CHAPTER III
EXPERIMENTAL

In this chapter, the experimental set-up for hydrogen permeation through the bare and platinum-filmed carbon steel tube is described. Details of all components including the materials and chemicals, equipments and experimental procedure follows.

3.1 Materials and Chemicals

- Carbon steel tubes, ASTM A179
- Hydrogen gas (Air Liquide Canada INC., Commercial grade)
- Hydrochloric acid (Fisher Scientific, Reagent grade 36.5-38%)
- Methanol (Fisher Scientific, A.C.S. Reagent grade)
- Acetone (Fisher Scientific, A.C.S. Reagent grade)
- Chloroplatinic acid hexahydrate (Sigma-Aldrich, A.C.S. Reagent grade)
- Sodium hydroxide (Fisher Scientific, A.C.S. Reagent grade 98.4%)
- Ethylamine anhydrous (The British Drug house, Laboratory reagent grade)
- Hydrazine monohydrate (Sigma-Aldrich, Reagent grade 98% N_2H_4 64-65%)

Tubing of carbon steel ASTM A179 was used for hydrogen permeation experiments. The chemical composition of carbon steel ASTM A179 as obtained from Metals Handbook, is shown in Table 3.1.

Table 3.1 Chemical composition of carbon steel ASTM A179

Element	Mass fraction (%)
Fe	Balance
C	0.06-0.18
Mn	0.27-0.63
Si	-
P	0.05
S	0.06
Cr	-

There were two sets of experiments conducted. One was using the bare carbon steel tube as a diffusing medium and the other was using the platinum-filmed carbon steel tube as a diffusing medium. The carbon steel tubes, 9.525 mm outside diameter and 1.651 mm wall thickness, were used for each set of experiments.

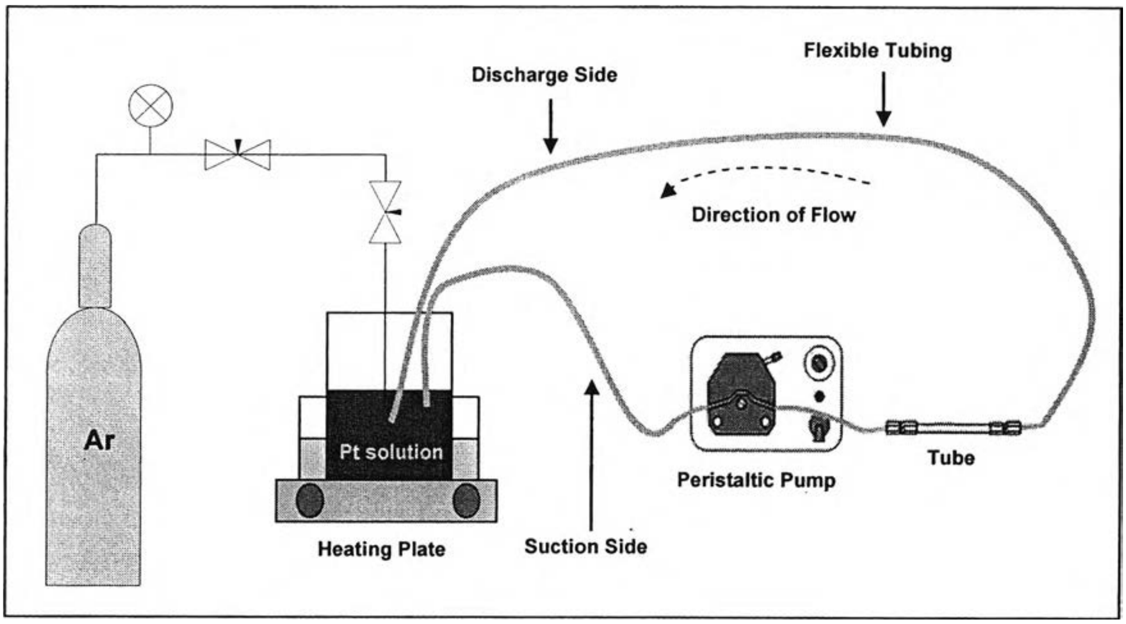
3.2 Equipment

The carbon steel tubes, ASTM A179, used in hydrogen permeation experiment had a 90° bend and were capped at one end with a Swagelok fitting. The other end of the tube was connected to a pressure gauge and a valve. The furnace is under trademark of Thermolyne; 120 Volts 50/60 Hertz 15 Amps and 1800 Watts. The peristaltic pump is under the trademark of Masterflex; 3 Amps 115 Volts 50/60 Hertz.

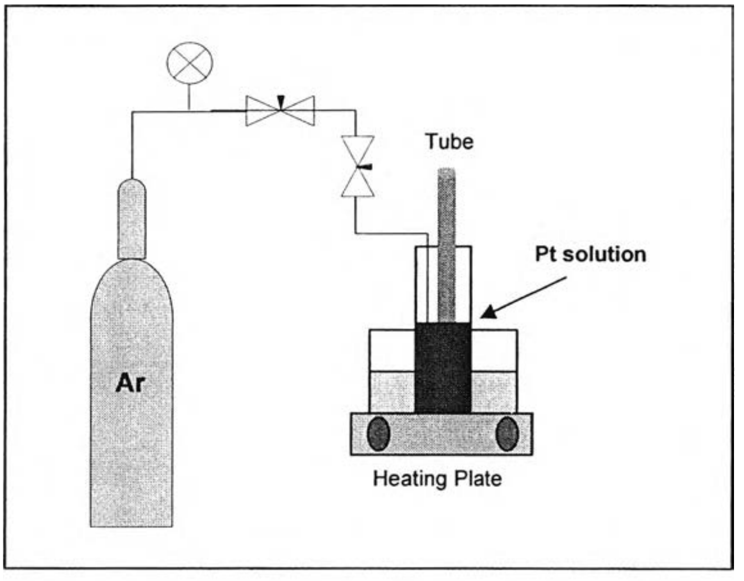
3.2.1 Coating Platinum on Carbon Steel Tube Surface

A flow procedure was used to coat platinum on the inside surface of the carbon steel tube. At a flow rate of 13 ml/s, prepared platinum solution at 35°C was passed through the carbon steel tubes in the test section as shown in Figure 3.1a. The solution was purged with Ar gas before starting to coat the tube surface so that during the coating the tube surface was free of oxygen in both the solution and the atmosphere.

The coating of platinum on the outside surface of the carbon steel tube was performed in a glass cylinder at 35 °C. Figure 3.1b shows a schematic diagram of the platinum coating procedure. In order to minimize the concentration of oxygen in both the solution and atmosphere, the Ar gas was purged into the prepared solution before and during the coating of platinum on the tube surface.



(a)



(b)

Figure 3.1 Schematic diagram for coating platinum on the surface of carbon steel tube (a) coating platinum on the inside surface (b) coating platinum on the outside surface.

3.2.2 Filmed Carbon Steel Tube Characterization

For the characterization of the coated carbon steel tubes, there were four types of equipment. Firstly, a Field Emission Scanning Electron Microscope (FESEM) was used for investigating the surface morphology. Se condly, Energy Dispersive Spectrometry (EDS) was used to determine the chemical composition of the surface. Thirdly, XRD analysis was used to identify the types of platinum film form on the surface. Finally, a Raman Microscope was used for identifying the types of oxide film formed on the platinum-filmed surface.

FESEM analysis was carried out in a Field emission SEM (Schottky electron gun) Hitachi SU-70 equipped with EDS. The EDS analyses were obtained from X-Act silicon drift X-ray detector with INCA Synergy software. FESEM images were collected with an accelerating voltage of 15kV and the beam current was approximately 3nA. The images and EDS data were obtained from FE-SEM lab housed at Planetary and Space Science Centre, University of New Brunswick.

XRD analysis was done on a Bruker AXS D8 Advance with a Cu anode X-ray tube. Scans were from 5 to 90 degrees 2-theta, 0.5-second counts at 0.02 degree steps.

Raman Spectroscopy was conducted in a Renishaw In Via Raman Microscope. The operating condition was 4-5 milliwatts of laser beam focused on the sample.

3.3 Experimental Procedures

The summarized procedure is shown in Figure 3.2. There were three main parts – hydrogen permeation experiments using bare carbon steel tubes with surface and kinetic barriers to hydrogen mass transfer by oxide films; experiments using platinum-filmed carbon steel tubes to eliminate surface resistances; and, characterization of the platinum-filmed carbon steel tube.

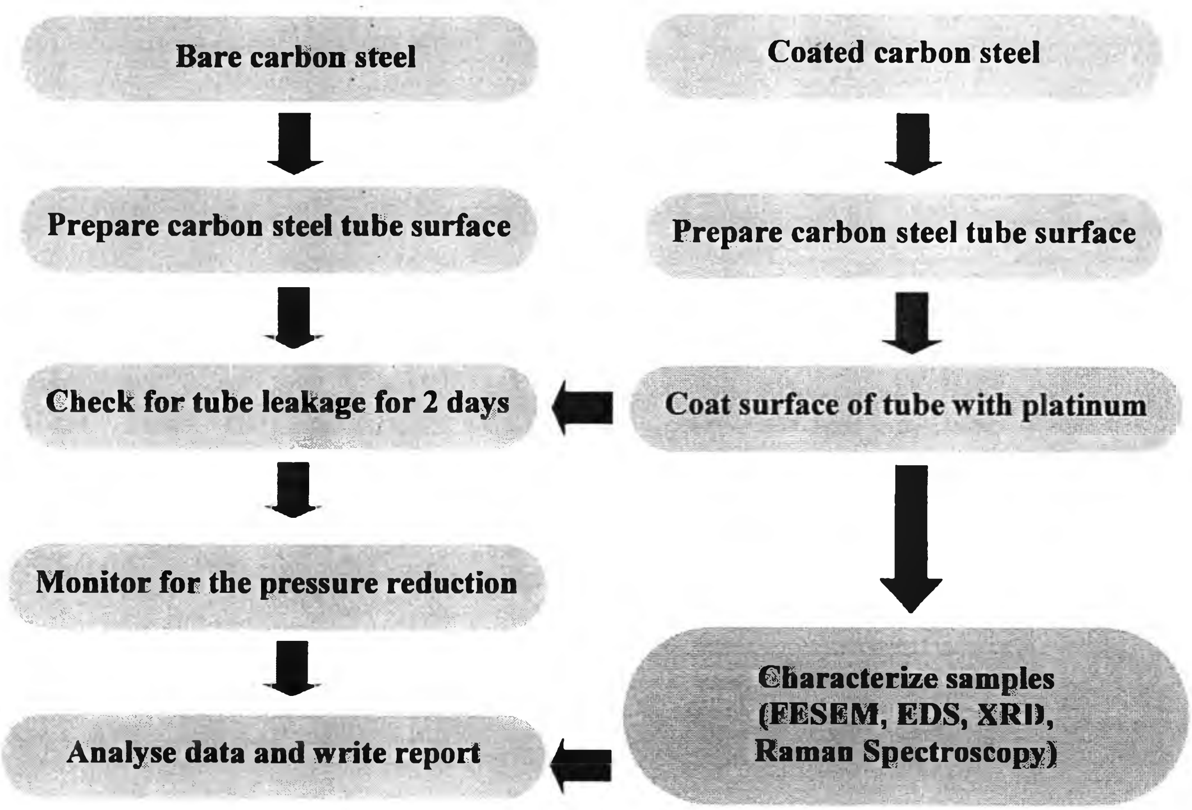


Figure 3.2 The summarized procedure for the experiments.

3.3.1 Hydrogen Permeation Experiment Using The Bare Carbon Steel Tube

• *Preparation of the carbon steel tube surface*

The carbon steel tube, ASTM A179, was cleaned before use in order to eliminate the oxide film that forms on the outside and inside steel surface. Accordingly, the tube was polished with 600 grit sandpaper on the outside surface and acid cleaning or pickling was performed on the inside surface. The equipment for acid cleaning is shown in Figure 3.3. The solution used was 10%HCl (v/v) solution. The acid was circulated through the tube for 5 minutes. Then deionized water (first rinse) was circulated through the tube for at least 5 minutes following by the second rinse of deionized water for at least 5 minutes. The tube was flushed thoroughly with fresh deionized water to ensure complete removal of the acid from both the inside and outside surfaces of the tube. The surfaces were then washed with methanol and acetone and blown dry with argon. Finally the tube was stored in a desiccator purged with argon gas.

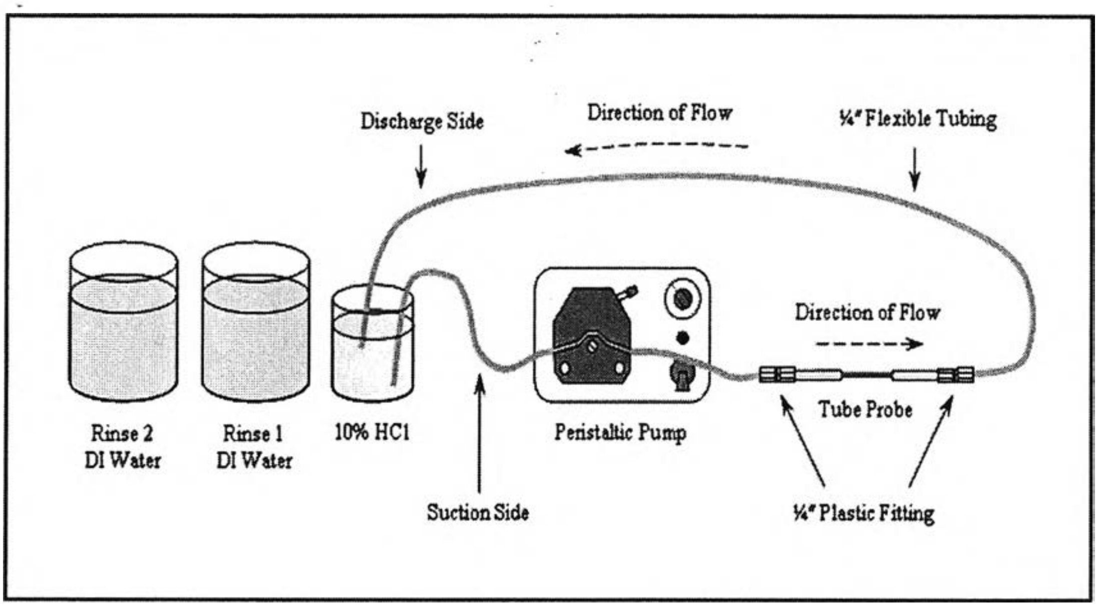


Figure 3.3 Schematic of the experimental setup for acid cleaning.

• *Checking for tube leakage*

After the tube was cleaned, all fittings were installed on the tube as follows. The carbon steel tube was capped at one end with a Swagelok fitting. The other end was connected to a pressure gauge and a valve as shown in Figure 3.4. The tube was charged with 100 psig of hydrogen gas for monitoring the reduction in pressure at room temperature for two days.

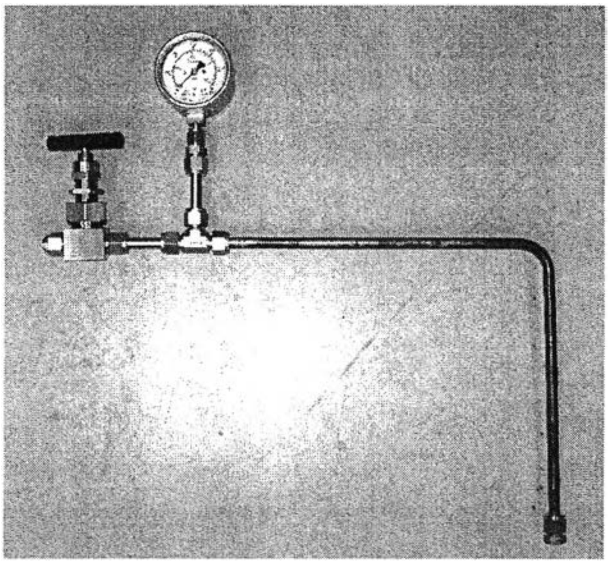


Figure 3.4 Carbon steel tube in the hydrogen permeation experiment.

• *Monitoring for the pressure reduction*

The position of the hydrogen-filled tube below the bend (see Figure 3.4) was placed in a furnace. The temperature of the furnace was gradually increased from room temperature to the temperature of interest. A K-type thermocouple was installed on the tube surface at the middle of the tube below the bend to measure the surface temperature of the tube during the experiment. The change in pressure inside the tube was recorded. The hydrogen diffusion rate and hydrogen diffusivity were determined from the reduction in pressure with time.

3.3.2 Surface and Kinetic Barrier to Hydrogen Mass Transfer Experiment

The experiments in this part were carried out in the same manner as those in the previous part for the hydrogen permeation experiment except that platinum was coated on the tube surfaces.

• *Preparation of carbon steel tube surface*

Before coating a tube surface, the tubes were prepared by using sandpaper and acid cleaning in order to eliminate the oxide film that forms on the outside and inside surfaces, as described in section 3.3.1.

• *Coating carbon steel tube surface*

The surface of the tube was coated by using hydrazine as a reducing agent in the platinum solution under the conditions of 35°C, following the procedure of Rhoda and Vines, 1969, described in Chapter II. The tubes were placed in the test section of the loop for 3 hours under flow conditions.

• *Hydrogen permeation experiment*

The experiment in this section was carried out in the same manner as the hydrogen permeation experiment; installing all fittings on the tube, charging with 100 psig of hydrogen gas and checking for tube leakage. The platinum-filmed tubes were used to investigate the effect of the platinum layer on hydrogen transport through the carbon steel.

3.3.3 Sample Characterization

The platinum-filmed tube cannot be directly analyzed. The filmed tube needs to be cut before the platinum layer formed on the inside and/or outside surface of the tube can be characterized. After the cut tubes were prepared, the platinum layers formed on the tube samples were evaluated by both visual inspection and surface characterization techniques.

The FESEM microscopy, EDS analysis and XRD analysis were performed on samples cut off the platinum-filmed carbon steel tube. The Raman Spectroscopy technique can change the phase of tube oxides because of the laser beam focused on surface. Therefore, the tube samples were characterized by this technique after other characterization techniques were completed.