CHAPTER III
EXPERIMENTAL SECTION

3.1 Coreflood experiment

A coreflood experiment was conducted to examine the effects of mass transport and surface reaction rate on wormhole formation in limestone. These parameters were modified by changing the fluid types, and pH. This investigation emphasized the relation on the Damköhler number and the wormhole structure. The injections were conducted with an organic acid, 0.5M acetic acid, 0.5M formic acid, and 0.5M maleic acid. In this study, HCl or an organic acid's salt was used to adjust the desired pH.

3.1.1 Core preparation

Carbonate cores used in these experiments were cut from a limestone slab by using a diamond core bit. Therefore, all of the cores were 3.80 cm in diameter and were cut to 10.20 cm in length using a diamond saw. The ends of the core were dipped into 0.1N HCl for removing the effects of contaminants on the migration into porous media. The core was completely dried, and weighted. Subsequently, the cores were vacuum, saturated with DI water at least one hour, and weighted again. The porosity was calculated from the difference between the wet and dry mass of the cores.

Elemental analysis of the limestone was conducted using Neutron Activation. This analysis was organized by technicians at the Phoenix

Memorial Laboratory at the University of Michigan. Results of the analysis are described in Fredd, 1998. The samples are composed primarily of calcium carbonate with impurities probably in the form (Al, Fe, Mg) and minerals such as dolomite [$CaMg(CO_3)_2$] and siderite [$FeCO_3$].

3.1.2 Coreflood apparatus

Linear coreflood experiments employed the apparatus shown schematically in Figure 2.1. All limestone samples were cut from a limestone slab in 3.80 cm in diameter and 10.20 cm in length. The core had porosities between 0.10 and 0.20 percent and permeabilities of 1.2 to 4.0 md. A sample was saturated with DI water and loaded into a standard Hassler cell. An overburden pressure of at least 2200 psi was applied to ensure that flow did not bypass the core. Before running each experiment, different flow rates of DI water were operated to inspect the permeability of each core. Subsequently, DI water was injected through the core at a desired constant rate controlled by an FDS-210 pump. When the system stabilized by the flow and temperature, acid injection was started from an accumulator containing an appropriate acid. The pressure drop across the length of the sample was monitored by a differential pressure transducer and recorded on a personal computer. The entire process had a back pressure of at least 1000 psi to retain CO_2 dissolved into its liquid phase. The experiment was terminated when the wormhole brokethrough the core, which was indicated by a insignificant pressure drop. The wormhole structures were imaged by using neutron radiograph (Lindsay *et al.*, 1990) and the Wood's metal casting technique (Hoefner and Fogler, 1988) are explained in later parts. The temperature of the processes was maintained at room temperature for all cases of acids.

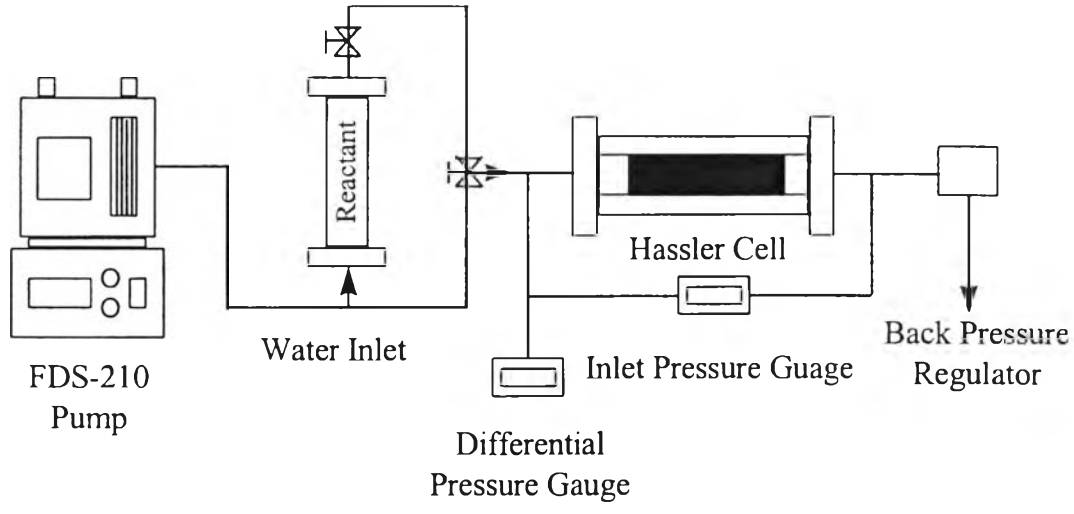

Figure 3.1 Schematic of a linear coreflood apparatus.

3.2 Neutronradiograph

Neutron radiography and the Wood's metal casting technique (Hoefner and Fogler, 1988) were applied to illustrate the wormhole structures formed during the linear coreflood experiments. The neutron radiography technique utilized a vacuum oven to remove moisture and evacuate the acidized cores at 100?C. At that temperature, the Wood's metal consisted of 50%Bi, 25%Pb, 12.5%Sn, and 12.5%Cd had been melted in a vacuum oven, and was then injected molten Wood's metal into those cores. The injection pressure was controlled to insure that the metal invaded only the pore spaces that were enlarged by dissolution. Afterward, the molten metal was allowed to solidify, forming a casting of the wormhole channels. The Wood's metal-filled cores were placed in a beam of thermal neutrons, and the film radiography method was used to record the flux onto a photographic film as shown in Figure 3.2. Wood's metal provides high contrast between the dissolution channels and the virtually transparent consolidated porous medium because it contains cadmium,

which is an excellent neutron absorber. Thermal neutrons cannot directly expose film, thus an intermediate screen was used to absorb the neutrons and generate a secondary form of radiation (such as electron, gamma rays, or visible light). In this experiment, a gadolinium oxisulphide (GdO_2S) screen was used to expose Kodak Azo^{TM} black and white film. A time required for exposing was 30 to 40 seconds. The photographic films were developed using standard procedures. This imaging technique is capable of detecting structures of the order of 0.5 microns.

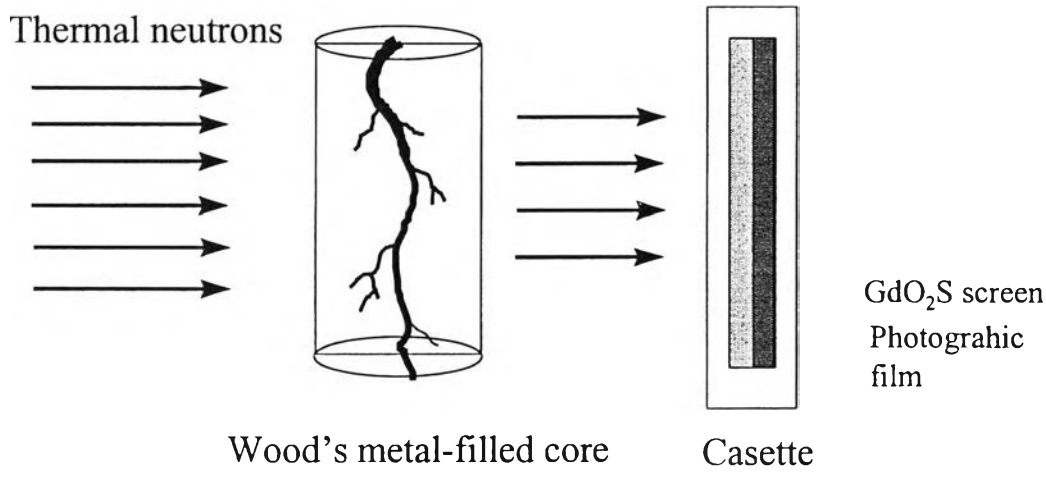

Figure 3.2 Schematic of a neutronradiograph.

3.3 Rotating Experiment

A rotating experiment was conducted to examine the effect on surface reaction. This investigation found by varying the rotating speed. Then, the parameter, k_r and K_{eff} were found. These parameters were modified by varying the fluid types, and pH. This investigation emphasized the relation on the Damköhler number and the wormhole structure. The injections were conducted with an organic acid, 0.5M acetic acid, 0.5M formic acid, and 0.5M maleic acid. In this study, HCl or an organic acid's salt was used to adjust the desired pH.

3.3.1 Reagent preparation

Italian marble was a represent as the calcite formation. By dissolving the sample with HCl, the sample was analyzed to be pure. A disk was cut into 5.3 cm in diameter and approximately 0.65 cm in thick. Then, the face of the sample was polished with 120, 320 and 400-mesh carborundum, respectively. The disk was soaked in 0.1 M HCl for 30 to 35 minutes and thoroughly rinsed with DI water for eliminating reproducibility problems associated with preparing the disk surfaces. These problems were observed only when the dissolution was influenced by the kinetics of the surface reaction i.e., disk preparation has no effect on the rate when the dissolution was mass transfer Fredd (1998).

Reactant solutions were prepared from deionized water and reagent grade chemicals. The same concentration of acetic acid, formic acid, and maleic acid at 0.5M were considered, as well as adjusted pH by adding strong acid or organic acid's salt.

3.3.2 Rotating disk apparatus

Rotating disk experiments were conducted by using the apparatus shown schematically in Figure 3.3. In designing a rotating disk reactor system, the disk should spin in an infinite volume and flow in the system must be laminar. Gregory and Riddiford (1956) demonstrated that the observed rate was independent of the vessel diameter when the vessel diameter was at least twice the disk diameter.

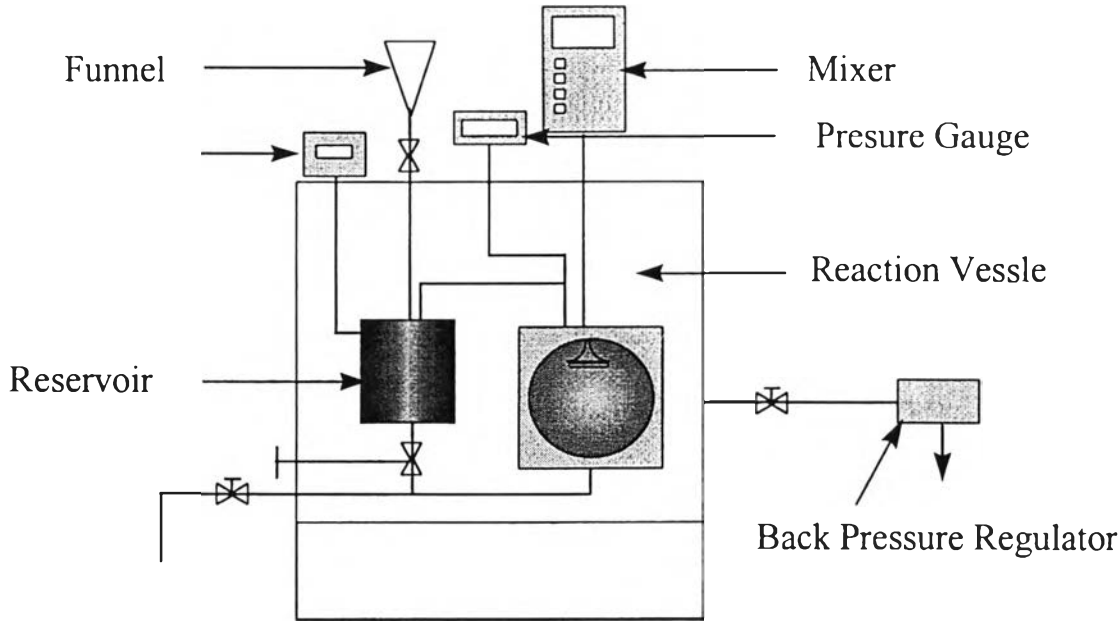

Figure 3.3 Schematic of a rotating disk experiment.

The reaction vessel and liquid reservoir were mounted in a laboratory oven to provide an insulated environment. The reaction vessel and magnetic rotator mechanism were designed to handle up to 6.9 MPa (1000 psig) and 150°C. They are described in detail by Boomer *et al* (1972). The calcite disk was attached to the rotator assembly using shrinkable Teflon tubing. The speed of the rotator was controlled with a LIGHTIN SI mixer with a range of about 200 to 1800 rpm. All of experiments were operated at the room temperature (21°C) in a nitrogen atmosphere at 5.5 MPa (800 psig). The high pressure was applied to retain gaseous reaction products (CO_2) which were a formation of gas bubbles in solution. These bubbles deviated the effect of the hydrodynamics in the vicinity of the rotating disk. During the experiments, ten small liquid samples were periodically withdrawn from the reactor and analyzed calcium content by using a Perkin Elmer model 3100 atomic absorption spectrophotometer (AAS). At the termination of the experiment the pressure was released and the system drained and flushed with distilled water. The

calcium content of the collected samples was used to determine the rate of reaction and the other parameters, k_r and K_{eff}. Also, the initial rate of dissolution was used in analysis in order to minimize the effects of changing surface area due to the formation of pits and irregular surface morphologies (Fredd, 1998).