CHAPTER I
INTRODUCTION

Corrosion of materials in elevated temperature aqueous environments is a significant problem in many industries. Stress-corrosion cracking (SCC) of primary system components in the nuclear industry is a serious problem, which has resulted in extensive plant outages and costly equipment replacement and repair. Recent examples of intergranular stress corrosion cracking (IGSCC) have occurred in operating boiling water reactor (BWR) piping (Indig, 1990), as well as cracking in in-core components of LWR's due to a combination of stress, radiation and a high temperature environment (Bosch *et al.*, 2004).

Over the years, an important application of high-temperature aqueous electrochemical technology has been understanding and controlling the environmental aspect of stress-corrosion cracking in nuclear reactors. It is of significant interest to understand corrosion mechanisms in order to help minimise corrosion problems. One of the key parameters for determining the corrosion behaviour of materials is the electrochemical corrosion potential of a metal or alloy exposed to aqueous solution. In order to investigate the electrochemical properties of materials in high temperature and pressure systems, suitable reference electrodes compatible with the operating conditions and system chemistry are required. There are several references available in the open literature where potentiometric techniques were used at temperatures up to about 450 °C (Macdonald *et al.*, 1992; Ito, *et al.*, 1995; Lvov, *et al.*, 1999; Kim and Andresen, 2003). Presently, two approaches have been employed for potential monitoring at elevated temperatures:

1) The use of an internal reference electrode operating within the high temperature environment.

2) The use of an external pressure balanced reference electrode (EPBRE) in which the electroactive element is kept at room temperature and connected to the high temperature test solution by means of a salt bridge.

The use of an external pressure-balanced reference electrode has received considerable attention and shall be considered in detail. Macdonald (1998) explained the main requirements to achieve the most suitable reference electrode for high temperature aqueous systems. Improvements in the silver/silver-chloride electrode have permitted electrochemical measurements in reactor piping systems and recently in the high radiation fields of the reactor core (Indig, 1990). Even though much research focused on developing high-temperature reference electrodes has been done over the past few decades, further work is needed since none have been made to withstand temperatures greater than 573 K (300 °C) for an extended period of time. It is observed that the higher the operating temperature, the greater the problems associated with reference electrode stability. Some problems include; destruction of the insulating polymer body, the stability of the reference electrode itself, and the difficulty in calculating the high-temperature reversible-electrode potential (Dobson *et al.*, 1971). Therefore, the goal of this work is to construct a reference electrode that has a long service life as well as a maximum operating temperature above those that are currently employed.

The main objective of this research is the first step toward this goal; the testing of the reproducibility and performance of the electrode up to 573 K. The work started with designing, constructing, and testing a high temperature reference electrode, which includes a correction for the thermal liquid junction potential. The silver/silver-chloride (Ag/AgCl) electrode was chosen for its ease of construction compared to other types of reference electrodes. The electrode was designed to maintain the electroactive element at low temperature in order to avoid thermal decomposition of the silver-chloride.

The stability of the electrode was examined by means of experiments conducted in a one litre titanium autoclave. The potential difference versus the standard hydrogen electrode (as deduced from a measurement against a reversible hydrogen electrode – i.e. Pt wire) was continuously monitored with increasing temperature. Comparing theoretical and experimental values verified the reliability and integrity of the electrode.

The correlation for correcting the measured potential versus the Ag/AgCl reference electrode onto the standard hydrogen electrode scale (SHE) was determined. A correction potential, E^{*}, was purposed by comparing the measured Ag/AgCl electrode potential with the theoretically calculated value to account for liquid junction potential (LJP), thermal liquid junction potential (TLJP), and all potentials due to temperature effects. The corrected potential was evaluated by the potential measurement of a carbon steel coupon against the Ag/AgCl reference electrode.