CHAPTER II
LITERATURE REVIEW

2.1 Oil Production and Related Problems

Most oil and gas wells today are drilled by rotary drilling method. The basic concept of rotary drilling is to make hole with a boring action. A bit rotates while it is in constant contact with the rock at the bottom of the hole. Part of the weight of the drill pipe above the bit rests on the bit while it is rotating to force it into the rock as it turns. More drill pipes are jointed together as the depth increases and become drill string. Drilling fluid is then pumped down the drill string and back to the surface in order to remove rock cuttings from the hole and cools the bit as it breaks up the rock at the bottom of the hole. This fluid also prevents the hole from caving by plastering its surface with a protective film of mud and prevents the escape of the oil and gas in the reservoirs. When the proper depth is reached, casing string is installed. Cement is pumped down the casing and out around the bottom of the casing so it can fill the annular space. After cement cure, the hole is then drilled again until it reaches the next depth. To bring oil up to the surface, oil must be replaced the capillary interstices of the porous reservoir. In young wells, oil can be delivered easily by natural pressure but this pressure will fall as the time passes leading to decrease in efficiency of oil production. To improve oil recovery the reciprocating plunger pump is installed in order to pump the oil moving to the surface. However, the decline in production capacity sometimes causes by other problems that cannot be solved by only pumping. Other techniques must be employed.

2.1.1 Formation Damage

Most formation damages occur in the region near the well bore which results in a decline in oil productivity. Formation damages may result from the plugging of the pore spaces by solid particles, by mechanical crushing or disaggregating of the porous media, by fluid effects such as the creation of emulsions or changes in relative permeability, or by biological damages.

2.1.1 Oil Well Stimulation

Two types of well treatments or stimulations are normally used.

2.1.2.1 Hydraulic Fracturing

Hydraulic fracturing is the method that improves the productivity by fracturing the formation and creates channels in the rock through which fluids can flow to the well bore. The fluid is injected until the fluid pressure become greater than the stresses inherent in the rock. This causes the rock to split apart. Fracturing fluid must be pumped into the fracture instantaneously to hold the fracture open. Although the concept of this method is quite simple, the pressures employed are so high that a lot of energy is required.

2.1.2.2 Acidizing

This technique enhances oil productivity by improving the drainage efficiency of the formation rock around the well bore. Acid injected into the channel dissolves soluble material resulting in a larger cross-sectional area of the channel. This increases the permeability and porosity of the reservoir formation.

Both organic and inorganic acids are used in this method. Organic acids are defined as derivatives of hydrocarbons with at least one carboxyl groups (-COOH). Organic acids commonly used in oil well stimulation are formic (HCOOH), acetic (CH_3COOH), oxalic, and citric. Inorganic acids are acids derived from mineral sources. Hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4), and sulfamic (HSO_3NH_2) are commonly used in treating. However, mineral acids are more preferable in the industries than organics since they are less expensive and have a greater strength.

There are four different kinds of acid treatments: acid soak or acid washing, high-pressure acidizing, acidizing through pre-existing fractures, and matrix acidizing.

a) Acid soak or acid washing is a process that cleans the surfaces of the well bore and equipment by acid without penetration into the formation.

b) High-pressure acidizing is the treatment in which acid is injected into the formation at a fracture pressure, a pressure high enough to fracture the formation rock. The purpose of this method is to make new flow paths into the undamaged zones of the reservoir rock resulted into more drainage surface area.

c) Acidizing through pre-existing fractures is the method that injects acid into the well bore through the channels created either naturally or by fracturing treatment.

d) Matrix acidizing is to inject acid into the flow channels of the formation at a pressure lower than the fracture pressure. No fracture occurs in this treatment. The acid radially penetrates the formation causing the flow channels to become larger. The soluble particles plugging the pore spaces are also dissolved and come out with spent acid.

2.2 Matrix Acidizing

Matrix acidizing is an oil well stimulation technique commonly used in the oil industry. In matrix acidization, an acid solution, either alone or mixed with another acid, is injected into the formation, where there is damage, to dissolve the mineral formation. The result is an increase in permeability in the near-well bore vicinity. This process is operated at a pressure below that which causes fracturing. The increase in production depends on the removal of the damaged zone.

This process consists of three main steps: preflush, main acid stage, and afterflush.

a) Preflush deals mostly with HCl, which is pumped to dissolve minerals, and serves as a buffer between acid system and formation brine.

b) Main acid stage is the main step of acidizing. Most fines and aluminosilicates are dissolved in this step. The type of acid used depends on rock mineralogy, produced-fluid compatibility, and petro-physics of the reservoir sand.

c) Afterflush or post flush uses generally HCl or ammonium chloride (NH_4Cl) to ensure that live acid can penetrate into the matrix. In heavy crude wells, xylene may be added before the preflush stage in order to dissolve and disperse heavy crude coating the matrix.

2.2.1 Acid Selection

The acid used in acidizing treatment is the key for success. Weak acid may be unable to handle the matrix formation while the stronger ones may cause serious problems from their over strength. The factors, which are suggested to be concerned before using acidizing in real scale, are the capacity of rock-dissolving, the spending time, the solubility of reaction products, the amount and pattern of metal corrosion, the compatibility of acid with reservoir fluids, the density and viscosity of spent acid, and the etching pattern. The type of acid used also depends on the kind of reservoir. In sandstone reservoirs, the treatment is usually performed with a mixture of HF and HCl, whereas in carbonate reservoirs (limestone and dolomites), HCl alone is used since HF is too strong so not only the plugging materials but the rock itself also reacts and dissolves.

2.2.2 Problems in Matrix Acidizing

Using matrix acidizing, a well can be stimulated; however, some reservoirs do not exhibit successful results. This is because of improper reactions of acids creating products which cause plugging. For example, in the case of sandstone wells in the Niger delta, some wells had no production increase and some even showed a decrease after acidizing. Problems from acidizing can be classified by their origin into four groups.

2.2.2.1 Clay swelling

The clay swelling results from ion exchange of sodium ions attached to the clays and ions of the injected fluid. When ion exchange occurs, the clays convert the

fluid into salt water. Exposure to this low-salinity brine can cause water-sensitive clays to swell and obstruct matrices. Smectite and mixed-layer (illite and smectite) are most water sensitive and are hence most likely to swell. Sand, feldspar, and kaolinite; on the other hand, are non-swelling.

2.2.2.2 Fine migration

Most fine migration problems result from the physics of flow. Since both kaolinite and illite are loosely bound and can be easily dispersed by production velocities, they are the two kinds of clay recently found to involve in this phenomenon.

2.2.2.3 Precipitation

Minerals that produce precipitates upon contact with acid (normally HF) are classified into three main groups: sodium-containing minerals, potassium-containing minerals, and carbonates.

Both sodium-containing and potassium-containing minerals precipitate silicon fluorides but with different degree of damage. Silicon fluorides produced by potassium-containing minerals have more plugging capability and occur closer to the well bore than those produced by sodium-containing minerals. They also precipitate in greater quantities. Fluosilicate precipitation can be found in illite, mixed-layer, and mica clays since they contain potassium while zeolites occasionally have precipitation caused by sodium (Golan and Whitson, 1991).

Carbonates precipitate calcium fluorides when contacted with live acid. However, the main problem with carbonates is aluminum fluorides, which precipitate upon contact of carbonates and spent acid. These aluminum scales can deposit in the matrix as well as in the well bore and cause very serious plugging problem.

2.2.2.4 Gel formation

The problem of gel formation results from clay instability. The clay decomposes in acid (usually HCl) and forms silica gel. This gel then forms polymerization and produces plugging colloidal particles. Chlorite and zeolites have the most probabilities to have this problem since they both are very unstable in acid. However, all clays have their own temperatures above which they are unstable in acid.

The problems occur in each kind of clays are listed in Table 2.1.

Table 2.1 Reactions with injected fluids

Mineral	Cation exchange capacity
Feldspar	Contains sodium and potassium. Fluosilicate precipitation and potassium feldspars can create major problems.
Carbonate	Consumes HCl acid and can cause precipitation of fluosilicates and aluminum from spent HF acid.
Illite	Can cause fines migration problems, is ion exchanging, and contains potassium, which can cause fluosilicate precipitation from spent HF acid.
Kaolinite	Can cause fines migration problems, disperses in freshwater, and causes plugging.
Smectite	Is ion exchanging and swells in freshwater.
Mixed-layer clay	Is ion exchanging, swells in freshwater, and frequently contains potassium, which can cause fluosilicate precipitation from spent HF acid.
Chlorite	Is ion exchanging and unstable in HCl acid.
Zeolite	Is ion exchanging, very unstable in HCl acid, and occasionally contains sodium, which can cause fluosilicate precipitation from spent HF acid.

2.3 Zeolite: Analcime

Zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. The ratio of Si and Al to oxygen equals to 1/2. Zeolites are naturally negatively charged and attract the positive cations that reside within. Since they contain large vacant spaces or cages in their structures, zeolites have low specific gravity and ability to adsorb some large molecules. The adsorption is somehow selected by the formation pattern of channels in the structure.

Analcime or analcite is a low-density crystalline mineral. The chemical formula of analcime is $[Na_{16}(H_2O)_{16}] [Si_{32}Al_{16}O_{96}]$ Murphy et al., 1996). The crystal parameter of analcime is cubic and the space group is Ia3d. Its framework (Figure 2.1) composes with strongly distorted T6-ring chairs. These T6-rings attached with each other by a 2-fold rotation axis. Its pore or channel sizes are approximately 1.6 to 4.2 A. Analcime composed with Si tetrahedral and Al tetrahedral. The Na ion sits at the Al tetrahedral location in order to balance the charge.
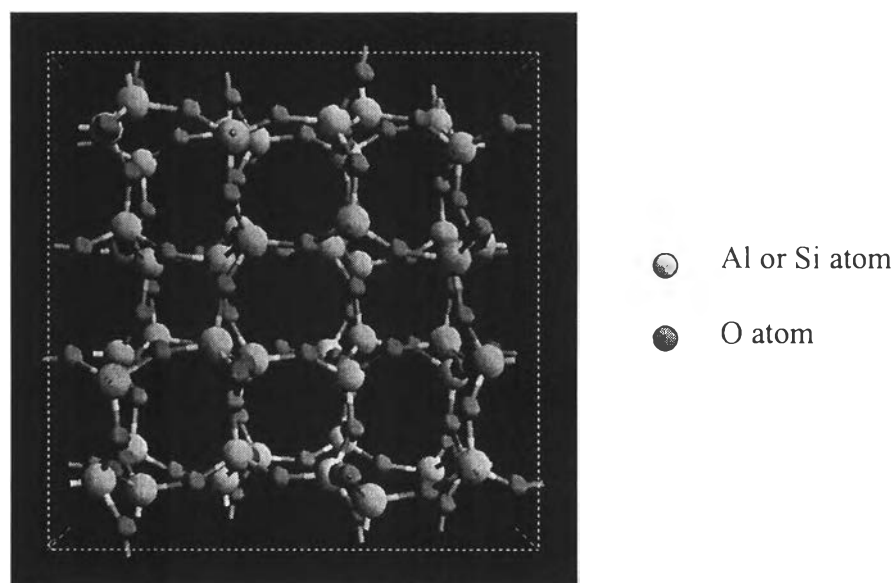

⊙   Al or Si atom

⊙   O atom

Figure 2.1   Framework structure of analcime.

The solubilities of analcime and clinoptilolite were determined in dilute, weakly alkaline, aqueous solution below 300°C at vapor-saturated pressures (Wilkin

and Barnes, 1998). Analcime from two different sources with a different Si/Al ratio was used in this study. The values of Gibbs free energies of formation, $\Delta G^{\circ}{}_{f}$ at 25°C and 1 bar for analcime were found to be -3089.2 (Si/Al = 2.02) and -3044.4 (Si/Al = 2.55). The increase in Al content in analcime was found to stabilize the aluminosilicate framework.

Underdown et. al. (1990) studied the acidization of analcime-cemented sandstone in the Gulf of Mexico. From this study, the results obtained indicated that analcime has a high solubility in HF. A white pasty gel was found to form with HF and HCl but not with acetic acid. Acetic acid was found to provide good stimulation of calcerous minerals and is compatible with zeolite mineral, analcime.

Murphy et al. (1996) studied the reaction kinetics and thermodynamics of aqueous dissolution and growth of analcime at pH close to 9. The experiment was conducted at low temperature (25°C) for up to 2.6 yr. Analcime dissolution and growth were found to be approximately stoichiometric. The dissolution reaction for analcime of generalized stoichiometry according to this study can be written as follows:

$$(NaAl)_{1+x}Si_{2-x}O_6 \cdot nH_2O \leftrightarrow (1+x)Na^+ + (1+x)Al(OH)^{4-} + (2-x)SiO_2 + [n - 2(1+x)]H_2O$$

(2.1)
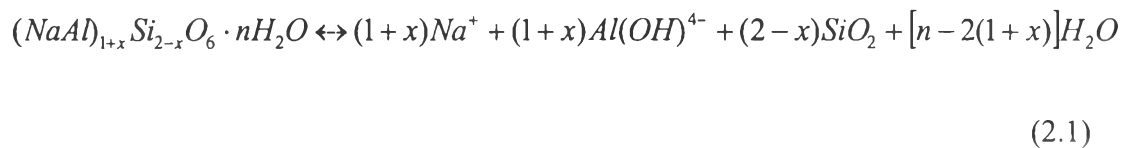
Where, n and x are coefficients expressing compositional variations.

2.4 Citric acid

Citric acid is a tribasic acid. The dissociation reactions of each proton are illustrated below:

$$C_6H_8O_7 \leftrightarrow C_6H_7O_7^- + H^+ \qquad pKa_1 = 3.128 \qquad (2.2)$$

$$C_6H_7O_7^- \leftrightarrow C_6H_6O_7^{2-} + H^+ \qquad pKa_2 = 4.761 \qquad (2.3)$$

$$C_6H_6O_7^{2-} \leftrightarrow C_6H_5O_7^{3-} + H^+ \qquad pKa_3 = 6.396 \qquad (2.4)$$

The increase in *pKa* values indicates the increase in bond strength between hydrogen atoms and the rest of the molecule in the four species in the sequence $C_6H_8O_7$, $C_6H_7O_7^-$, $C_6H_6O_7^{2-}$ and $C_6H_5O_7^{3-}$.

These species are present in different concentrations depending on the pH of the solution. The abundance of each species could be calculated by a known procedure (Marinovic and Despic, 1997) using the value of pK_a as shown in Figure 2.2.

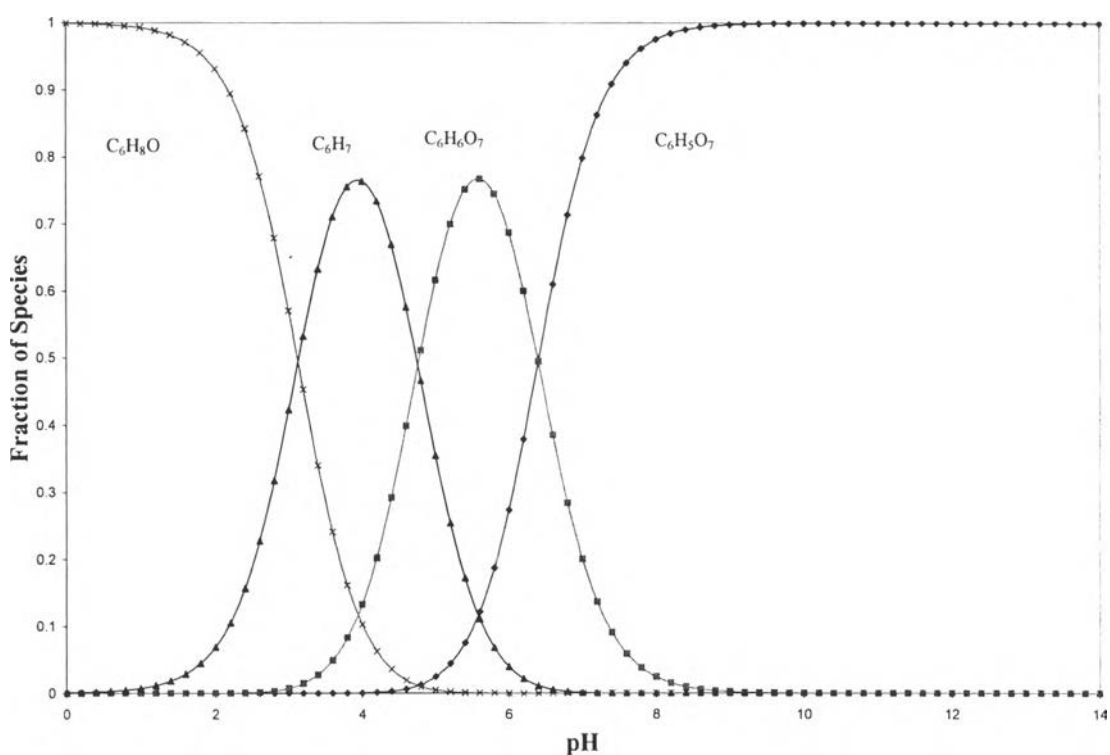**Figure 2.2** Deprotonation of citric acid.

It was found that pH values of prevailing concentration of one of the species are <1.3 for $C_6H_8O_7$, 4.0 for $C_6H_7O_7^-$, 5.55 for $C_6H_6O_7^{2-}$ and >8.5 for $C_6H_5O_7^{3-}$.

Yokel (2002) has found that the citrate can enhance Al removal by its chelating property. Since the citrate species was found to have the properties of Al chelation it is possible that it can also be a Si chelator, therefore, it is one of the new alternatives for acidization.

Other chelating agents, such as EDTA, have been shown to enhance the dissolution reaction of carbonates with acetic acid (Fredd and Fogler, 1998).

2.5 Reaction Mechanisms

Many reaction mechanisms for various kinds of acid have been developed in the dissolution of different types of alumino-silicates. However, the application of those mechanisms is limited to the dissolution of zeolite alumino-silicates such as analcime. The general form of the overall dissolution reaction of an alumino-silicate (M-Al-Si) in a strong acid (HX) may be written as shown below:

$$M - Al - Si + HX \leftrightarrow Al^{3+} + SiO_2 \cdot 2H_2O + M^+ + X^- + H_2O \qquad (2.5)$$
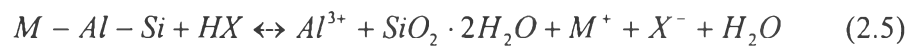
Where M represents other cations such as Na, K and X can be I, Cl or Br. The most abundant products may be $Al^{3+}X^-$, $SiO_2.2H_2O$ (hydrated silica), other salts (M^+X^-) and water (Shuchart et al., 1995). Therefore, the dissolution reaction of analcime ($Na_2O\,Al_2O_3*4SiO_2\,2H_2O$) in hydrochloric acid can be written according to equation (2.6) as shown below:

$$Na_2O \cdot Al_2O_3 * 4SiO_2 \cdot 2H_2O + 3HCl \leftrightarrow 2AlCl_3 + 4SiO_2 \cdot 2H_2O + 2NaCl + 4H_2O$$

$$(2.6)$$
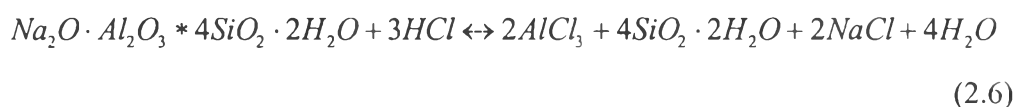
Other reactive intermediate such as $SiCl_4$ may exist in the system. The exact mechanism requires more research.

For multiprotonic acid such as citric acid, the product of the reaction may exist in many different patterns since the acid reacts with its different forms. The overall reaction is difficult to describe by a single equation. The possible products are hydrated silica, $Si^{4+}(C_6H_7O^-)_4$, $Si^{4+}(C_6H_7O^{2-})_2$, $Si^{4+}_3(C_6H_7O^{3-})_4$, $Al^{3+}(C_6H_7O^-)_3$, $Al^{3+}_2(C_6H_7O^{2-})_3$, $Al^{3+}(C_6H_7O^{3-})$, $Na^{1+}(C_6H_7O^-)$, $Na^{1+}_2(C_6H_7O^{2-})$, $Na^{1+}_3(C_6H_7O^{3-})$. However, the variety of the product is limited by the pH of the system since the

dissociation of citric acid is also depend on the pH of the system as shown in Figure 2.1.

2.6 Reaction Kinetics

Equation (2.7) illustrates the general mole balance on a batch reactor for the dissolution of an alumino-silicate in acid (Fogler, 1999):

$$-\frac{d[ion]}{dt} = -r_{ion} = -r_{ion}^{''} a \rho_s \tag{2.7}$$

Or,

$$-\frac{dM_{ion}}{dt} = -r_{ion}^{'} \tag{2.8}$$

Where, $[ion]$ = Concentration of Al, Si or Na in the solution at time t, mmole/dm^3

$-r_{ion}$ = Rate of disappearance of Al, Si or Na per initial total volume of solid, mmole/dm^3/min

$-r_{ion}^{'}$ = Rate of disappearance per mass of undissolved solid, mmole/g/min

$-r_{ion}^{''}$ = Rate of disappearance per initial reactive surface area, mmole/dm^2/min

a = Solid particle surface area per unit mass, dm^2/g

ρ_s = Density of solid particle, g/dm^3

M_{ion} = Mole of dissolved solid particle per mass of undissolved solid particle at time t, mmole/g

t = Time, min

Assuming that the dissolution is an elementary reaction, the rate law on a basis of solid reactant becomes:

$$-r_{ion} \sim k[Acid]^\alpha \tag{2.9}$$

Let,

$$k = a_s k^{''} \qquad (2.10)$$

Where,

$$a_s = a\rho_s \qquad (2.11)$$

And,

$$\frac{d[ion]}{dt} = r^{''}_{ion} a_s \sim k[Acid]^\alpha \qquad (2.12)$$

Where, $[Acid]$ = Concentration of acid at time t, mmole/dm^3

α = Reaction order with respect to the hydrogen ion

a_s = External particle surface area per volume of reaction mixture, dm^2/dm^3

$k^{''}$ = Specific reaction rate, dm^3/dm^2/min

k = Specific reaction rate, min^{-1}

2.7 The Shrinking Core Model

The shrinking core model can be used to describe the dissolution of a particle for the case in which the particle does not break-up (Fogler, 1999).
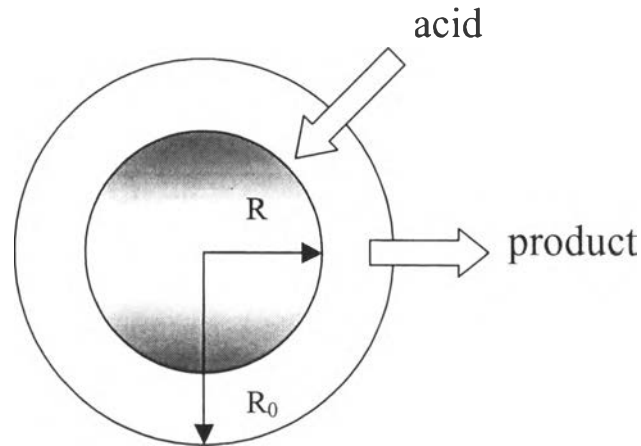
Figure 2.3 The shrinking core model for the dissolution reaction of analcime in acid.

Considering the case where the particles are completely consumed (monodispersed solid particle), let A and B represent the acid and analcime solid particles, respectively. In this case, A must diffuse to the surface to react with B at the liquid-solid interface. Assuming that the reaction is zero-order respect to B and first-order respect to A, the rate of mass transfer to the surface and the rate of surface reaction can then be written as:

$$W_{Ar} = k_c \left(C_A - C_{AS} \right) = -r''_{AS} = k_r C_{AS} \tag{2.13}$$

Where, W_{Ar} = Molar flux of species A, $\text{mmol/dm}^2\,\text{s}$

$-r''_{AS}$ = Rate of disappearance of species A per unit area, $\text{mmol/dm}^2\,\text{s}$

k_c = Mass transfer coefficient, dm/s

k_r = Specific reaction rate, s^{-1}

C_A = Concentration of species A in the bulk solution, mmol/dm^3

C_{AS} = Concentration of species A at the surface, mmol/dm^3

Eliminating C_{AS}, equation (2.14) is then obtained:

$$W_{Ar} = -r_{AS}^{''} = \frac{k_c k_r}{k_c + k_r} C_A \qquad (2.14)$$

For the case of small particle and negligible shear stress at the fluid boundary, the Sherwood number (Sh) is approximately 2 or

$$k_c = \frac{2D_e}{D} \qquad (2.15)$$

Where, D is the diameter of the dissolving particle (dm) and D_e is the effective diffusivity (dm^2/s). Substituting equation (2.15) into equation (2.14) and rearranging yields

$$-r_{AS}^{''} = \frac{k_r C_A}{1 + k_r/k_c} = \frac{k_r C_A}{1 + k_r D/2D_e} = \frac{k_r C_A}{1 + D/D^*} \qquad (2.16)$$

Where, $D^* = 2D_e/k_r$

A mole balance on the solid B particle can be written as

$$r_{BS}^{''} \pi D^2 = \frac{d(\rho \pi D^3/6)}{dt} \qquad (2.17)$$

Where, ρ is the molar density of species B. If 8 mols of A dissolve 1 mol of B, then $-r_{AS}^{''} = -8r_{BS}^{''}$. After differentiation and rearrangement, equation (2.17) becomes,

$$\frac{dD}{dt} = -\left[\frac{2(-r_{AS}^{''}/8)}{\rho}\right] = -\frac{k_r C_A}{4\rho}\left(\frac{1}{1 + D/D^*}\right) \qquad (2.18)$$

$$\frac{dD}{dt} = \frac{\alpha}{1 + D/D^*}$$ (2.19)

Where,

$$\alpha = \frac{k_r C_A}{4\rho}$$

At time t = 0, the initial diameter is D_i. For the case of excess concentration of A, integrating equation (2.19) yields the following relationship between diameter and time:

$$D_i - D + \frac{1}{2D^*}\left(D_i^2 - D^2\right) = \alpha t$$ (2.20)

2.8 Basic Principle of Diffusion

The diffusion of matter is generally expressed by Fick's first law of diffusion

$$J = -D\frac{\partial c}{\partial t}$$ (2.21)

Where, D is defined as diffusivity.

Two different diffusion phenomena may be distinguished; mass transfer (transport diffusion) and Brownian molecular motion (self-diffusion).

Diffusion in small pore zeolites and carbon sieves shares many common features with surface diffusion. The steric and other effects associated with the proximity of the wall need to be taken into consideration to develop the model.

2.9 Crystal Dissolution

The dissolution of crystal was observed in order to develop a model to describe the mechanism (Lasaga and Luttge, 2001). This pit plays the major role as a nucleating agent for holes. The dissolution rate was found to be related to the radius of the dislocation defect.

Yamamoto, et al (1996) studied the dissolution of zeolite in acid and alkaline aqueous solution by AFM. They found that the dissolution occurs layer by layer that is the uppermost layer was attacked and dissolved completely before the attack begins with another layer. The dissolution was also found to be due to the pore structure.

The dissolution of dicalcium phosphate dehydrate was found to be resulted from the nucleation and the growth of different types of pits (Kanzaki, et al, 2002). The difference in crystal plane was found to affect the dissolution process.

The process of crystal dissolution can theoretically be considered as a combination of three steps: volume diffusion, surface reaction or surface disintegration, and heat transfer (Al-Jibbouri and Ulrich, 2002). However, this process is frequently described by only diffusion step. Therefore the dissolution rate is derived as a function of the density of the solution and the concentration of the solute.