

Element	% Composition				
	Carbon steel I	Carbon steel 5LX42	Carbon steel 5LX60	304 Stainless Steel	316 Stainless Steel
Al	0.023	0.033			
Sn	<0.005	0.033			
Pb	<0.01				
Si	0.018	0.26	0.27	0.46	0.2555
Ni	0.014			8.08	10.0150
Fe	99.559				
Mn	0.27	1.04	1.38	1.80	1.5880
P	0.009	0.011	0.016	0.034	0.0360
S	0.005	0.001	0.004	0.0004	0.0020
Co	<0.005				
Cu	0.030	0.01		0.48	0.4495
Ti	<0.002	0.003			
Cr	0.019	0.011		18.26	16.7910
V	<0.005	0.062	0.004		
C	0.049	0.15	0.007	0.027	0.0210
Mo	0.002	0.002		0.43	2.0090
Nb	<0.001				
B	<0.0005	0.0001			
Zr	<0.005				
Ca	0.002	0.002			
N		0.004		0.07	0.0493
Cb		0.002			
Density (g/cm^3)	7.87	7.87	7.87	7.94	7.98

Solvents used for the present study are Monoethanol Amine (MEA) and Monoethylene Glycol (MEG) of AR grade.

3.2 Mass loss method

Mass loss analysis, a direct measure of corrosion is the simplest and longest established method of estimating corrosion losses in plant and equipment. A weighed sample of the metal or alloy under consideration is introduced into the process and removed after a reasonable time interval. The coupon is then cleaned of all corrosion products and reweighed. The mass loss is converted to a total thickness loss, or average corrosion rate using proper conversion equations.

Methodology

3.2.1 Rotating Cage method

Rotating Cage is a promising and reliable method to simulate pipeline flow under laboratory conditions by rotating the specimens at speeds up to 1500rpm.This methodology may be used to evaluate the corrosion rate of eight metals simultaneously. Rotating Cage is

- Inexpensive
- Compact
- Hydrodynamically characterized
- Provides various flow conditions

ASTM G184-06 provides the standard practice for using rotating cage.

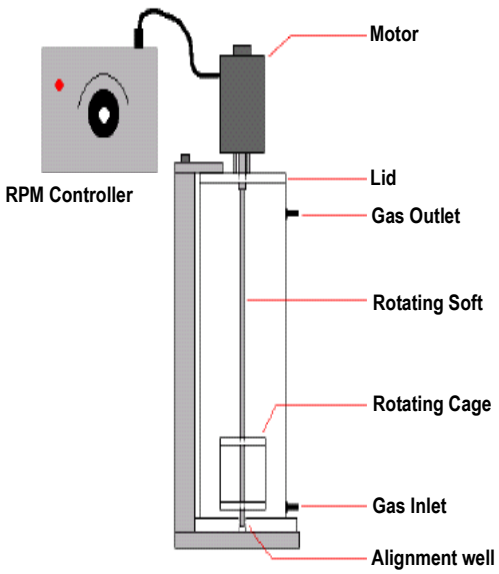

Figure 7. Schematic diagram of the rotating cage

Figure 7, shows the schematic diagram of the rotating cage systems which was fabricated in accordance with the ASTM standards. The vessel (typically150mm diameter) is manufactured from acrylic. A PTFE base is fitted at the bottom of the container. At the centre of the base, a hole is drilled into which the lower end of a string rod is placed to stabilize the stirrer and coupons. Typically, eight coupons (each of 15mm length, 19mm width and 3mm thickness, and a surface area of about 34.14cm^2) are supported between two PTFE disks (of 80mm diameter) mounted 75mm apart on the stirring rod.

Depending on the rotation speed, the volume of the container and the fluids used, the flow pattern can be classified into four zones and are pictorially represented in figure 8 **(ASTM G170-1a).**

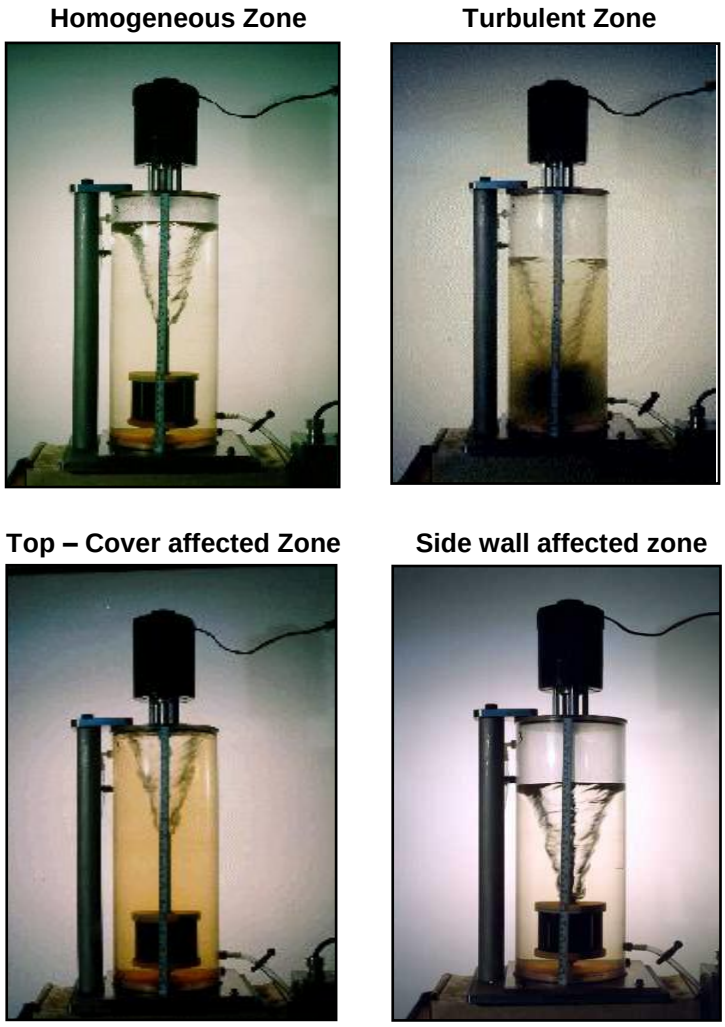

Figure 8. Flow patterns in rotating cage

1. **Homogeneous Zone:** Vortex dimensions that have been observed increases with rotation speed.

2. **Side-wall affected Zone:** Vortex length increases, but the width has reached the side and collides with the wall.

3. **Turbulent Zone:** Vortex length penetrates into the rotating cage unit and creates turbulent flow.

4. **Top – Cover affected Zone:** The liquid level oscillates and rises to the top, pushing the flow pattern due to the backward movement of the fluids,and changing the flow pattern.

Prior to the experimental studies in rotating cage**,** the instrument was standardized using synthetic ocean water as per ASTM **D 1141.**

3.3 Preparation of Reagents

3.3.1 Preparation of substitute ocean water (for 10.0 L)

About 245.34g of NaCl was dissolved in 9L of water followed by the addition of 40.94g of anhydrous sodium sulphate to this solution. 200ml of stock solution # 1 which consists of 555.6g/l of $MgCl_2.6H_2O$, 57.8g/l of $CaCl_2$ (anhydrous) and 2.1 g/l of $SrCl_2.6H_2O$ was added to the above solution. To this solution 100ml of stock solution # 2 containing 69.5g/l of KCl, 20.1 g/l of $NaHCO_3$,10 g/l of KBr,2.7 g/l of H_3BO_3 and 0.3g/l of NaF. Finally the solution was made up to 10 litres. The pH of the solution was adjusted to 8.2 using 0.1NaOH.

Throughout the study a constant volume of four litres of test solution was taken. All the solutions were prepared in deionised water. The test media used for the present investigation were

- NaCl solution – 1%, 5%, 15% and 30% concentrations.
- 4 M MEA solutions in NaCl (966ml of MEA+3034ml of NaCl solution of 1,5,15 and 30% concentrations).
- 4 M MEG solutions in NaCl (892ml of MEG+3108ml of NaCl solution of 1,5,15 and 30% concentrations).

Test solutions were deoxygenated by passing nitrogen gas for 4hours to reduce the oxygen content followed by pre-saturation of the solution with CO_2 for 4 hours at the rate of 4bubbles/second (to ensure proper deoxygenation and pre-saturation as per ASTM G 202 procedure) and the solutions were kept under deoxygenated conditions.

For the study with 4M MEG, an additional impurity of oxygen was also considered. Therefore, the test solution was oxygenated for 4 hours and then followed by pre-saturation of the solution with CO_2 for 4 hours at the rate of 4bubbles/second.

3.4 Experimental Procedure

Experiments were carried out using the atmospheric Rotating Cage to evaluate the corrosion of all the metals. ASTM standards G170, G184, and G202 provide detailed descriptions of this methodology and a procedure to conduct rotating cage experiments.

The experimental setup is shown in Figure and (b). Experiments were performed in a Rotating cage with 4 litres of deareated and pre CO_2 saturated NaCl solution. Eight identical coupons of dimensions 7.5 x 1.9 x 0.3cm were supported between two PTFE disks (of 80-mm diameter) mounted 75 mm apart on the stirring rod.

Inlet 2 of rotating cage was closed initially and inlet 1 was connected to the container of the prepared NaCl solution. The solution was pumped into the apparatus without allowing the entry of oxygen and then the inlet 1 should be closed. This time is considered as the start of the experiment. Now through the inlet 2 a continuous blanket of CO_2 was maintained through the apparatus throughout the experiment in order to avoid oxygen contamination. The speed controller was used to set the rotation speed and was kept constant at 500rpm. Each experiment was run for 24, 48, 72 and 96 hours for 1%, 5%, 15% and 30% of NaCl concentrations under CO_2 environment. The coupons were then washed with distilled water dried and reweighed.

Methods for preparing specimens for tests and removing specimens after the test were followed as described in ASTM G 1-90.

Figure 9. (a) Rotating cage at constant 500rpm

Figure 9. (b) Samples mounted between PTFE disks

3.5 Measurement of pH

After the completion of each run with various parameters, the pH of the solution was measured using pH meter of ADWA Model 1030.

3.6 Corrosion Rate

The loss in mass was determined and average results from three specimens were reported. The corrosion rate was calculated as per ASTM G1 standard using the following formula.

$$\text{Corrosion rate (mpy)} = \frac{3.45 \times 10^6 \times \text{mass loss (grams)}}{\text{Density (g/cm}^3\text{)} \times \text{Area (cm}^2\text{)} \times \text{Time (hours)}}$$

3.7 Surface Morphology

The change in surface morphology of the samples after the exposure to different test media was characterized by metallurgical microscopy and scanning electron microscopy.

3.7.1 Metallurgical microscope

After the exposure to the different test media for a specific period of rotation, the metals were washed with water and then rinsed in acetone and dried. The corroded surface of carbon steel I, carbon steel 5LX 42, carbon steel 5LX 60, 304 SS and 314 SS coupons and their polished samples were characterized by inverted metallurgical microscope KOZO optics model XJM 404T.

3.7.2 Scanning electron microscopy

One common method to investigate the nature of corrosion products is SEM analysis. The appearance of the coupons at the end of the mass loss study was recorded by scanning electron microscope. For SEM analysis, the samples after washing with water and rinsing with acetone to remove excess moisture on sample surfaces were dried using compressed air. The samples are typically mounted in low-shrinkage epoxy under vacuum prior to grinding and polishing to 0.05µm using colloidal silica.

Figure 10

Scanning Electron Microscope

The mounted specimen is then coated with a thin layer of palladium for electronic conduction purposes prior to SEM examination. Samples were put in a FEI NanoSEM 650 Scanning Electron Microscope equipped with a light element Energy-dispersive X-ray detector (EDS) for composition analysis in and away from the corrosion pits. Secondary electron images were collected along with EDS spectra from various locations on each specimen. The metal samples subjected to 96 hours in the lowest and highest concentration of different test media studied were analyzed.

3.7.3 Statistical Analysis

Three way ANOVA was done for the experimental results for different metals, test media of various concentrations and period of rotation at a 5% level of confidence in order to determine the significance of the three variables – metal type, concentration of the solutions and period of rotation on the corrosion rate using AGRES STAT Software version 7.01.