

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Acidizing

Acidizing is one of the successful methods for stimulating both carbonate and sandstone formation usually found a petroleum reservoir. The importance of this petroleum recovery in carbonate formation is concerned as about one third of the world's petroleum reserves found in limestone. This technique is usually characterized through acid injection rates and pressures into two categories. Injection rates above fracture pressure are termed as fracture acidizing, while those below fracture pressure are termed as matrix acidizing.

Fracture acidizing affects the rapid injection into the carbonate formation at a rate higher than the reservoir matrix can be accepted. This rapid injection produces a buildup in wellbore pressure until it is large enough to overcome compressive earth stresses and the rock's tensile strength. This pressure at which the rock fails allows a crack or fracture to be formed. Continued fluid injection fluid enhances the fracture's length and width. Acid is then injected into the fracture to react with the formation and create a flow channel extending deeply into the formation and remaining open when the well is placed back on production processes. Unfortunately, the productivity after treatments is often difficult to predict because the fracture acidizing strongly corresponds to many parameters. They are the fracture geometry, fluid temperature, acid penetration distance along the fracture for conditions

predicted in both fracture geometry and temperature, and the flow capacity of the fracture created by acid reaction with the walls of the fracture. Moreover, the problems are the unstabilized flow for a significant period of time in low-permeability reservoir, and turbulent flow in the reservoir, thereby reducing fracture flow capacity. In addition, fluids and additives such as undissolved fines, surfactant or polymer used in the treatment can restrict productivity due to reduce fracture flow capacity. Another limitation is no application in sandstone formation. An acidized sandstone well at fracture pressure may break down natural vertical permeability barriers. This problem causes leaking unwanted gas or water from adjacent zone after completion or within a few months after completion processes

On the other hand, matrix acidizing is determined as the injection of acid into the formation porosity at a pressure at less than the pressure at which a fracture can be opened. The objective is to greatly enhance or recover the permeability very near the wellbore, rather than affect a large portion of the reservoir. This treatment technique is defined as the injection of acid into the formation for dissolving the formation reduction such as the rock particles or materials plugging the pore spaces. The dissolution results lead to an increase in the permeability or fluid conductivity, consequently allowing oil or gas to flow more readily. This removal of severe plugging in sandstone, limestone [CaCO<sub>3</sub>], or dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>], can result in a very large increase in well productivity. Otherwise, this treatment tends to leave zone barriers intact if pressures are maintained below fracture at which preventing water or gas production. Thus, it often will elevate oil production without increasing the percentage of either water or gas produced. Furthermore, matrix acidizing can apply into both formations, sandstone and carbonate.

Sandstone formations are often sequentially treated with a preflush, a mixture of hydrofluoric and hydrochloric acid, and an afterflush. A preflush usually applies hydrochloric acid 5-15% by weight to reduce the possible redamaging of the formation by precipitation of insoluble sodium and potassium fluorides or fluosilicates. Following the preflush, a mixture of acids is then injected. This mixture is chosen because of its ability to dissolve clays, also will react with most constituents of naturally occurring sandstone, including silica, feldspar, and calcareous material. HCl will not react with these materials but this strong acid is still required to keep the pH low, thereby reducing the precipitation of HF reaction products. Finally, an afterflush is generally utilized to isolate the reacted HF from brine that may be used to flush the tubing, to displace spent acid into the formation, and to restore water wettability of the formation.

In carbonates, matrix acidizing treatments normally employ 15% or 37% by weight hydrochloric acid. The high reaction rate of this strong acid with limestone or dolomite results in the formation of large flow often called wormholes. These wormholes typically penetrate a few feet (0.3 to 2 m) radially into the formation. Although the depth of stimulation is not as significant as with fractures, these wormholes stimulate the near-wellbore region where the majority of flow resistance associated with the radial geometry is manifested. Therefore, the effectiveness of these treatments is firmly dependent upon the formation of wormhole. These structures of wormhole are varied with fluid/rock systems and acid injection rates. Therefore, many researchers have tried to discover the relation of these systems.

## **2.2 Wormhole formation**

Typically, the effectiveness of matrix acidizing is dependent upon the success of wormhole formation. Then, the importance of the wormhole channel must be considered. Several researchers investigated the wormhole formation involving the complication phenomenon.

Scheidegger (1960) reviewed capillary models and found that to predict those quantities related to the geometric structure of a porous media, an empirical correction factor (tortuosity) must be introduced. Schechter and Gidley (1969) used a capillary model for describing the growth function of wormhole. However, the design of a treatment requires a basic knowledge of all the phenomena involved. The comprehension of wormhole induces various steps. These include a chemical reaction between a fluid and various solids, and the flow of a liquid through a porous medium. Early investigators recognized the significant influence of mass transfer on wormhole formation in limestone (William *et al.*, 1970; Nierode and William, 1971). This influence has served as a basis for many of the theories describing wormhole formation. Daccord and Lemanczyk (1987) recommended a dimensionless kinetic parameter  $P$ , defined as the ratio of the flux of molecules provided by molecule diffusion over the flux of molecules consumed by the surface reaction. This quantified parameter can describe the mixed kinetics. The kinetic parameter approached zero when the whole reactions are governed by mass transfer kinetics. On the other hand, this value approached infinity when they are governed by surface kinetics. Furthermore, Daccord *et al.*, (1989) investigated the water/plaster of Paris ( $\text{CaSO}_4$ ) system and reported the dissolution to depend on Peclet number. The Peclet number is defined as the ratio of transport by convection to transport by diffusion. A similar dependence on the Peclet number was observed by Mostofizadesh *et al.*, (1994) for the HCl/limestone system. Frick *et al.*, (1994) also studied the HCl/limestone system and combined the concepts of fractal geometry with the dependence on the Peclet number. Wang *et al.* (1993) and

Huang *et al.* (1997) investigated HCl/carbonate systems and proposed that the optimum injection rate occurred at a transition between reaction rate and fluid-loss limited regime. Despite mass transfer having a major influence on wormhole formation, diffusion plays only a minor role in their theory.

Hoefner and Fogler (1988) examined HCl/carbonate systems and demonstrated that the reaction rate and diffusion coefficient both play important roles in determining the wormhole structure. They found that the structure of the dissolution channels depends significantly on the injection conditions and fluid/rock properties and is governed by the Damköhler number (Hekim *et al.*, 1982) for flow and reaction. The Damköhler number is defined as the ratio of the net rate of dissolution by acid to the rate of convective transport of acid. When the dissolution is limited by the rate of mass transfer (e.g., the dissolution of limestone by HCl), the Damköhler number is given by

$$Da_{mt} = \frac{aD_e^{2/3}l}{Q} \quad (2.1)$$

where  $D_e$  is the effective diffusion coefficient,  $Q$  is the flow rate,  $l$  is the pore length, and  $a$  is a constant depends on the carbonate sample. On the other hand when the dissolution is limited by the rate of mass transfer (e.g., the dissolution of dolomite by HCl), the Damköhler number is given by

$$Da_{rxn} = \frac{ak_r dl}{Q} \quad (2.2)$$

where  $k_r$  is the surface reaction rate constant and  $d$  is the pore diameter. The dissolution of dolomite by HCl is reaction rate limited below about 50 C (Lund *et al.*, 1973).

Hoefner and Fogler (1988) observed that a minimum volume of the fluid was required for channel breakthrough (i.e., optimum conditions for wormhole formation) when the Damköhler number was varied over several orders of magnitude. This observation is consistent with the existence of an optimum injection rate for constant fluid/rock properties because the Damköhler number is inversely proportional to the injection rate. At high Damköhler number or low injection rates, the reactant is consumed on the inlet flow face of the core. However the volumes of fluid required to breakthrough are high, permeability increases are negligible. The lower Damköhler number leads the reactant penetrate into the porous matrix and enlarge flow channels. Unconsumed reactant reaches the advancing tips of the channels and a dominant wormhole is eventually formed. The wormhole provides significant permeability increases and requires a minimum volume of fluid to permeate the rock matrix. As the Damköhler number is reduced further, flow channels become more highly branched as fluid is forced into smaller pores. Dissolution occurs over a high surface area, which results in an increase in the fluid volume required to breakthrough. Thus, there is an optimum Damköhler number at which the least amount of reactant fluid is required for channel breakthrough. Wang *et al* (1993) also presented the existence of the optimum injection rate.

### **2.3 Well Stimulating acids**

The basic types of acids used in carbonate stimulation can be classified as mineral acids, organic acids, powdered organic acids, and retarded acid systems. All these, with the exception of the hydrofluoric, hydrochloric-

hydrofluoric and formic-hydrofluoric acid mixtures, are used to stimulate carbonate formation. HF acid should never be used in carbonate formations because of causing the insoluble precipitate,  $\text{CaF}_2$ .

### 2.3.1 Mineral acids

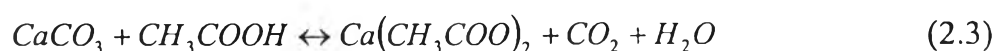
#### *Hydrochloric acid*

Most acid treatments of carbonaceous formations overwhelmingly employ hydrochloric acid (HCl). Normally, it is used as 15% by weight HCl; however, acid concentration may vary between 5% and about 35% by weight. HCl will dissolve limestone, chalk, dolomite, and most other carbonates.

In addition, the continued use of HCl results in the severe problems. The principle disadvantages are its high corrosivity on wellbore tubular goods. The high corrosivity is especially significant and expensive to control at high temperature. Also, aluminum- or chromium-plated metals, often found in pumps, are easily damaged. Generally, the application will dictate whether a less corrosive acid than HCl is required.

### 2.3.2 Organic acids

The principle virtues of the organic acids are their lower corrosivity and easier inhibition at high temperature. Despite, the carbonate dissolution is be restricted by the reversible reaction. The conversion of the reactants into products is not complete as a result of the accumulation of the products such as acetic acids presented by Daccord (1987).



Carbon dioxide ( $\text{CO}_2$ ) is a weak acid in water and prevents the complete dissociation of acetic acid. Acetic acid has used as a substitute of mineral acids more than several years.

### *Acetic acid*

Acetic acid was the first of the organic acids to be employed in appreciable volumes in well stimulation. It is commonly available as a 10% by weight solution in water. At this concentration, the products, calcium and magnesium acetates, are generally soluble in spent acid. Other advantages of acetic acid in comparison to HCl are:

1. Acetic acid is naturally sequestered against iron precipitation.
2. It does not cause embrittlement or stress cracking of high strength steels.
3. It will not corrode aluminum.
4. It will not attack chrome plating up to 200°F.

### *Formic acid*

Formic acid is substantially stronger than acetic acid, though appreciably weaker than HCl. Likewise, formic acid reacts to an equilibrium concentration in the presence of its reaction products.

The apparent principle advantage of formic acid over acetic acid is cost compared with their molecular weight. Although, more corrosive than acetic acid, formic acid corrodes uniformly and with less pitting than HCl. An effective inhibitor is available for its use at temperature as high as 400°F.

#### 2.3.3 Powdered acids

Powdered acids have been limited use in the well stimulation. They are superior to other acids as the result associated with their portability to remote locations in powdered form. *Sulfamic acid and Chloroacetic acid* can be hauled to the location as a dry powder and then mixed with water. Both of them are substantially more expensive than HCl on an equivalent dissolving power defined as the ratio the volume of rock dissolved per volume of acid reacted.



Because the amount of  $\text{CaCO}_3$  dissolved by one pound of sulfamic acid is only about one-third that dissolved by an equal weight of HCl.

#### 2.3.4 Acid mixtures

##### *Acetic-Hydrochloric Acids and Formic-Hydrochloric Acids*

These acids have been designed to exploit the dissolving power economies of HCl while attaining the lower corrosivity (especially at high temperature) of the organic acids. For example, small amounts of formic acid are often added to HCl to increase the effectiveness of the corrosion inhibitor.

##### *Chemically Retarded Acids*

These acids are often prepared by adding oil-wetting surfactants to acid in an effort to create a physical barrier to acid transfer to the rock surface. The additive must adsorb on the rock surface and form a coherent film. Use of these acids often requires continuous injection of oil during the treatment.

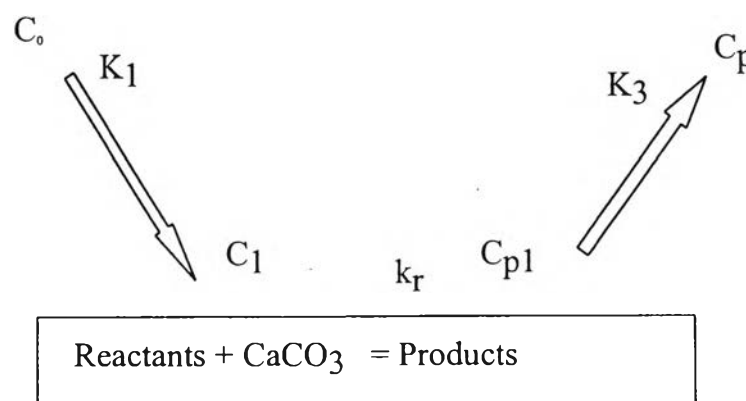
##### *Emulsified Acids*

Emulsified acids can contain the acid as either internal or external phase. The higher viscosity created by emulsification and the presence of the oil can retard the rate of acid transfer to the rock. This reduction in transfer rate, and its corresponding reduction in acid reaction rate, often can increase the depth of acid penetration.

## **2.4 Development of Comprehensive Dissolution Kinetics of Acidizing Processes**

Several investigators have tried to simplify the model for accessing the highest effectiveness of acidizing treatment. They primary studied on sandstone

acidizing with linear cores which did not show any instabilities because the flow was considered as pistonlike. (Fredd, 1998). They also believed that factors, which had effects as macroscopic formations, are the kinetics limited by surface reactions and reactions on the surface. Many models considered either a unique reactive species (Lund and Fogler, 1976; McCune and Fogler, 1976) or various species with different reactivities (Hekim et al. 1982, Taha et al, 1984). Fredd (1998) also formulated these mechanisms, which consisted of many factors. This model can primarily predict the optimum condition (acidic species, and injection rates), providing the suitable condition and the highest effectiveness for a wide range of solid-liquid systems. The overall carbonate dissolution mechanism has been modeled as three sequential steps as shown in Figure 2.1. These relative steps consist of mass transfer of reactants to the carbonate surface, reversible surface reactions, and mass transfer of products away from the carbonate surface. To simplify the illustration of this development, the surface reaction have been generalized as



**Figure 2.1** Schematics of carbonate dissolution mechanisms.

Assuming this dissolution is a first order reaction and heterogeneous chemical reaction due to the interaction between two phases. The rate of dissolution ( $r_D$ ) is given by

$$r_D = k_r \left( C_i - \frac{C_{pi}}{K_{eq}} \right) \quad (2.5)$$

where  $k_r$  is the effective forward reaction rate constant,  $K_{eq}$  is the effective equilibrium constant, and  $C_i$  and  $C_{pi}$  are the reactants and products at the solid-liquid interface, respectively. The effective reaction rate and equilibrium constants for this generalized reaction depend on the pH and the type of species presented.

At steady state, the rates of the three sequential steps are equal and the rate of reactant consumed ( $r_A$ ) is given by

$$\begin{aligned} r_A &= \nu r_D \\ &= K_1 (C - C_i) \\ &= \nu k_r \left( C_i - \frac{C_{pi}}{K_{eq}} \right) \\ &= \nu K_3 (C_{pi} - C_p) \end{aligned} \quad (2.6)$$

Where  $\nu$  is the stoichiometric ratio of reactants consumed to products produced, and  $K_1$  and  $K_3$  are the mass transfer coefficients for reactants and products, respectively. These expressions are solved simultaneously for the interface concentrations, which are then substituted back into equation (2.6). The concentration of products in the bulk solution at steady state is given by

$$C_p = \frac{(C_0 - C)}{\nu} \quad (2.7)$$

where  $C_0$  is the initial reactant concentration. Making the additional substitution for  $C_p$  in equation (2.6), the rate of reactant consumption can then be expressed as

$$r_A = \kappa \left[ C - \frac{C_0}{1 + \nu K_{eq}} \right] \quad (2.8)$$

where the overall dissolution rate constant,  $\kappa$ , depends on the sum of resistance in series and is given by

$$\kappa = \frac{1 + \frac{1}{\nu K_{eq}}}{\frac{1}{K_1} + \frac{1}{\nu k_r} + \frac{1}{\nu K_{eq} K_3}} \quad (2.9)$$

The dissolution of porous media is then modeled as the dissolution of a representative cylindrical tube. The cylindrical tube represents the dominant flow channels within the porous media (i.e., the wormhole). Convection and reaction in the tube are included in the reactant mass balance, where equation (2.8) is used for the rate of reactant consumption. Solution of the reactant mass balance equation resulted in an expression for the concentration profile along the length of the channel, which was dependent upon the Damköhler number.

$$\frac{C}{C_0} = \frac{1 + \nu K_{eq} e^{-Da}}{1 + \nu K_{eq}} \quad (2.10)$$

Here, the Damköhler number is defined as

$$Da = \frac{4l\kappa}{du} = \frac{\pi dl\kappa}{Q} \quad (2.11)$$

where  $d$  and  $l$  are the diameter and length of the capillary tube, respectively.  $u$  is the superficial velocity in the capillary tube. Because the length and diameter of the wormhole change with time, equation (2.8) gives an average Damköhler number for a wormhole of length  $l$ . This Damköhler number includes the effects of reactants transport, the reversible surface reaction, and the products transport. Physically, it provides a measure of the amount of reactant being consumed on the walls of the wormhole, as opposed to being transported to the tip of the wormhole where it can be consumed efficiently.

To determine the overall dissolution rate constant, the mass transfer coefficients are obtained from Levich's solution of the convective diffusion equation for laminar flow in a cylindrical tube (Levich, 1962). The average mass transfer coefficient along the length of a tube is given by

$$K_{mt} = 1.86D_e^{2/3} \left( \frac{u}{dl} \right)^{1/3} \quad (2.12)$$

where  $K_{mt}$  is for either reactants or products ( $K_1$  or  $K_3$ ), depending on the value of the diffusion coefficient. Because the capillary tube represents the wormhole channels, measured diameters of these channels are obtained from neutron radiograph and used for the diameter of the capillary tube. Typical diameters were on the order of 0.06 cm. The length of the tube was assigned a representative length of the wormhole (one-half the length of the core).