4. ANALYTICAL METHOD

Electrochemical method was chosen because of its simplicity, high accuracy and high repeatability. The only requirement was that the collector test section had to be electrically non-conducting. HDPE was selected as standard pipes were available and extrusion or butt welding technique could be employed. Further, the use of small electrodes do not obstruct the flow.

4.1 Principle of Electrochemical measurement

The electrochemical method followed in the present work is similar to those employed to study mass transfer, for example, Shaw and Hanratty (1964), Lin et. al (1951), Aggarwal and Talbot (1979). The method involves essentially applying a DC potential across a pair of electrodes immersed in an indifferent electrolyte containing reacting ions. The pair of electrodes comprises of a small electrode (cathode) and a relatively large electrode (anode).

In the present case, the small electrode or the cathode called the test electrode, was made of a copper wire 1.4 mm in diameter. It was mounted in the HDFE pipe such that 3mm was projecting inside the pipe. The larger electrode or the anode, called the reference electrode, was made of copper pipe 50 mm nominal diameter and 60 mm long. The electrolytic solution chosen was 0.5 N NaOH, as the indifferent electrolyte, and equimolar (0.01 N) concentration of reacting species of potassium ferro- and ferricyanide.

When DC potential is applied, the reactions at the electrode involves two steps : movement of ions from the bulk of the solution to the surface of the electrode, and chemical and physical changes occuring at the surface the electrode. When the first step becomes rate determining in the electrode process, the conditions are those resulting in the so-called concentration polarisation. Movement of ions between the bulk of the solution and the electrode-solution interface can occur in two ways - diffusion due to concentration gradient at the electrode, and ionic migration due to the potential field. In a stagnant solution, the steady rate of discharge for a certain species of ions, in the present case ferricyanide, can be expressed as follows :

$$\frac{i}{n_i F A} = -DL \frac{dC}{dx} - C u \frac{d\phi}{dx} \qquad (4.1)$$

The first term on the right hand side of the equation represents the rate of diffusion due to concentration gradient and the second term accounts for the rate of ionic migration.

Ordinarily, a stagnant solution cannot be obtained experimentally because of natural convection, so that the problem is complicated by solution movement. A quantitative treatment is difficult due to indefinite thickness of diffusion layer in contact with the electrode. If the effect of ionic migration is eliminated, the electrode process becomes simpler and is amenable to quantitative treatment.

In order to eliminate the effect of ionic migration, an indifferent electrolyte, in the present case sodium hydroxide, is added. The indifferent electrolyte does not react at the electrode, is present in relatively high concentrations and has high conductivity in comparison with ferro- and ferricyanide ions reacting at the electrodes. There will be then no sharp potential gradient at the electrode. Since the conductivity is high, $d\phi/dx$ will be approximately zero, and the ionic migration term can be neglected.

For the present study the reduction of ferricyanide ion in a sodium hydroxide solution on a copper electrode results in the following reactions at the electrodes:

At the cathode, $Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-}$ (4.2)

At the anode, $Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + e$ (4.3)

The electrode reactions are very rapid and electrode materials are inert to the solution. There is diffusion both of the reacting materials towards the electrode and of the reacted material back towards the solution. The integrated form of eqn (4.1) neglecting the migration term can be expressed as :

$$\frac{i}{n_i F A} = \frac{D_L}{B} (C - C_s) = k_L (C - C_s) \qquad (4.4)$$

When the limiting value of I_l,the polarisation current, is reached on a polarised electrode, on increasing the DC potential, C_s becomes zero, i.e. when ferricyanide ions react at the surface at a rate equal to their maximum rate of transport to the surface. When the current asymptotes to the limiting value, an increase in DC potential does not affect this value, untill a second regime is reached when hydrogen is liberated from the cathode causing further increase in the current. All experiments were done under limiting current conditions in the absence of hydrogen liberation. When dilute solutions of ferrocyanide and ferricyanide are used, eqn 4.2 will be valid.

Lin et. al (1975) observed that limiting current is affected by the flow rate of the electrolytic solution. In fact the polarisation curve becomes steep beyond a certain flow rate (for oxidation of ferro-cyanide and quinone reduction) such that the constant limiting current value is no longer observed. The flow rate at which this occurs is termed as the 'critical flow rate'. For reduction of ferricynaide the critical flow rate occurs at a very high Reynolds number. Lin further observed that the limiting current relationship with the flow rate (or Reynolds no.) is affected by the ferricynaide concentration and temperature. The effect of concentration can be appreciated from eqn 4.4 also, which implies that the limiting current is proportional to the concentration. Temperature affects the diffusivity and thus the limiting current.

Based on Lin's observation, it is, therefore, possible to correlate the flow rate or velocity in the collector riser tubes with the limiting current. Once this relationship is known, it is possible to measure flow distribution in a collector comprising of several riser tubes in parallel by measuring the limiting current. The relationship between flow rate and limiting current is obtained in Chapter 5.