

CHAPTER II

LITERATURE SURVEY



2.1 Oil Production and Problems

The common method of oil recovery used in most of the regions of the world is rotary drilling. In order to bring the oil to the surface, oil must be replaced through the capillary interstices of the porous reservoir. In a wellbore, the production capacity decreases by formation damage in the wellbore, causing a narrow pore and occurrence of several problems after oil well stimulation (Russell, 1951).

2.1.1 Problems in Oil Production

2.1.1.1 *Matrix formation*

Fines migration problems resulting from the physics of flow involve two kinds of clay: kaolinite and illite. Both clays are loosely bound and can be easily dispersed by production velocities near the well bore (Gdanski, 1999).

2.1.1.2 *Clay swelling resulted from ion exchange on clay*

Ion exchange occurs between formation minerals and injected brines. Sodium ions are often attached to the clays but these ions can become exchanged with ions of injected fluid. When ion exchange occurs, the clays convert the injected fluid to 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 the most water sensitive and hence the most prone to swelling after ion exchange. In contrast, sand, feldspar and kaolinite are not prone to swelling. Zeolite minerals will not swell, but they have high ion-exchange capacities. Such minerals are likely to contain sodium that could contaminate spent HF acid or quickly transform 2% KCl into weak salt water (Gdanski, 1999).

2.1.1.3 Plugging problems caused by clay instability during acid treatment

Clay can react with HCl acid to form silica gel. Zeolite is very unstable in HCl. The plugging problems are caused by silica gel that polymerizes and creates plugging colloidal particles (Gdanski, 1999).

2.1.1.4 Minerals precipitation

Minerals are likely to form matrix-blocking precipitates during sandstone acidizing treatments. Feldspar and clay contain three main mineral groups, namely: sodium-containing minerals, potassium-containing minerals, and carbonates that can form significant precipitates upon contacting with HF acid. Sodium-containing minerals will precipitate fluosilicate. Potassium-containing minerals will precipitate fluosilicate closer to the well bore and in greater quantities. The fluosilicate produced by potassium-containing minerals has more plugging capacity than the fluosilicate produced by sodium-containing minerals. Illite, mixed-layer, and mica clay contain potassium, which can cause fluosilicate precipitation from spent HF acid. Zeolites occasionally contain sodium, which can cause fluosilicate precipitation from spent HF acid. Silica gels are found to precipitate as a result aggressive reaction of HCl with zeolite (Gdanski, 1999).

Carbonate containing minerals will precipitate calcium fluorides upon contacting with live HF acid. However, the formation of calcium fluorides does not cause a problem. The main problem with the carbonates is that they will precipitate aluminum fluorides, which can deposit in the well bore and the matrix (Gdanski, 1999).

2.1.2 Treatment Methods

There are two treatment methods for the well stimulation:

2.1.2.1 Fracturing

Fracturing is a treatment method to create a conductive fracture extending from the well bore into the reservoir to increase the effective well bore radius (Schechter, 1992).

2.1.2.2 Matrix acidizing

Matrix acidizing is the injection of acid into the formation porosity at a pressure less than the pressure at which a fracture can be opened. Stimulation is usually accomplished by removing the effect of a damage formation around the well bore by enlarging the pore spaces and dissolving particles plugging these spaces (Schechter, 1992).

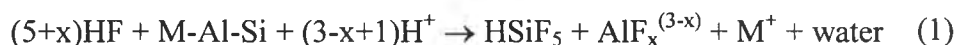
2.2 Acid Treatment

Matrix acidizing is a chemical stimulation method in which acid removes damage and increases permeability near the well bore. The acid acts by dissolving minerals that make up the original formation matrix, as well as pore plugging materials that result from mud invasion or fine migration.

2.3 Acid – Aluminosilicate Reactions

Acid reactions with minerals are termed *heterogeneous reactions* because they occur at a boundary between the solid and the liquid rather than in the bulk liquid phase. The first step is acid transfer to the reactive surface by diffusion, flow-induced mixing (forced convection), mixing resulted from density gradients (free convection) or fluid loss into the formation. Once the acid reaches the rock surface, the rate of the second step is determined by the kinetics of the surface reaction. Finally, the reaction products may be transported away from the surface (Golan and Whiton, 1991).

Gdanski (2000) studied the primary reaction of HF with aluminosilicates. The reaction can be written in the general form as:



The rate law of HF on sand is given by

$$\text{Rate} = \frac{d[\text{HF}]}{dt} = -k_s[\text{HF}]^{\alpha_s}[\text{H}^+]^{\beta_s} \quad (2)$$

Where α_s is HF reaction order for dissolution of sand, SiO_2 dissolution

β_s is HCl reaction order for dissolution of sand, SiO_2 dissolution

k_s is specific reaction rate

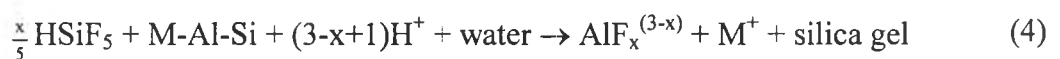
$[\text{HF}]$ is hydrofluoric acid concentration

$[\text{H}^+]$ is the bulk proton molar concentration

The rate law of HF on clay, feldspar and silica gel film is given by

$$\text{Rate} = \frac{d[\text{HF}]}{dt} = -k_1[\text{HF}]^{\alpha_1}[\text{H}^+]^{\beta_1}[\text{CLAY}] \quad (3)$$

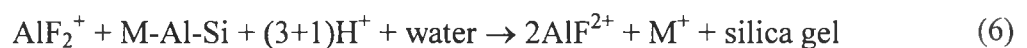
Gdanski (1999) studied the secondary reaction of HF with an aluminosilicate, which can be written in the general form



The rate law for the secondary reaction has recently been determined as:

$$\text{Rate} = \frac{d[\text{HSiF}_5]}{dt} = -k_2[\text{HSiF}_5]^{\alpha_2}[\text{H}^+]^{\beta_2}[\text{CLAY}]\text{Film}^{\gamma_1} \quad (5)$$

Gdanski (1998) studied the tertiary reaction of HF with an aluminosilicate, which can be written in the general form as



The rate law for the tertiary reaction has recently been determined and is given by Equation 7.

$$\text{Rate} = \frac{d[\text{AlF}_2^+]}{dt} = -k_3[\text{AlF}_2^+]^{\alpha_3}[\text{H}^+]^{\beta_3}[\text{CLAY}]\text{Film}^{\gamma_3} \quad (7)$$

Where α is the reaction order for the first reactant

β is the reaction order for the second reactant

k is the reaction rate constant

$[\text{H}^+]$ is the bulk proton molar concentration

$[\text{HF}]$ is the bulk hydrofluoric acid molar concentration

$[\text{CLAY}]$ is the clay concentration (grams of clay to ml of fluid)

$[\text{HSiF}_5]$ is the bulk fluosilicic acid concentration

$[\text{AlF}_2^+]$ is the bulk aluminum difluoride ion concentration

M is all other cations

Film describes the silica gel filming effect

γ is filming order

$$\text{Film} = \frac{\text{CLAY}}{\text{CLAY} + \text{PPT} \cdot \text{CF}} \quad (8)$$

Where PPT = amount of silica gel residue in grams in a column element

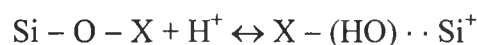
CF = effective coverage factor for the silica gel coating

CLAY = amount of clay (grams) in an element

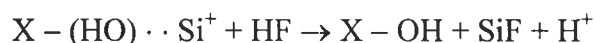
Turner (1964) studied the kinetics of acid dissolution of montmorillonite and kaolinite. The data from this investigation of the digestion of kaolinite and montmorillonite in 10 to 30 percent HCl showed that the acid-dissolution of metal ions from the crystal lattice of these clay minerals obeyed pseudo first-order kinetics with respect to acid concentration and temperature over the ranges investigated. The dissolution process involved a complete dissolution of a part of the crystal lattice

rather than a preferential removal of lattice metal cations. As the dissolution progresses the solution become saturated with silica. Subsequent silica dissolved from the lattice would, then, immediately precipitate from the solution as amorphous silica.

Lund (1974) studied the dissolution of two feldspars in HF and HCl mixtures. Two feldspars, a sodium-feldspar and potassium feldspar were used in this study. The dissolution rate experiments were performed using a rotating disk apparatus. It was found that when strong acids, such as a mixed acid of hydrochloric acid and hydrofluoric acid, two parallel reaction paths may exist for the dissolution process. Hydrogen ions are strongly adsorbed on the surfaces of minerals such as α -quartz, rutile (Al_2O_3), and clays because of the polar nature of the Si-O and Al-O bonds. In the lattice network, oxygen will have a negative charge relative to silicon and aluminum, and hydrogen ions may, therefore, be adsorbed by the Si-O-Si and Si-O-Al group in the following manner:



The adsorption has the effect of decreasing the bond strength between silicon and oxygen; then the reaction of HF with the group should be considerably facilitated:



Yang and Xu (1997) studied the states of aluminum in zeolite β and influence of acidic or basic medium. The states of aluminum in zeolite β were investigated in detail by using FTIR spectroscopy. From the results, they concluded that the state of aluminum and the change of these state in acid or base were also determined by the nature of compensating cations in zeolites. The high deformability of framework of zeolite β occurs when protons, which posses high electron affinity from hydrochloric solution, are located at cationic sites, leading to the breakage of Al-O bond and the removal of aluminum. Therefore, zeolite β is

subjected to dealumination in acidic medium. The process of alumination extraction can be proposed briefly as shown in Figure 2.1.

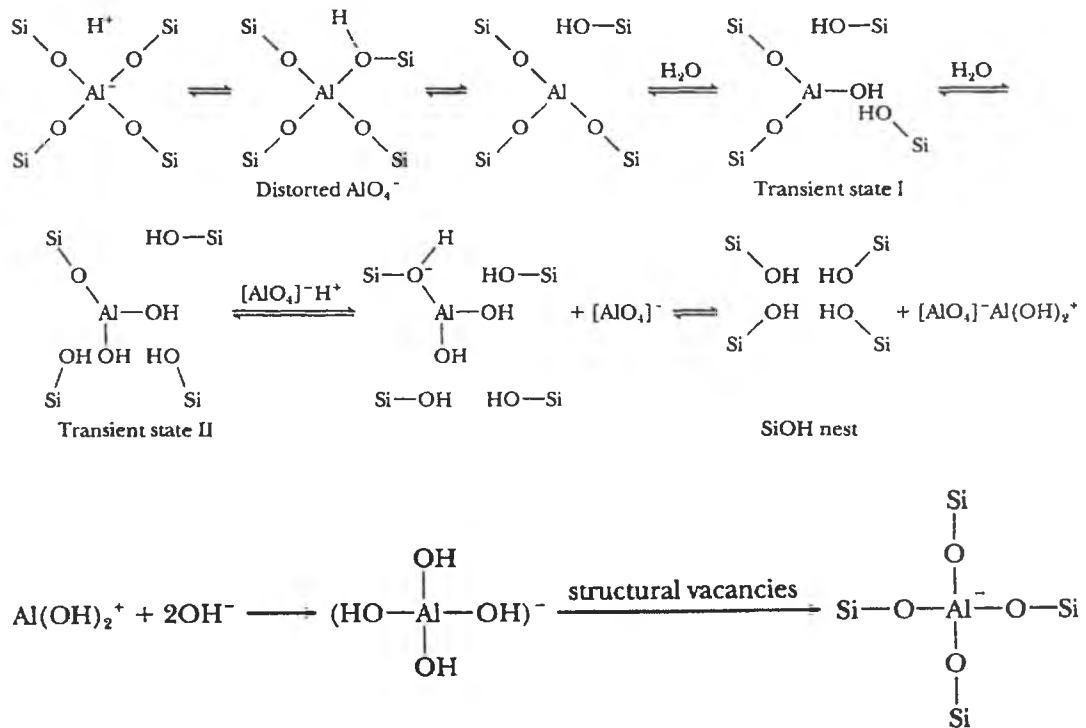


Figure 2.1 The process of dealumination of zeolite β in HCl solution (Yang and Xu, 1997).

Underdown *et al.* (1990) studied the acidization of analcime-cemented sandstone in the Gulf of Mexico. The results obtained from the experiments indicated that analcime has a high solubility in HF and a strong tendency to form hydrated gels in concentrated HCl. A white pasty gel was found to form with HF and HCl but not with acetic acid. Acetic acid provides good stimulation of calcareous minerals and is compatible with the zeolite mineral, analcime.

2.4 Zeolite

Zeolite is a crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by large ions and water molecules, both of

which have considerable freedom of movement to permit cation exchange and reversible dehydration (Smith, 1963).

The fundamental building block of all zeolites is a tetrahedral of four oxygen anions surrounding with silicon or aluminum ions. These tetrahedra are arranged so that each of the four oxygen anions is shared in turn with another silica or alumina tetrahedron. The crystal lattice extends in three-dimension, and the -2 oxidation state of each oxygen is accounted for. Each silicon ion has its $+4$ charge balanced by the four tetrahedral oxygens and the silica tetrahedral are therefore electrically neutral. Each alumina tetrahedron has a residual charge of -1 since the trivalent aluminum is bonded to four oxygen anions. Therefore, each alumina tetrahedron requires a $+1$ charge from a cation in the structure to maintain electrical neutrality. Figure 2.2 shows the development of zeolite structures. The silica and alumina tetrahedra are combined into more complicated secondary units, which form the building blocks of the framework zeolite crystal structures (Byrappa and Yoshimura, 2001).

There are over 46 naturally occurring zeolite minerals, belonging to some major structure types. In a number of offshore oil wells, the discovery of the common occurrence of the zeolite mineral analcime as sandstone cement has contributed to an overhaul of standard completion and stimulation procedure in the field (Byrappa and Yoshimura, 2001).

2.4.1 Analcime

Analcime is a low-density, hydrated sodium aluminum silicate. The chemical formula of analcime is $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. The Si/Al ratio of sedimentary and analcime varies between 2.0 and 2.9 (Hay, 1966). The framework density is $18.6 \text{ T}/1000\text{A}^3$. The cubic structure consists of 4-, 6- and 8- rings linking in such a way as to give sixteen large interconnected cavities which form non-intersecting channels and a second series of twenty-four smaller individual cavities. Sixteen of the small cages are occupied by sodium cations, and the large cages are occupied by water molecules (Sacha, 1959). Analcime is generally classified with the zeolite family of minerals. It occurs as a primary mineral in some silica-poor volcanic rocks

and as a secondary cement and alteration mineral within vugs in basaltic volcanics, in tuffaceous deposits, and in volcanic-rich sandstones. Analcime is thermally stable (note its occurrence as a primary volcanic phase), but in sandstone with zeolite cement analcime is an intermediate step in burial diagenesis. Analcime is a low density phase (2.3 g/cc), with a significant water content (8% wt/wt) (Underdown *et al.*,1990).

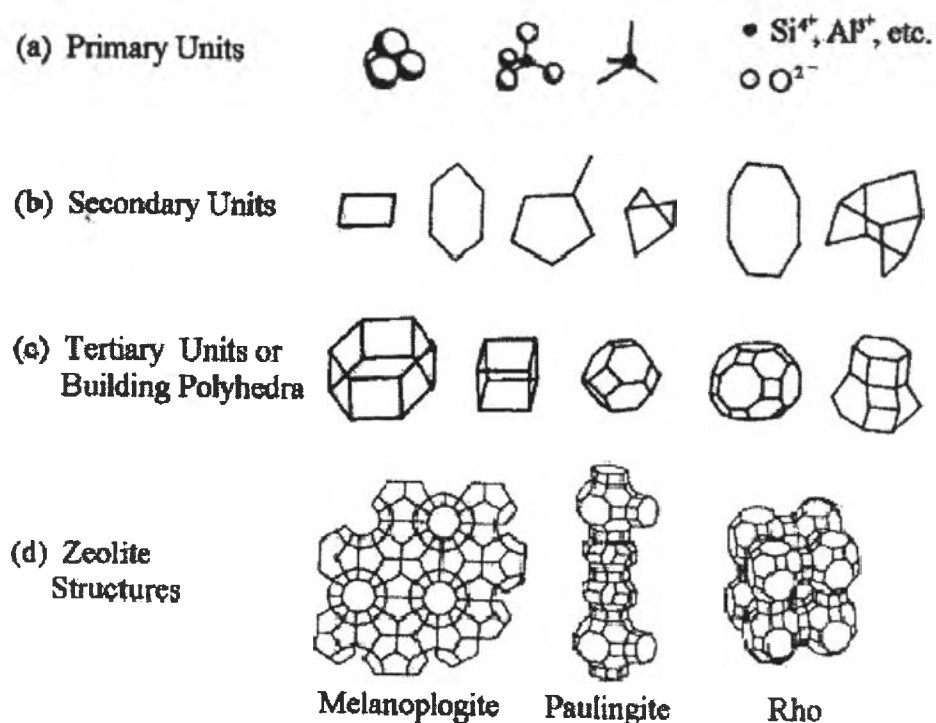


Figure 2.2 Development of zeolite structures (Koyama and Takeuchi, 1977).