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# APPENDIX A
# DETAILS OF COREFLOOD EXPERIMENTS

## Core Preparation

Carbonate cores were cut from a limestone slab. Their porosity ranged between 0.10 and 0.20, as well as permeability between 1.2 and 4.0. The permeability was calculated by applying Darcy's equation presented in equation A.1.

$$K = \frac{Q\mu L}{\Delta P} \tag{A.1}$$

where $K$ is the permeability, $Q$ is the injection rate, $\mu$ is the fluid viscosity, and $L$ is the lenght of the sample. The components of the cores were analysed at the Phoenix Memorial Laboratory, the University of Michigan. The samples were composed primarily of calcium carbonate ($CaCO_3$) with impurites probably in forms of clay (Al, Fe, Mg) and other minerals such as dolomite [$CaMg(CO_3)_2$] and siderite [$FeCO_3$]. The analysis results are listed in Table A.1.

**Table A.1** Elemental composition of limestone analysed by Neutron Activation Method

| Element | Ppm | Element | ppm |
|---|---|---|---|
| Al | 264 | Mn | 64.9 |
| As | 1.1 | Mo | 0.6 |
| Ba | 14.8 | Na | 136 |
| Ce | 0.4 | Sc | 0.1 |
| Co | 0.3 | Sm | 0.1 |
| Cr | 6.8 | Th | 0.1 |
| E | 0.02 | U | 0.3 |
| Fe | 1330 | V | 1.7 |
| La | 0.6 | Yb | 0.04 |
| Lu | 0.02 | Zn | 28.2 |
| Mg | 3412 | | |

**Data Analysis**

According to the coreflood experiment, the primary data collected during the experiment was the pressure drop along the core as a function of the volume of fluid injected. The progress of wormhole formation was examined by the reduction of pressure drop when compared to the initiate time. Figure A.1 expresses the relation between pressure drop and pore volumed injected The decrease was then transformed to the ratio of permeability at any time to initiate as shown in equation A.2.

$$\frac{k_0}{k} = \frac{\mu \Delta P}{\mu_0 \Delta P_0} \qquad \text{(A.2)}$$

where the subscript *0* represents initial values. The average viscosity of fluid in the core during the displacement was estimated by assuming plug flow (i.e., the viscosity was assumed to change linearly from that of DI water to that of the injected fluid between 0 and 1 pore volumes of fluid injected). In this study, the pore volumes to breakthrough was defined at a permeability ratio of 100. These results were verified by images from neutron radiographs. Figure A.2 demonstrates that the pore volumes to breakthrough at different permeability ratios ranging from 10 to 100. It should be noted that at low injection rates where conical shaped channels, with large diameter and little branching was observed in this study, the pore volumes to breakthrough was calculated based on a core length equivalent to the depth of dissolution (determined from neutron radiographs). Actual breakthrough could not be achieved because a majority of the core would be dissolved leaving no support for the overburden sleeve, thereby causing a loss of overburden pressure and/or damage to the sleeve.

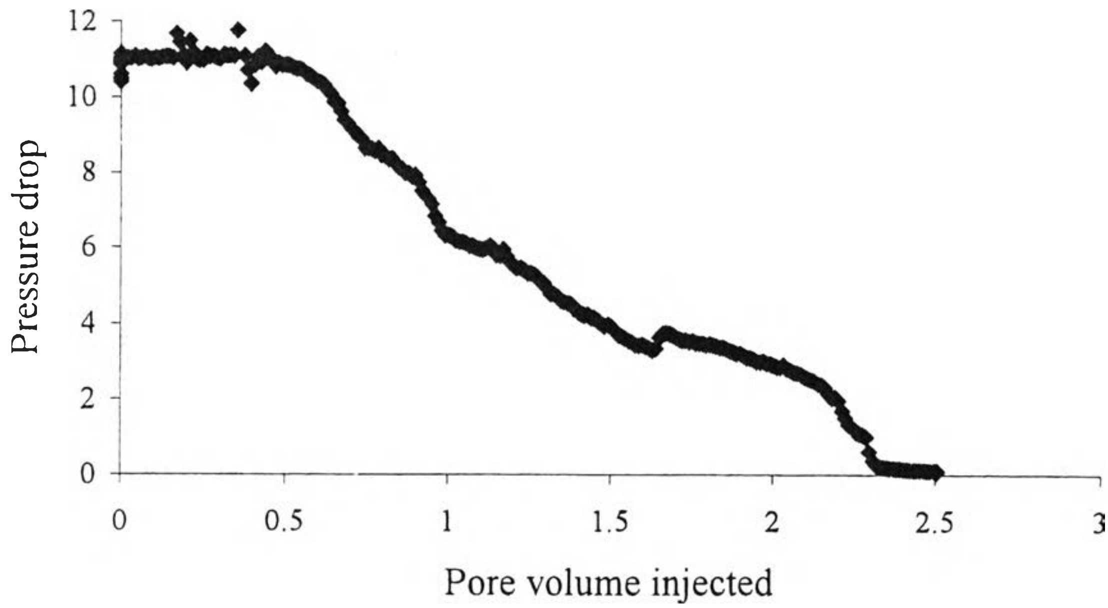


**Figure A.1** Correlation between pore volumes injected and pressure drop of maleic acid 0.5M at 0.2 cc/min.

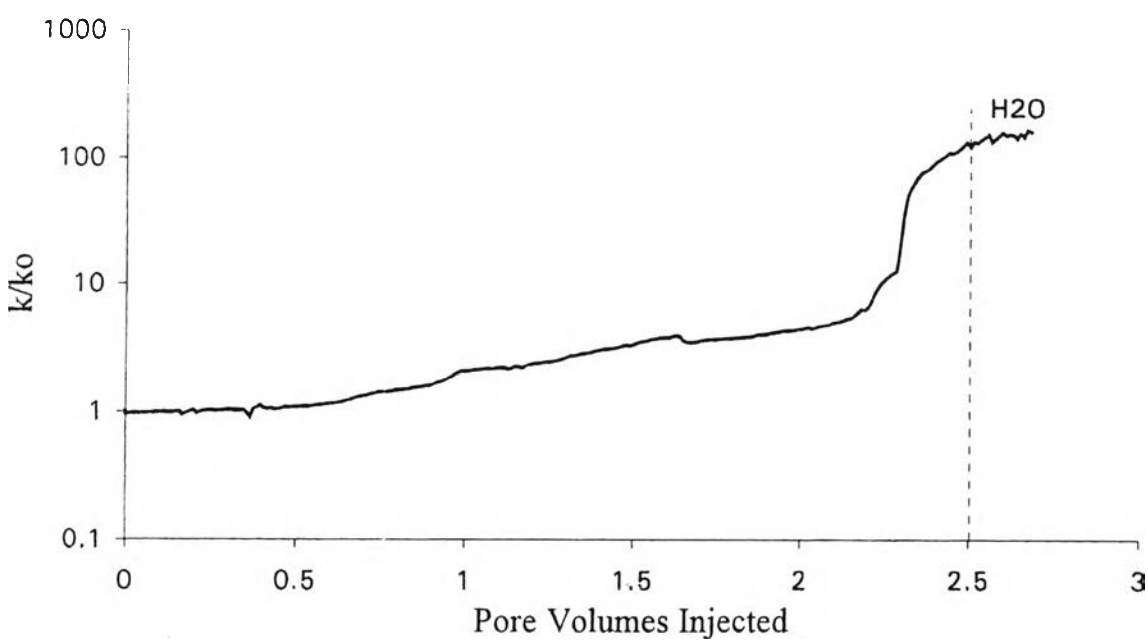


**Figure A.2** The relation between the pore volumes to breakthrough at various permeability ratio of maleic acid 0.5M at 0.2 cc/min.

# APPENDIX B
# ROTATING DISK EXPERIMENT

A rotating disk experiment was used to determine the influent parameter relating to calcite dissolution. This reaction is heterogeneous consisting of reactant transport to surface, reversible surface reaction, and products transport to bulk fluid. The experimental procedure was explained in chapter 3.

The rate of dissolution presented in equation B.1 showed the effect of total resistance κ in series.

$$r_D = \kappa\left[C_{T.H} - \frac{C_{T.M}}{K_{eff}}\right] \tag{B.1}$$

where κ depends on the sum of resistance in series and is given by

$$\kappa = \frac{1}{\frac{\nu}{K_1} + \frac{1}{k_r} + \frac{1}{K_{eff}K_3}} \tag{B.2}$$

$$K_{eff} = \frac{K_c}{C_{T.CO(i)}} \tag{B.3}$$

$$K_c = \frac{C_{T.M(i)}C_{T.CO(i)}}{C_{T.H(i)}} \tag{B.4}$$

and $\nu$ is stoichiometric ratio of reactants consumed to products produced, $k_r$ is the effective forward reaction rate constant, as well as $K_1$ and $K_3$ are the mass transfer coefficients for reactant and product, respectively. The total concentration of reactants ($C_{T.H}$) and products ($C_{T.M}$ and $C_{T.CO}$) are listed in the case of calcite dissolution with acetic acid.

$$C_{T.H(i)} = C_{H^+(i)} + C_{HAc(i)}$$

$C_{T.M(i)} = C_{Ca^{+2}(i)} + C_{CaAc^{+}(i)} + C_{CaHCO^{3+}(i)} + C_{CaOH^{+}(i)}$

$C_{T.CO(i)} = C_{HCO3^{-}(i)} + C_{CO3^{-2}(i)} + C_{CO2(i)} + C_{H2CO3(I)} + C_{NaCO3^{-}(I)}$

From equation (B.1), the unknowns in these expressions are the effective surface reaction rate constant and the effective equilibrium constant.

The kinetic parameters were evaluated by linearizing equation (B.1) with respect to the square root dependence on the rotating speed in the mass transfer coefficients. The linearization gives

$$\frac{1}{r_D} = \frac{1}{k_r\left[C_{T.H} - \dfrac{C_{T.M}}{K_{eff}}\right]} + \frac{\left[\dfrac{\nu}{K_1^*} + \dfrac{1}{K_{eff}K_3^*}\right]}{\left[C_{T.H} - \dfrac{C_{T.M}}{K_{eff}}\right]}\frac{1}{\sqrt{\omega}} \qquad \text{(B.3)}$$

where $K_i^* = Ki/\omega^{1/2}$. Equation (B.3) suggests that the reciprocal of the rate of dissolution should vary linearly with the reciprocal of the square root of the rotating speed, provided the underlying assumptions are valid. Consequently the unknown parameters can be solved to verify the influence of calcite dissolution reaction.

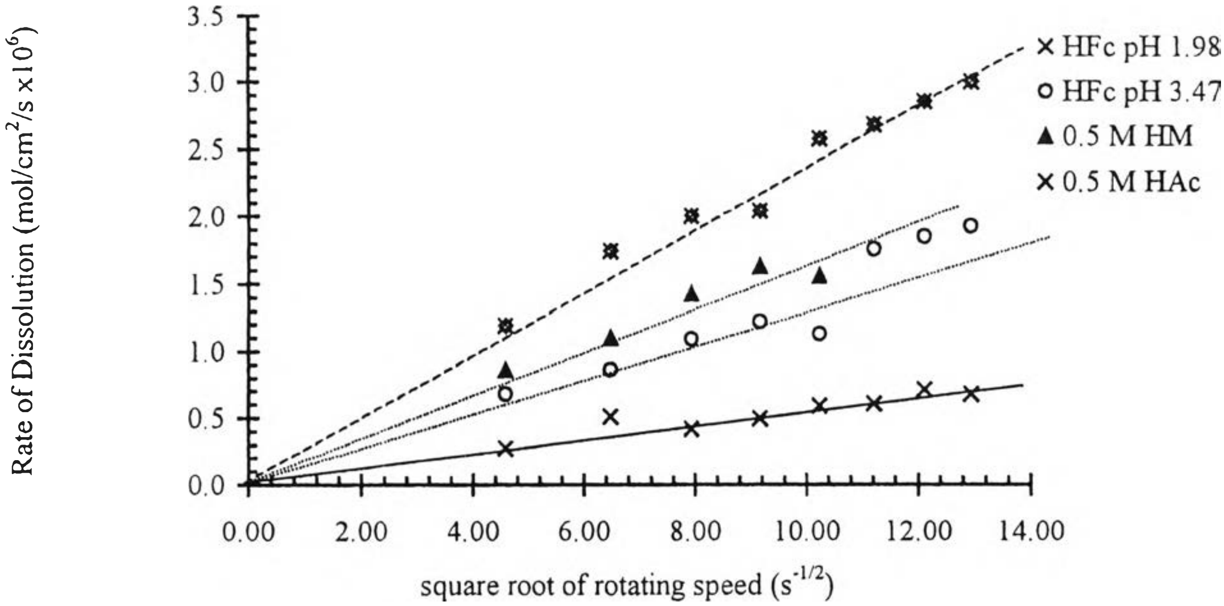


**Figure B.1** Effect of a variety of stimulating fluids and pH on the rate of dissolution.

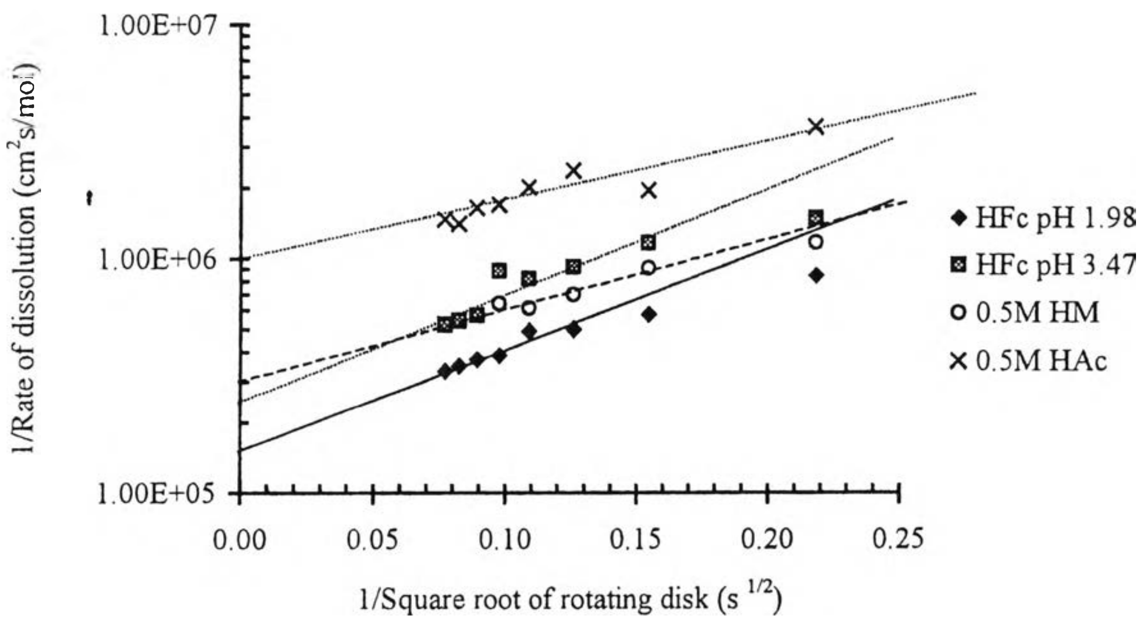


**Figure B.2** Correlation between the reciprocal of rotating speeds and the reciprocal of rate of dissolution as demonstrated by the linearized rate expression.

# APPENDIX C
# NEUTRONRADIOGRAPHS

The neutron radiographs in this section show the effect of varying pH at the same concentration 0.5M. Acetic acid was adjusted pH by mixing with hydrochloric acid and sodium acetate for decreasing and increasing pH, respectively. Formic acid was also increase by adding sodiumformate. All the chemical reagents were the laboratory grade. The coreflood experiments were operated at the room temperature.

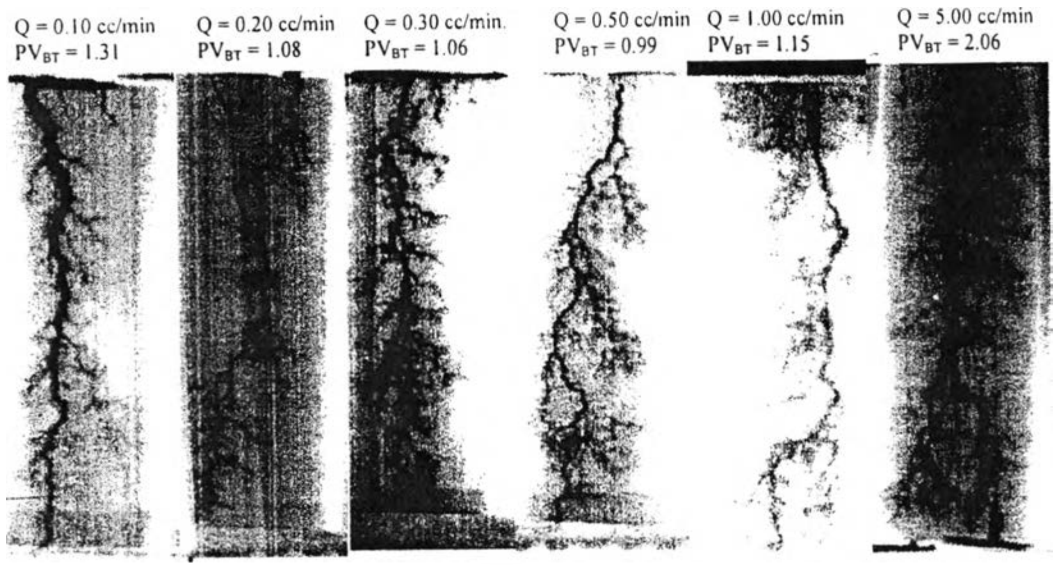


**Figure C.1** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M acetic acid and pH = 0.3.

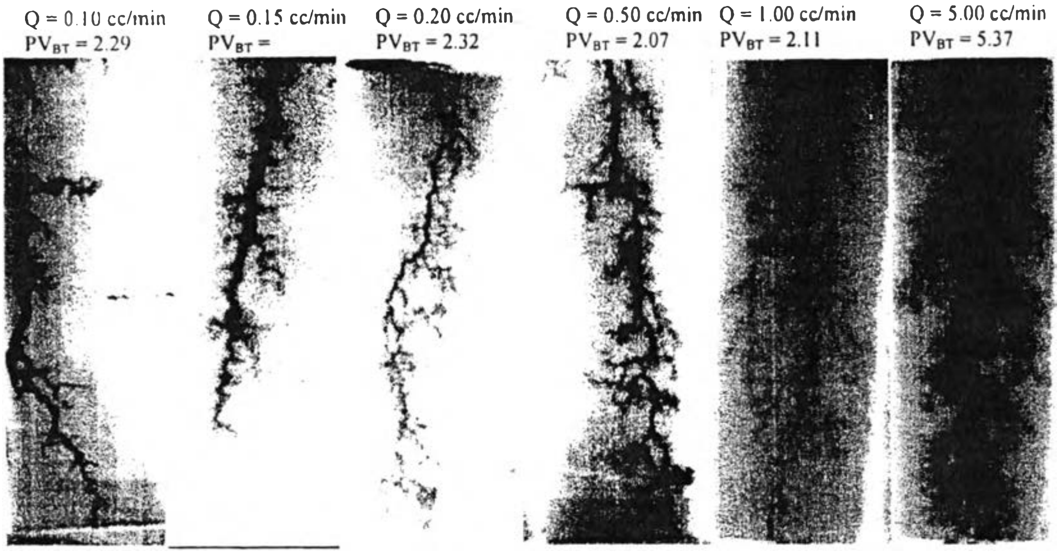


**Figure C.2** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M acetic acid and pH = 1.1.

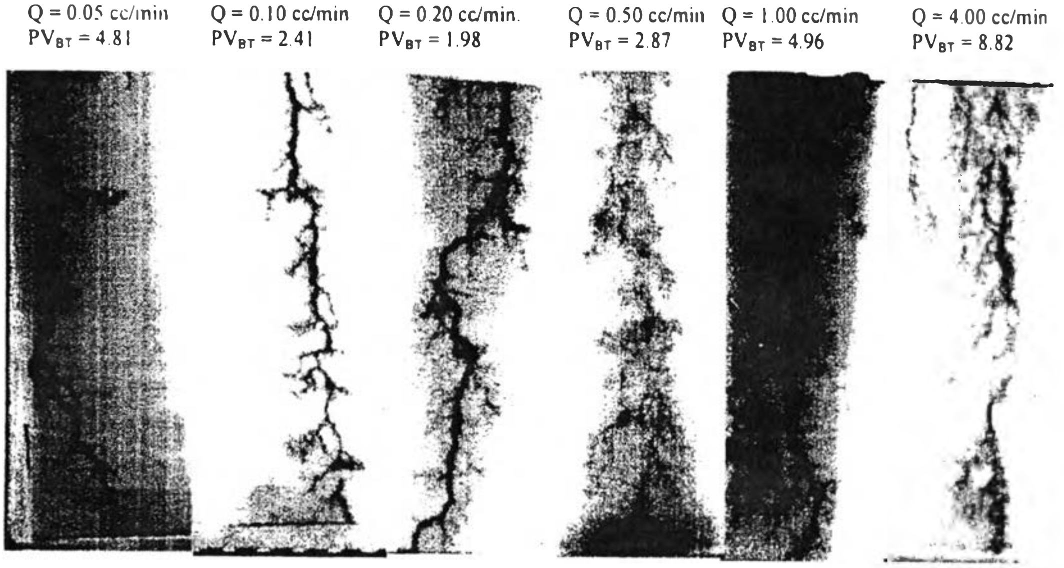


**Figure C.3** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M acetic acid and pH = 2.6.

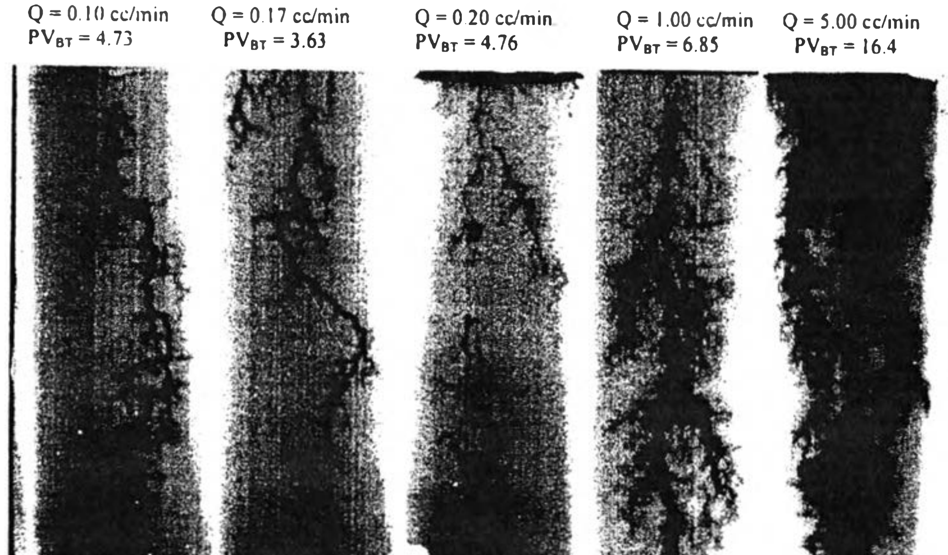


**Figure C.4** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M acetic acid and pH = 4.3.

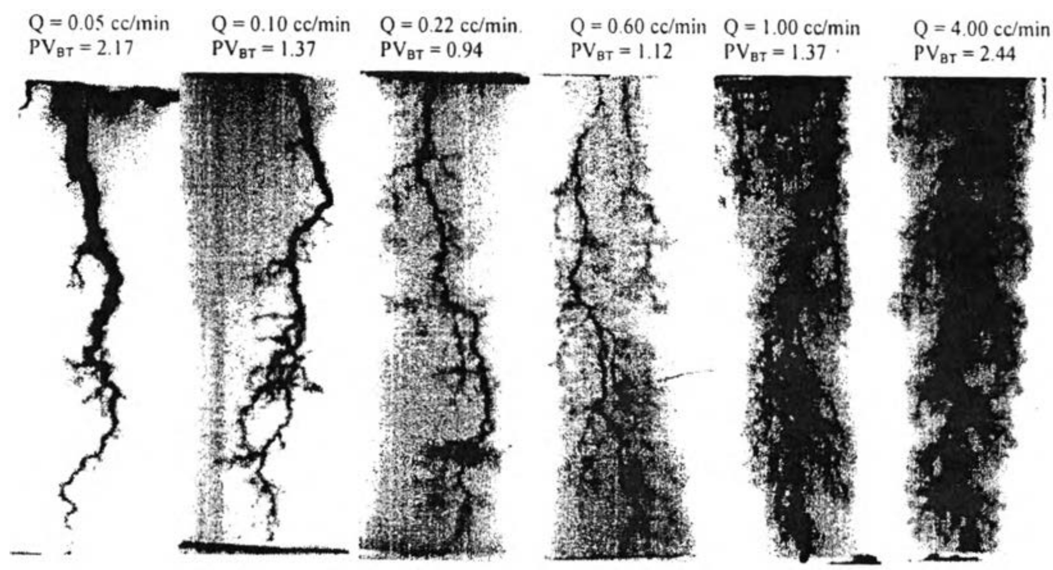


**Figure C.5** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M formic acid and pH = 2.0.

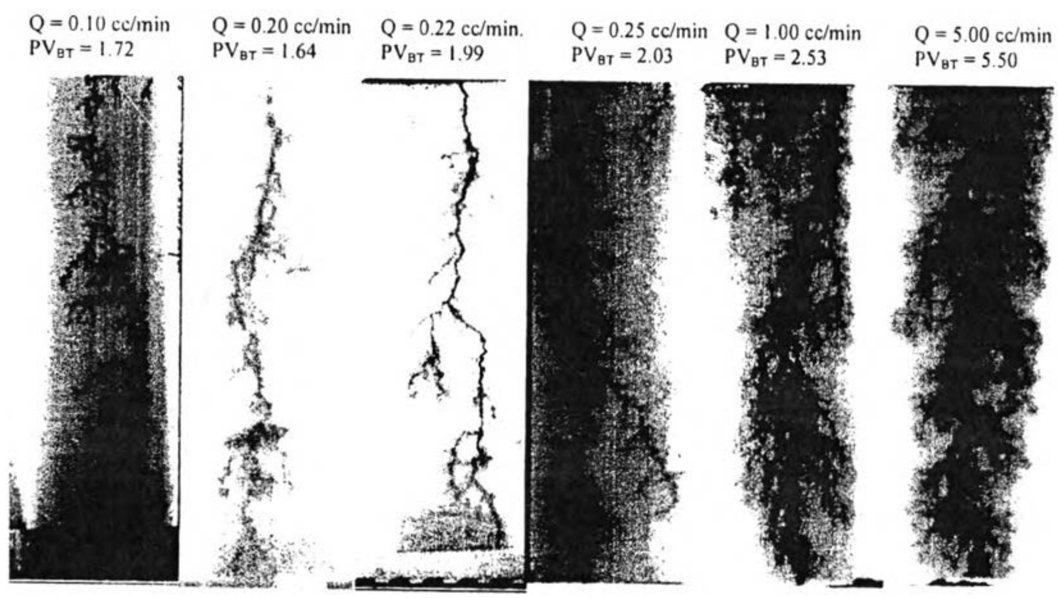


**Figure C.6** Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M formic acid and pH = 3.5.

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