CHAPTER IV
RESULTS AND DISCUSSION

Permeability (k) and porosity ($\emptyset$) are the crucial indices for indicating the success of wormhole formation. Therefore, the permeability curves corresponding with the progress of wormhole channels in the various stimulating fluids are presented in Figure 4.1. A core is assumed to absolutely breakthrough when the ratio at least 100 of the permeability at any time to the initiate permeability. At this point, the pore volumes to breakthrough are defined. The permeability curves of all stimulating fluids are similar in tendency. In other words, the pore volumes to breakthrough are calculated by the volumes of rock consumed in the reactions. These origins start at the unity and increase until they reach over 100 of permeability ratio. However their trends were similar in progress, they have different slopes. The steeper the curve is, the less the number of pore volume to breakthrough are. The relationship between the pore volumes injected and the permeability ratio for different injection rates is shown in Figure 4.2. Therefore, the stimulating fluid properties and injection rates are greatly potential factors for the structures of wormhole formation.

4.1 Effect of Stimulating Fluids

4.1.1 Effect of acid types on permeability

Acetic acid, formic acid and maleic acid were injected into the limestone cores to formulate an optimum injection rate. This effective injection rate exhibits the minimum volume of acid required to penetrate the desired distance (10.2 cm). Figure 4.1 presented the relation between permeability response and pore volume injected. Various stimulating fluids were employed at the same rate 1.0 cc/min. In these experiments, maleic acid provided the less number of pore volumes injected at 1.0, while formic and acetic acids were 1.1 and 5.0, respectively. Hydrochloric acid was still good as the stimulating fluid by giving the pore volumes injected around 1.5. All the stimulating fluids had the same dissolving number, which defined as the mass of solid per unit mass of acid reacted. This result corresponds with acid properties because formic acid is slower-reacting organic acid, but it is a stronger acid than acetic acid (Kalfayan, 1996). In the case of maleic acid, it had the least number of pore volumes injected. This result might come from the carboxylic groups (R-COOH). Maleic has two carboxylic groups, whereas the other has only one. But, it is not necessary that more carboxylic groups are more effective in the wormhole formation. Fredd (1998) demonstrated by applying chelating agents, which have many carboxylic groups. Acetic acid provided the less number of pore volumes injected when compared with the chelating agents, which have up to four carboxylic groups.

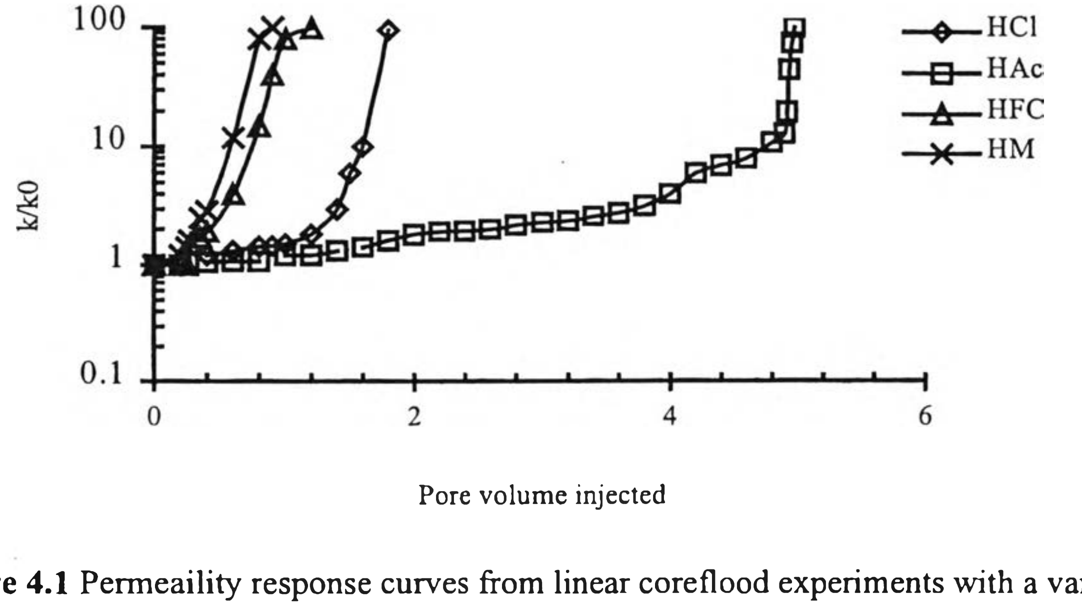

Figure 4.1 Permeaility response curves from linear coreflood experiments with a variety of stimulating fluids at 1.0 cc/min.

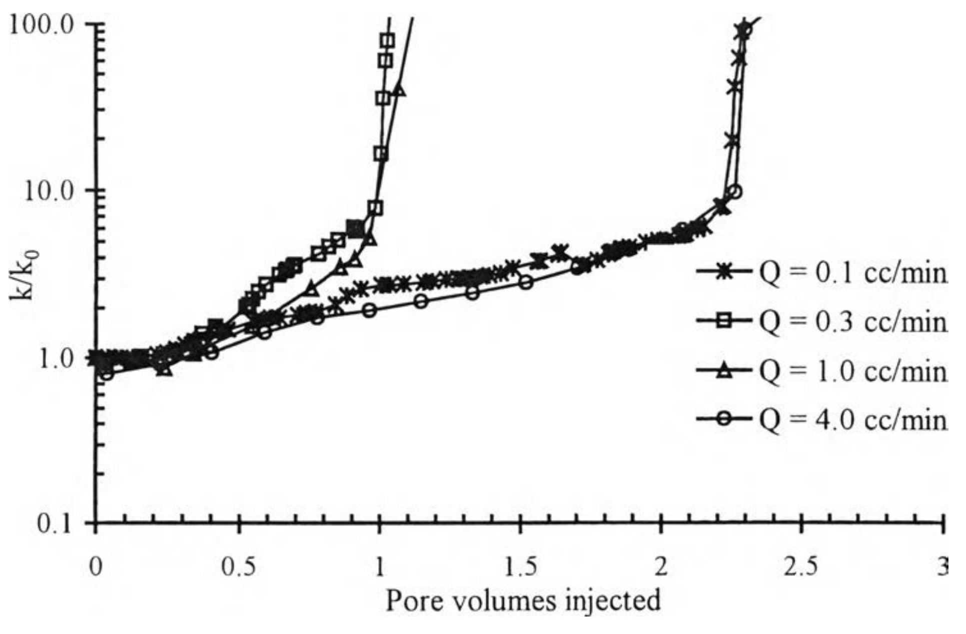

Figure 4.2 Permeability reponse curves from linear experiments with different injection rates of HFc 0.5M.

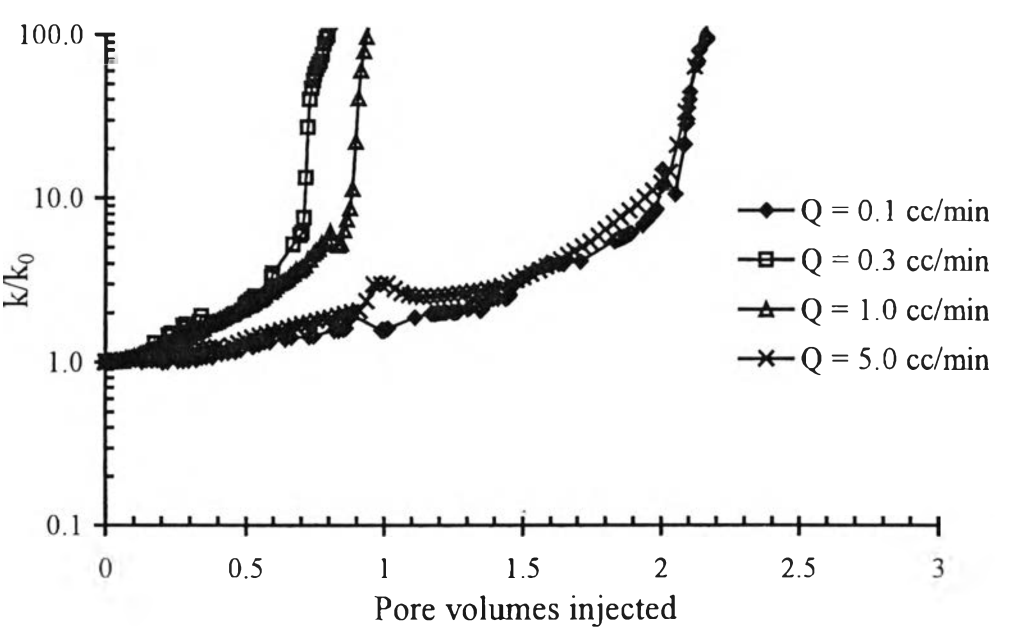

Figure 4.3 Permeability response curves from linear coreflood experiments with different injection rates of HM 0.5M.

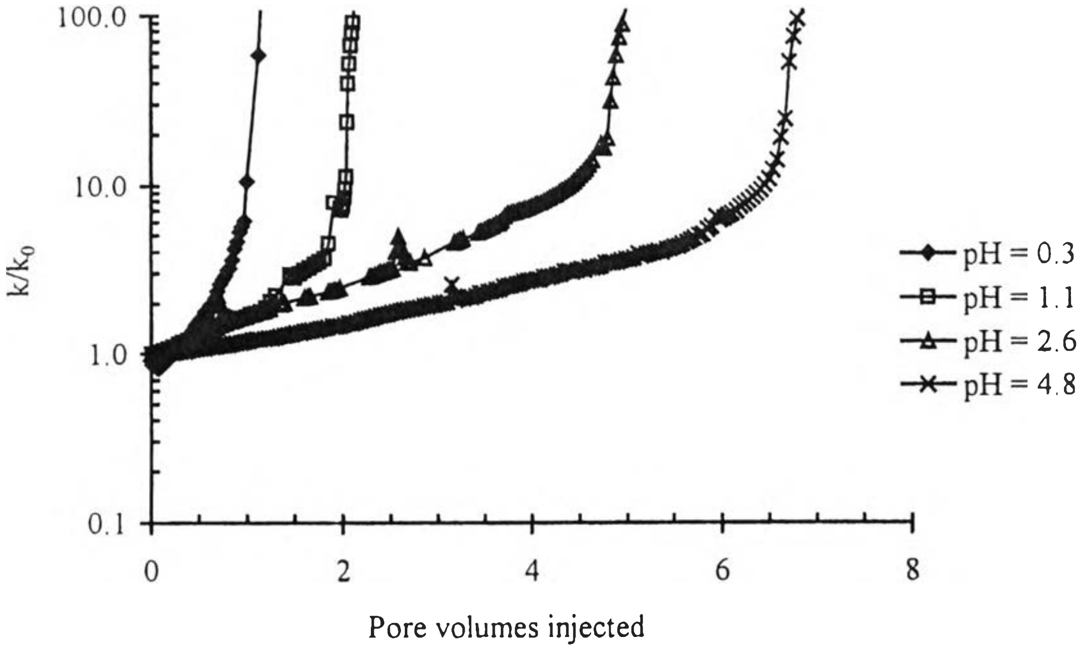

Figure 4.4 Permeability response curves form linear coreflood experiments with various pH of HAc 0.5M.

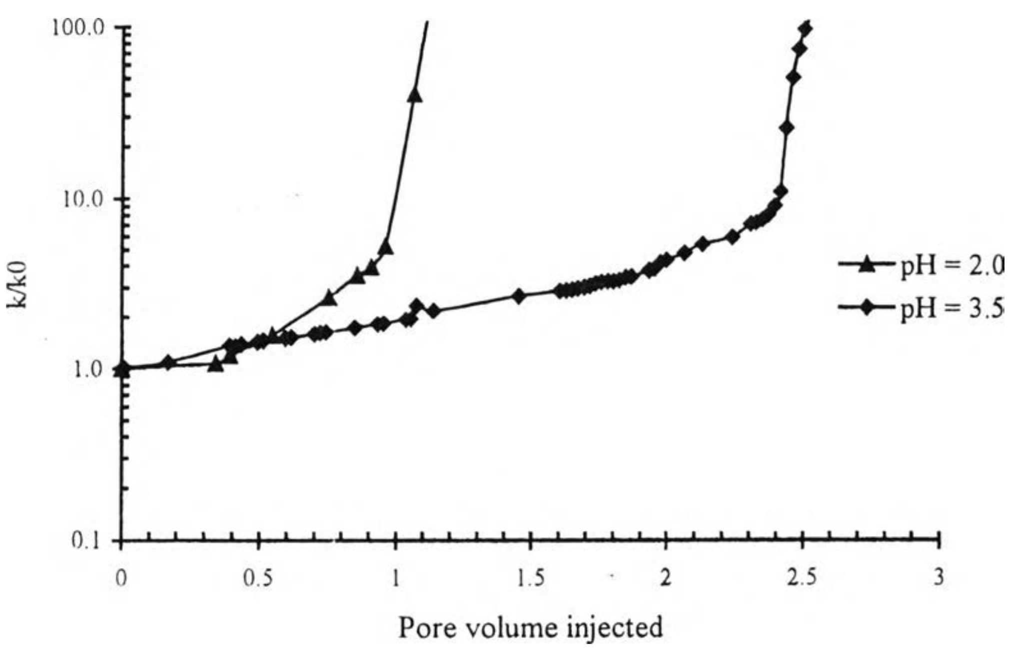

Figure 4.5 Permeability response curves from linear coreflood experiments with various pH of HFc 0.5M.

4.1.2 Effect of injection rates on permeability

The dependence of the number of pore volumes to breakthrough on the injection rate is shown in Figure 4.5. At low injection rates, the acid easily reacted with calcite surface. Therefore, the large number of pore volumes to breakthrough were excess consumed. When the injection rate was increased, the volume of pore volumes to breakthrough gradually decreased and reached the minimum of pore volumes to breakthrough. This point is an optimum injection rate. At higher injection rates, the number of pore volumes to breakthrough continuously increased due to the formation of increasingly branched dissolution structure or ramified structure. This tendency from the range of extremely low to extremely high injection rate can be observed with all of stimulating fluids. In addition, the optimum injection rates also were found at approximately 0.24, and 0.20 cc/min for formic acid, and maleic acid, respectively.

4.1.3 Effect of pH on permeability ratio

Graphs plotted between the injection rate and pore volumes to breakthrough for different pH of acetic acid and formic acid are also showed in Figure 4.6. In the case of acetic acid. The optimum injection rate slightly increased from 0.2 to 0.4, when the pH is increased. Formic acid system presented the slightly similar optimum injection rate at 0.2 to 0.3 cc/min. This results correstpond to the amount of hydronium, which directly affect with reaction on calcite surface. When pH value increase, the amount of hydronium are lower. Therefore, the optimum injection rate increase flong with increasing pH values.

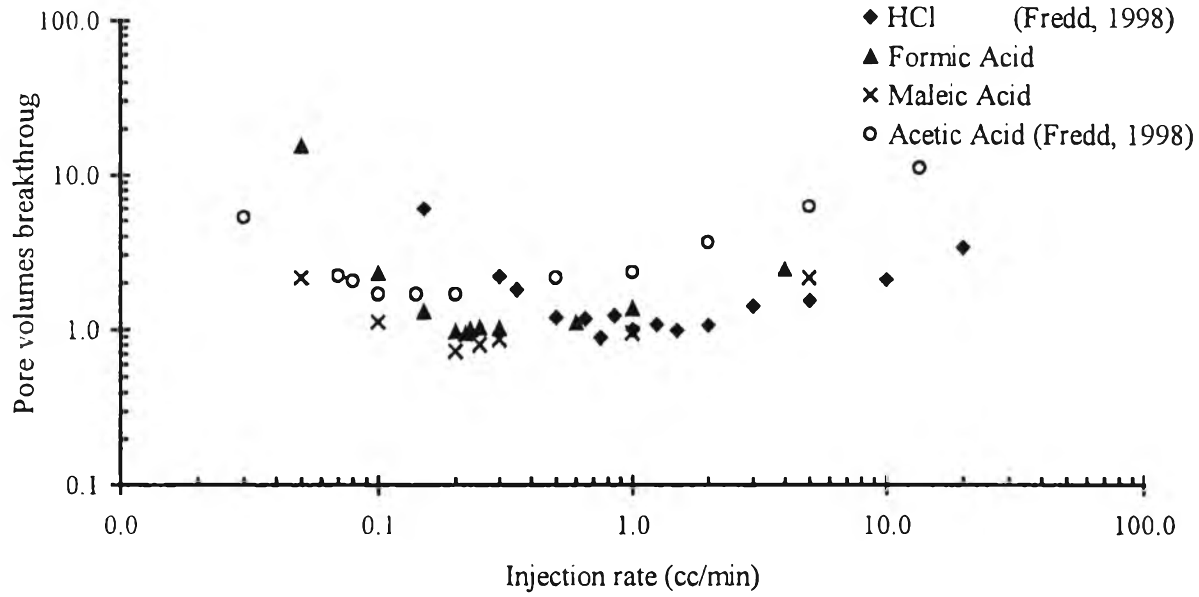

Figure 4.6 The relation between injection rates and pore volumes to breakthrough for a variety of stimulating fluids at 0.5M.

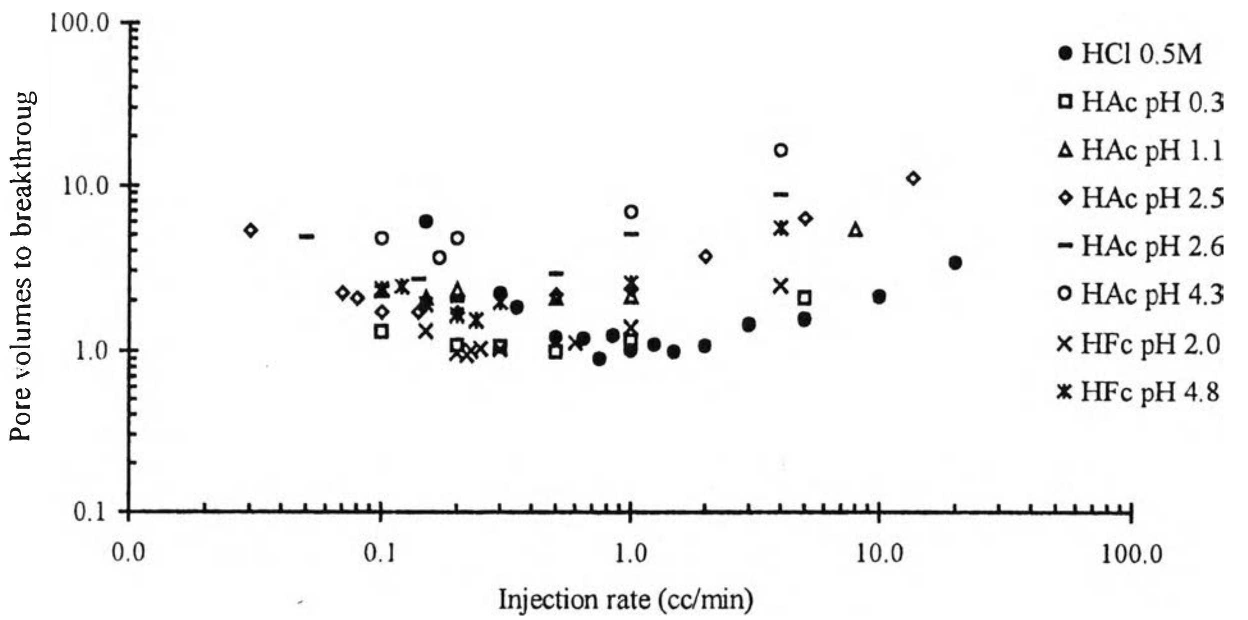

Figure 4.7 The relation between injection rates and pore volumes to breakthrough for various pH of acetic acid and formic acid at the same concentration 0.5M.

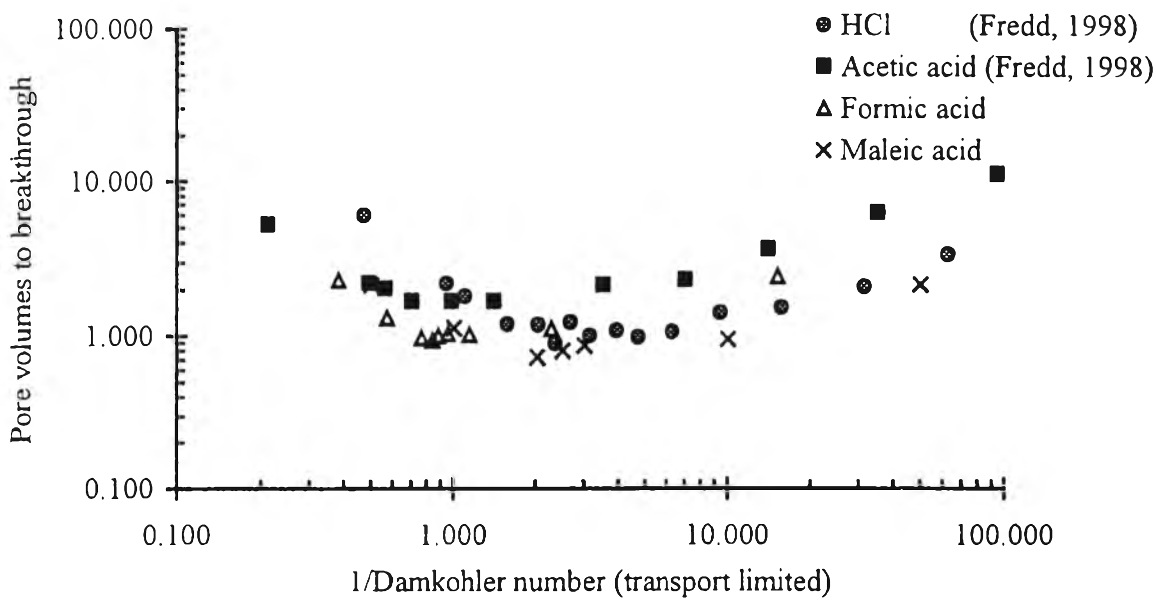

Figure 4.8 Comparison of the number of pore volumes to breakthrough for a variety of stimulation fluids at the same concentration 0.5M.

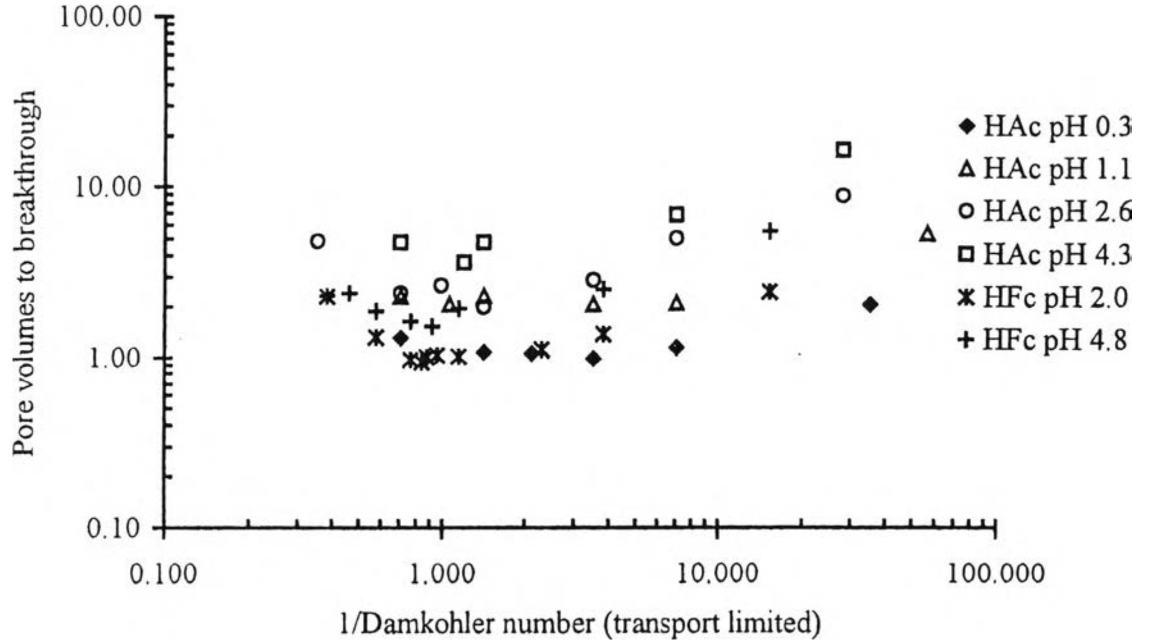

Figure 4.9 Comparison of the number of pore volumes to breakthrough for various pH of acetic acid and formic acid at the same concentration 0.5M.

4.2 Relationship between Damköhler Number and Pore Volumes to Breakthrough

Figure 4.7 shown the data consisted of the optimum Damköhler number (or injection rate) which recommended by previous investigators (Hoefner and Fogler, 1988; Wang *et al.*, 1993; Mostofizadesh and Economides, 1994; Frick *et al.*, 1997; Huang *et al.*, 1997) in the hydrochloric acid systems. This trend is consistent with changes in the number for the mass transfer limited dissolution. The diffusion coefficients of weak acids decreases from formic acid, acetic acid to maleic acid as 1.5×10^{-5}, 1.1×10^{-5}, and 0.9×10^{-5} cm^2/s, respectively. In this figure, the phenomenon of wormhole formation depending in the Damköhler number for flow and reaction (Hoefner and Fogler, 1988). The diagram was plotted between the pore volumes to breakthrough and the reciprocal of the Damköhler number calculated from equation (2.1) assuming dissolution limited by the transport of reactants to surface. The Damköhler number has been designed based on the macroscopic dimensions of the wormhole, diameter, and wormhole length. Unfortunately, the minimum of each curves do not respond at the same value of the Damköhler number. However, a single dominant wormhole channel is still observed. In other words, the Damköhler number defined by the equation (2.1) does not describe the wormhole structure formed by the various fluid/rock systems.

This discrepancy is explained by kinetic study. It revealed that the dissolution of limestone by an organic acid might be affected by the rate of mass transport of both reactants and products, as well as the rate of surface reaction. Because of this reason, the Damköhler number defined by the equation (2.1) does not provide a general description of the dissolution phenomena. Therefore, the effects of the sequential steps, the transport of reactants to the surface, the kinetics of the reversible surface reaction, and the transport of products away from the surface must be considered simultaneously to describe the phenomena of wormhole formation.

In addition, all of the organic acids used in these experiments were adjusted pH by adding sodiumacetate, and sodiumformate for shifting acetic acid, and formic acid, respectively.

The Damköhler number defined by equation (4.8) includes the effects of reactant transport to the surface, reversible surface reaction, and products transport away from the surface. This Damköhler number was shown to dictate the type of wormhole structures that were formed by a wide range of fluid/porous medium systems. The parameters used to calculate the overall dissolution rate constant are listed in Table 4.1. Furthermore, the effective surface reaction rate constant and the effective equilibrium constant were obtained from the independent kinetic studies using a rotating disk (Appendix B).

Table 4.1 Parameters used to calculate the overall dissolution rate constant

	D_e [cm^2/s]	k_r [cm/s]	K_{eff} [-]
HAc(1)	$1.1x10^{-5}$	$5x10^{-3}$	$1.6x10^{-1}$
HFc	$3.0x10^{-5}$ (2)	$4.45x10^{-3}$	1.48
HM	$0.7x10^{-5}$ (3)	$1.45x10^{-1}$	$3.54x10^{-1}$

(1) Estimated from the Strokes-Einstein equation.

(2) From Robert S. Schechter, "Oil well Stimulation", 1st ed., Prectice Hall, 1992.

(3) Estimated from the Wilkes-Chang equation.

Figure 4.10 exhibits a modified Damköhler number at which the number of pore volumes to breakthrough is minimized. *Note the x-axis still represents an increase in the injection rate.* The modified optimum Damköhler number occurs at approximately 0.29 for wide range of fluid systems. This value can be compared with the previous result. The dependence of the wormhole number structure on the Damköhler number is shown in Figure 4.11 and 4.12. The Damköhler number can classify each picture into three parts, the low, the optimum, as well as the high Damköhler number.

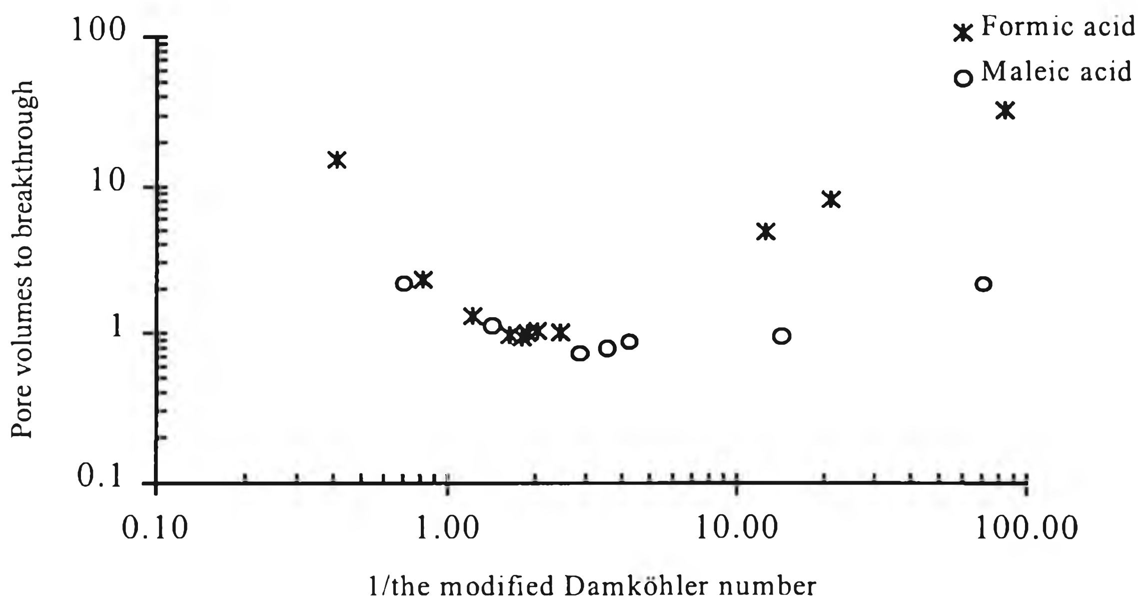

Figure 4.10 Comparison of the number to breakthrough plotted the inverse of the modified Damköhler number as defined by equation (4.8).

At the high Damköhler number, it still represents the low injection rate because the Damköhler number is inversely function to the injection rate. Wormhole structure has a larger channel than the single dominant channels obtained at the intermediate Damköhler number. As the low Damköhler number, the increasing channel branching was observed. Sometimes this structure is called as ramified structure. This tendency of structure transformation also is the same as previous investigators (Hoefner and Fogler (1988); Fredd and Fogler (1998)).

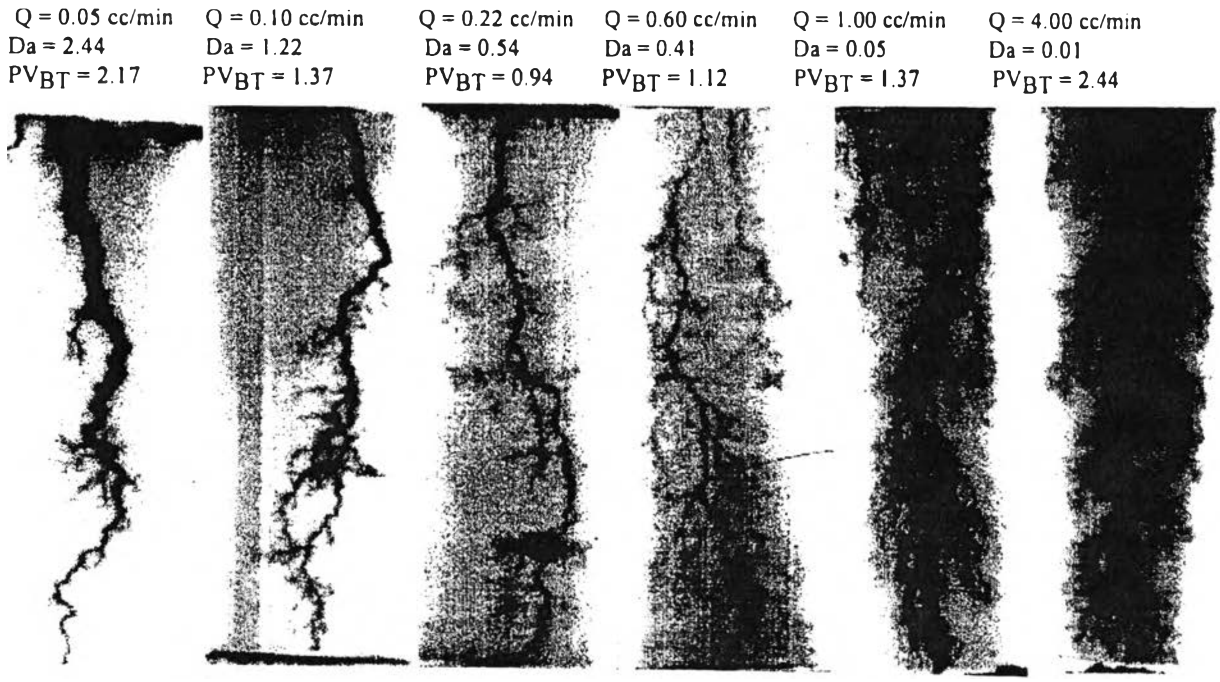

Figure 4.11 Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M formic acid.

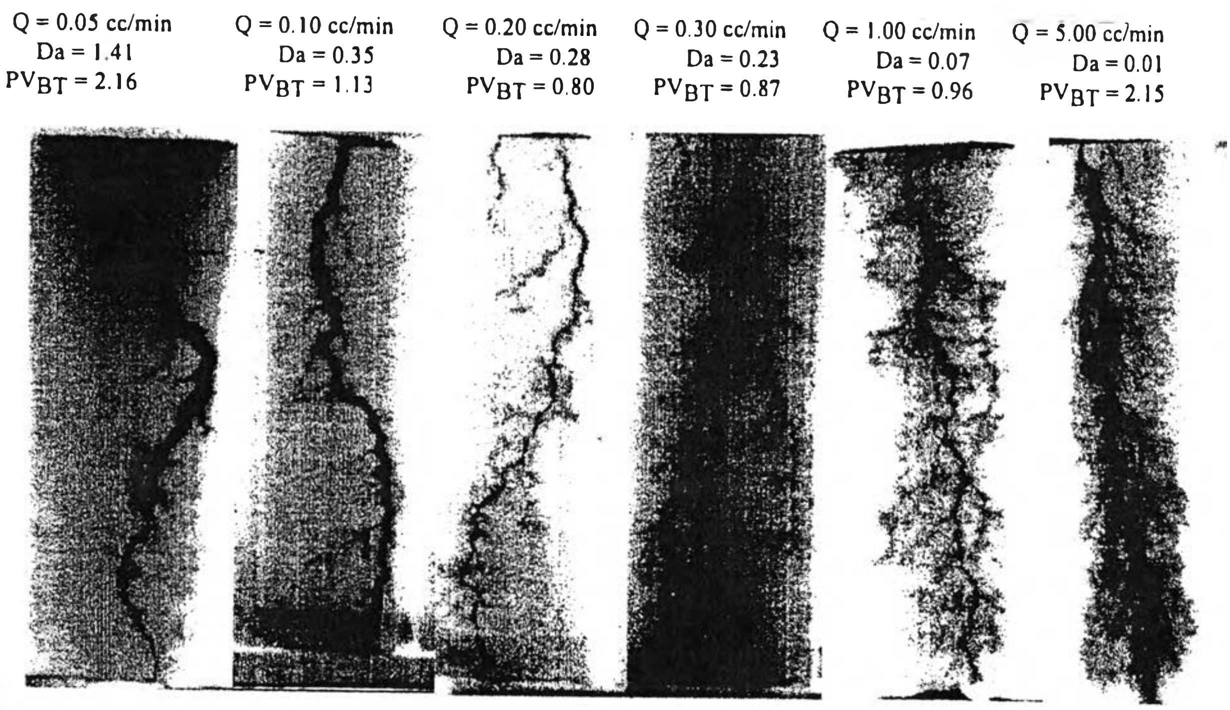

Figure 4.12 Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M maleic acid.

The neutron radiograph results in increasing pH from 0.3 to 4.8 in the acetic acid systems are shown in Figure 4.13. However, the whole wormhole structures negligibly differ at the same Damköhler number (Fredd, 1998), the pore volumes to breakthrough increased along with the increase of pH. This trend is caused by the reduction of hydrogen ion to attack the calcite surface. Consequently, the pore volumes to breakthrough increased.

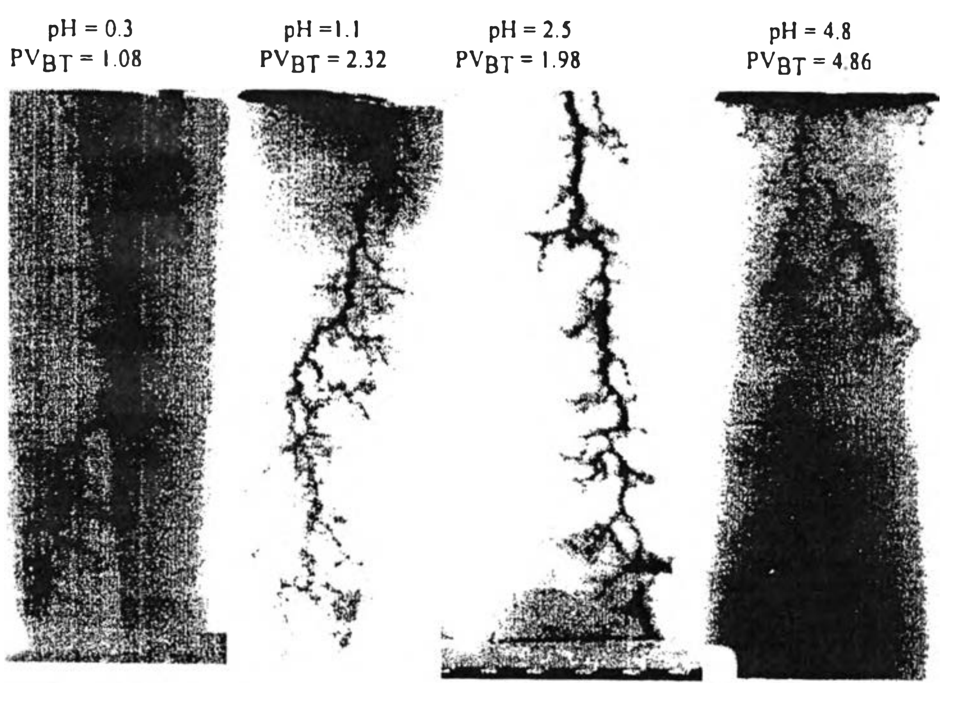

Figure 4.13 Neutron radiographs of wormholes formed during the dissolution of limestone by injection 0.5M acetic acid at various pH.