# CHAPTER II
# BACKGROUND AND LITERATURE SURVEY

## 2.1 Problems in Oil Production (Pore Reduction Causes)

### 2.1.1 Fines Migration

Fines migration is a production problem that can be minimized by tailoring stimulation treatment to a formation's minerals. Most fines migration problems result from the physics of flow and involve two kinds of clays: kaolinite and illite. Both clays are loosely bound and can be easily dispersed by production velocities near the wellbore (Gdanski, 1999).

### 2.1.2 Clay Swelling Due to Ion Exchange

Ion exchange occurs between formation minerals and injects 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 ions exchange. In contrast, sand, feldspar and kaolinite are not prone to swelling. Zeolite minerals do 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).

### 2.1.3 Gel Formation

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

### 2.1.4 Minerals Precipitation

Minerals that produce precipitates upon contact with HF acid are classified into three groups: sodium-containing minerals, potassium-containing

minerals, and carbonate. Sodium-containing minerals will precipitate fluosilicate. Potassium-containing minerals will precipitate fluosilicate closer to the wellbore and in greater quantities. Fluosilicate precipitation can be found in illite, mixed layer, and mica clays since they contain potassium that can. Zeolites occasionally contain sodium, which can cause fluosilicate precipitation with spent HF acid (Golan and Whitson, 1991). Silica-gel is found to precipitate as a result of aggressive reaction of HCl with zeolite (Gdanski, 1999).

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

## 2.2 Oil Well Stimulation

Any operation that results in a reduction in the formation skin effect is known as stimulation. Stimulation can be accomplished in two ways. First is stimulation by removing formation damage and second by bypassing formation damage. There are three primary methods of stimulation.

### 2.2.1 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 wellbore. The fluid is injected until the fluid pressure becomes greater than the stresses inherent in the rock. This causes the rock to spill 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 (Schechter, 1992).

2.2.2 Acid Fracturing

This technique is used on carbonate formations only. The treatment is similar to hydraulic fracturing except that no propellant is required. In acid fracturing the bottle hole treating pressure is greater than the breakdown pressure. Hydrochloric acid is viscosified with polymer for this method. The acid etches the faces of the fracture creating surface roughness which props the fractre open following the treatment.

2.2.3 Matrix Acidizing

This technique is used to remove formation damage due to drilling mud invasion, clay swelling and clay migration. In matrix acidizing the bottle hole treating pressure must be less than the fracturing pressure. It is a near wellbore treatment normally, less than 1 meter. of rock around the wellbore is affected. However matrix acidizing cannot reduce the formation skin factor below zero.

## 2.3 Matrix Acidizing of Sandstone

The simple aim of matrix acidizing is to improve production by dissolving formation damage or creating new pathways within several inches to a foot or two around the borehole. This is done by pumping treatment fluid at relatively low pressure to avoid fracturing the formation. Compared with high-pressure fracturing, matrix acidizing is a low-volume, low-budget operation.

Besides the basic quartz grains, sandstone contains other silico-aluminate compounds that are often located in the pore space and provoke flow restrictions. Sandstone occasionally contains carbonates, metallic oxides, sulfates, sulfides or chlorides, and amorphous silica . They may also have drilling mud cement filtrates from invasion.

Hydrofluoric acid (HF) is the only common acid that dissolves siliceous minerals. Therefore, all formulations used in matrix sandstone acidizing involve hydrofluoric acid or its precursors. The most commonly used acid system is "mud acid" a mixture of hydrochloric and hydrofluoric acids in variable proportions. This composition is prepared either by diluting concentrated formulations or by reacting

ammonium bifluoride with hydrochloric acid. The minimum concentration ratio between HCl and HF is 9:1 (Gdanski, 2000).

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

2.3.1 Preflush

An HCl solution is usually used as a preflush when acidizing sandstone with mud acid. Various acid strengths can be used depending on the formation, to accomplish the following.

Displace brine from the wellbore when a ammonium chloride spacer is not used; to avoid contact between HF acid and any formation brine containing K, Na, or Ca.

Dissolve a maximum amount of carbonate to minimize $CaF_2$ precipitation. Acetic acid can replace HCl to dissolve carbonates. It acts as low pH buffer and complex agent, which helps minimize the tendency for iron compounds to precipitate as HCl is spent.

2.3.2 Main Acid Stage

Main acid stage is the major step of matrix acidizing. Most fines and alumino-silicate are dissolved in this step. The type of acid used depends on rock mineralogy, produces-fluid compatability, and petro-physics of the reservoir sand.

2.3.3 Postflush

Postflush generally uses 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 postflush stage in order to dissolve and disperse heavy crude coating the matrix.

## 2.4 Dissolution of Alumino-Silicates in Acid Solution

Alumino-silicates are defined as those minerals that contain tetrahedrally coordinated aluminum and silicon. Alumino-silicate minerals may contain octahedrally coordinated aluminum as well. Each oxygen atom within a tetrahedron is shared with a neighboring tetrahedron. The result is a continuous framework of silicon and aluminum tetrahedron (or aluminum octahedron). The net charge in a silicon tetrahedron is zero. However, aluminum has an oxidation number of +3, which results in a net charge in an aluminum tetrahedron of -1. Hydrogen ions may bond to bridging oxygen atoms between silicon and aluminum tetrahedral in order to satisfy the net charge.

The result is a bridging hydroxyl group, which can be found in the structure of some common clays (e.g., kaolinite). Minerals constructed about a three-dimensional network of cross-linked $SiO_4$ tetrahedral are classified as tecto-silicates. Within the tecto-silicate class, the zeolite group is made up of crystalline alumino-silicates. Zeolites are commonly used as ion exchangers, molecular sieves, and catalysts. In zeolites, neighboring silicon and aluminum tetrahedron form secondary rings (or secondary building units) as shown schematically in Figure 2.1. Furthermore, secondary building units can be combined to form framework components (e.g., the sodalite cage). The components can then be combined to form larger and more complicated zeolite frameworks.

Both zeolites and clays are alumino-silicates. The primary difference is in their crystalline structures. The crystalline structures of many clays, such as Na-feldspar ($NaAlSi_3O_8$), are non-micro porous. However, zeolites have three dimensional crystalline structures (comparable to a honeycomb) consisting of a network of interconnected tunnels and cages, in which acid may be able to diffuse and react. The zeolite framework remains rigid as water molecules diffuse in and out of these small pores. Zeolite pore sizes are nearly uniform and in the order of 10 Å, which allows the crystal to act as a molecular sieve. In zeolite minerals, loosely bound cations, such as $Na^+$, $Ca^{2+}$, or $K^+$, exist within the alumino-silicate framework to satisfy the total charge. Water exists in the void spaces between adjacent silicon and aluminum tetrahedron in hydrated zeolites (e.g., the zeolite analcime).

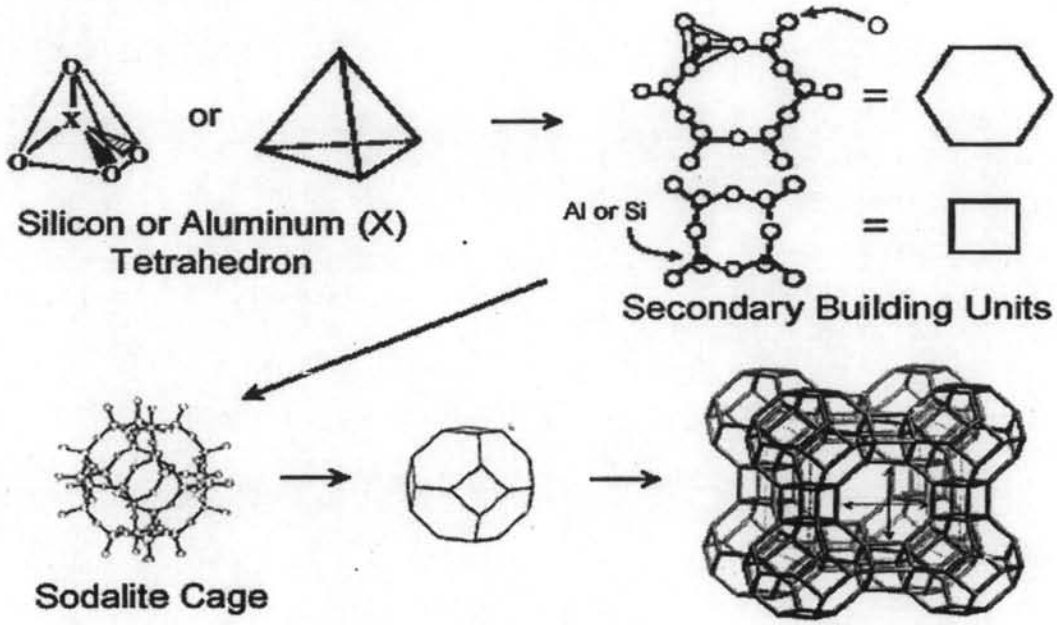


**Figure 2.1** The zeolite framework constructed from silicon and aluminum tetrahedron (zeolite type 4A).

Lasaga *et al.* (2001) postulated that crystal dissolution begins at natural defects (or nucleation sites) on the surface. Furthermore, a dissolution step-wave model was developed using Monte Carlo simulations in which the rate of dissolution was derived as a function of a critical defect radius on a crystal surface. However, no such models have been developed for the dissolution of zeolite minerals. Other researchers have used high-resolution imaging techniques, such as atomic force microscopy, to study the dissolution of heulandite (a natural zeolite).

Yamamoto *et al.* (1996) argued that protons or hydroxide ions diffuse into the micro porous channels resulting in the removal of the topmost alumino-silicate layer from the zeolite framework. Yet, no dissolution kinetics were developed to support the proposed reaction mechanism.

Filippidis *et al.* (1996) observed that low-silica zeolites (natrolite and thomsonite) reached equilibrium in acidic and alkaline solutions at a faster rate than did higher-silica zeolites (heulandite and stilbite). However, no quantitative analysis

was provided. Furthermore, a rate law model for the dissolution process was not developed.

Previous researchers have assumed that the dissolution of zeolite minerals found in oil-bearing formations follows a power rate law model. In addition, it was postulated that the simultaneous precipitation of silicon inhibits the dissolution reaction (Gdanski *et al.,* 1998, 2000).

Much of the previous research in the area of alumino-silicate dissolution has focused on layered (or non-micro porous) alumino-silicates, such as chlorite, illite, and kaolinite. In these cases, it has been shown that acid attacks the mineral at the planar surfaces and edges. The mechanism in which acid attacks zeolite minerals is not well understood. An extensive amount of literature has been published on the dissolution of sandstone formations in acidic solutions( Kline and Fogler, 1981).

Kline *et al.* (1981), Lund *et al.* (1975) were among the first of researchers to study the dissolution of alumino-silicate or sandstone minerals in hydrofluoric and hydrochloric acids.

LeBlanc *et al.* (1987, 1989) proved that significant errors in reaction kinetics may result when assuming monodisperse particles rather than polydisperse particles for mineral dissolutions in slurry reactors. Alternative stimulation fluids, such as chelating agents (chemicals that form coordination compounds with metal cations in solution), for the dissolution of carbonate formations have been investigated by Fredd and Fogler (1998) as well.

Naturally occurring zeolites can be found throughout the world. The zeolite mineral analcime is naturally occurring and found in oil-bearing formations in the Gulf of Mexico region.

In analcime, $Na^+$ ions occupy the irregular framework channels (dPore = 1.6x4.2 Å, dEff = 2.6 Å) and are surrounded by an oxygen octahedron. There exist approximately 2 silicon tetrahedrals for every 1 aluminum tetrahedron within the theoretical framework of the zeolite analcime. Cations within a zeolite framework are loosely bound to surrounding oxygen atoms from neighboring aluminum tetrahedron and water molecules, which allows the exchange of cation species with those existing in solution( Yakomori and Idaka, 1998).

Underdown *et al.* (1990) noted the existence of analcime in an oil-bearing formation in the Gulf region in which an acid stimulation was followed by a decline in well productivity.

The dissolution kinetics of zeolites in alkaline solutions have been studied by previous researchers (Cizmek *et al.,* 1991, 1992, 1995; Murphy *et al.,* 1996; Ragnarsdottir, 1993). Only a handful of experimental studies have examined the dissolution of zeolites found in sandstone formations, and none have presented reaction kinetics or mechanisms for pure systems in the low pH range (pH < 1). This information is necessary in order to accurately predict stimulation treatments in the field.

## 2.5 Silica Precipitation

To initiate precipitation, the solution must be supersaturated. This supersaturation can be reached by various method such mixing solutions containing reactants or by changing solubility by increasing or decreasing temperature. So, the precipitation takes place in two stages : nucleation and growth of these nuclei to macroscopic scale. It is not easy to detect formation of sub-micronic nuclei, and generally both nucleation and growth occur simultaneously in solution. Other processes could also occur during all the aging time of particle in the mother liquor, especially, agglomeration, disruption, Oswald ripening.

Thus, the amount of solute precipitated, the size and distribution size of particle change every time, making it very difficult to analyze the results. However, numerous models have been developed in order to describe each elementary process and they allow to predict the behavior of supersaturated solutions and crystal evolution. The theoretical representation of those phenomena needs the introduction of thermodynamical, kinetic, geometric data, mass transfer, heat transfer, and numerical resolution methods.

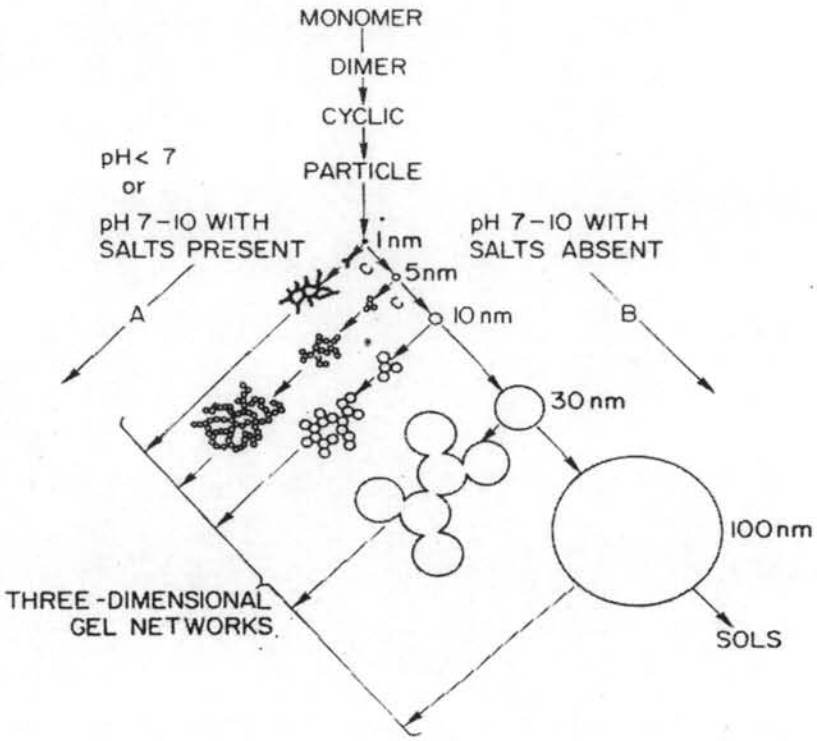


**Figure 2.2** Polymerization behavior of silica. In basic solution (B) particles in sol grow in size with decrease in number; in acid solution or in presence of flucculating salts (A), particles aggregate into three-dimensional networks and form gels.

The polymerization behavior of Si has been previously studied as shown in Figure 2.2. A solution of silicic acid monomer ($SiO_2.2H_2O$) polymerizes by condensation to form dimmer and higher molecular weight species when the concentration in water is greater than the solubility of $SiO_2$ (~100-200 ppm). The rate of polymerization is proportional to the concentration of $H^+$ below pH of 2 in the early stags of polymerization, rapid condensation leads to cyclic structures, which link together to form larger three-dimensional molecules. Eventually, spherical particles are formed. At pH between 7 and 10, the particles continue to grow without aggregation due to the negatively charged surfaces (i.e., particle surfaces become neutral) and three dimensional gel networks form (Iler, 1979).

Colloidal silica donates stable dispersions or sols of isolated particles of amorphous silica. This definition excludes solutions in which small Si-polymer

molecules or particles are unstable. Discrete colloidal particles are formed as a result of Si polymerization. Colloidal Si particles may aggregate through gelling, coagulation or flucculation. In coagulation, Si particles exist in relatively "closed-packed clumps". The silica is more concentrated than in the original sol, and the result is a dense precipitate. In flocculation, Si particles are linked together by bridges in which the structure is less dense than that of coagulation. (Iler, 1979).

Silica precipitated as a result of matrix acidizing treatments has been referred to in the oil industry as "hydrate silica" (Underdown, *et al.,* 1990). Other authors have all referred to precipitated silica as " silica gel " (Gdanski, 2000). Recently, (Gdanski and Shuchart, 1998) have described silica precipitate as "colloidal silica gel" and other current industrial researchers have labeled it as "amorphous silica" (Frenier and Ziauddin, 2002). Experimental studies have not been published in which precipitated silica resulting from the dissolution of sandstones has been identified. No research has attempted to question whether or not the precipitated silica is a colloidal gel formed as a result of polymerization. Furthermore, no attempts have been made to study the effects of silica precipitation on the reaction kinetics and mechanisms of zeolite dissolution. Gdanski and Shuchart (1998) hypothesized that precipitated silica gel slows the attack of acids on alumino-silicates by forming a thin film at the liquid-solid interface. However, Hartman and Fogler (2005) said silica precipitation does not inhibit the dissolution of aluminum atoms from zeolite.

## 2.6 Chelating Agent

Chelating agents can be defined as organic compounds which complex or sequester metal ions. The word chelate derives from the Greek root "chela" meaning the claw of a lobster. The chelating agent removes a metallic ion from a solid salt and holds it in solution. By forming a soluble complex from an insoluble compound.

The chelating agent or ligand must have at least two functional groups, bidentate, capable of bonding to the metal atom. In this bond the ligand is an electron-pair donor and the metal an electron-pair acceptor, this is known as co-

ordination bonding. The functional groups can be acidic or basic. An acidic group loses a proton and coordinates with a metal atom. Since the loss of a proton is pH dependant, so is the ability of a particular acid to act as an effective chelating agent. A basic group contains an atom carrying a lone pair of electrons which may interact with the metal ion, these basic groups are called co-ordination groups.

The functional groups must be so located in the ligand that the formation of a ring including the metal atom is possible: The process of ring formation is known as chelation. The word chelate describes the ring. Chelation changes, often profoundly, the chemical and physical characteristics of the constituent metal ion and ligand and has far reaching consequences in the realms of chemistry and biology.

In general, for a chelating ligand which contains *Z* donor atoms all capable of coordination to a single metal ion, Z-1 chelate rings will be formed and the larger the value of *Z* the greater the stability of the resulting complex. The enhanced stability associated with chelation is called the chelate effect. The size of the ring can also effect the stability of the chelate complex. The rings usually have five or more sides, smaller rings are possible only on rare occasions.

The properties of metal ions also affect chelate formation. The metal ions vary in their number of co-ordination sites. The major determining factors are the oxidation state (or valence) of the metal atom, the charge of the metal atom and the number of available bonding orbitals.

Chelating reactions work fastest when both the chelating agent and the metal to be chelated are present in solution. Factors that influence the preference of a chelating agent for one ion over another, such as pH and stability of the formed complex, are taken into account in a number called conditional stability constant. This is practical expression of the chelate strength for a certain metal ion with a certain chelating agent.

The chelating agent prefers to chelate metal ions with the highest conditional stability constant, which form a more stable complex. However, any excess of chelating agent will chelate the next favourable metal ion. Since the conditional stability constant is pH dependent, pH can be used as a means of increasing the selectivity of a solution for one ion over another.

2.6.1 Citric acid

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

$$C_6H_8O_7 \leftrightarrow C_6H_7O_7^- + H^+ \qquad pK_{a1} = 3.128 \quad (2.1)$$

$$C_6H_7O_7^- \leftrightarrow C_6H_6O_7^{2-} + H^+ \qquad pK_{a1} = 4.761 \quad (2.2)$$

$$C_6H_6O_7^{2-} \leftrightarrow C_6H_5O_7^{3-} + H^+ \qquad pK_{a1} = 6.396 \quad (2.3)$$

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

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 using the value of $pK_a$ as shown in Figure 2.3.

Bennett *et al.* (1991) has found that the citrate can enhance quartz dissolution and increase silicon solubility by its chelating property. Therefore, it might be an alternatives fluid for acidization.

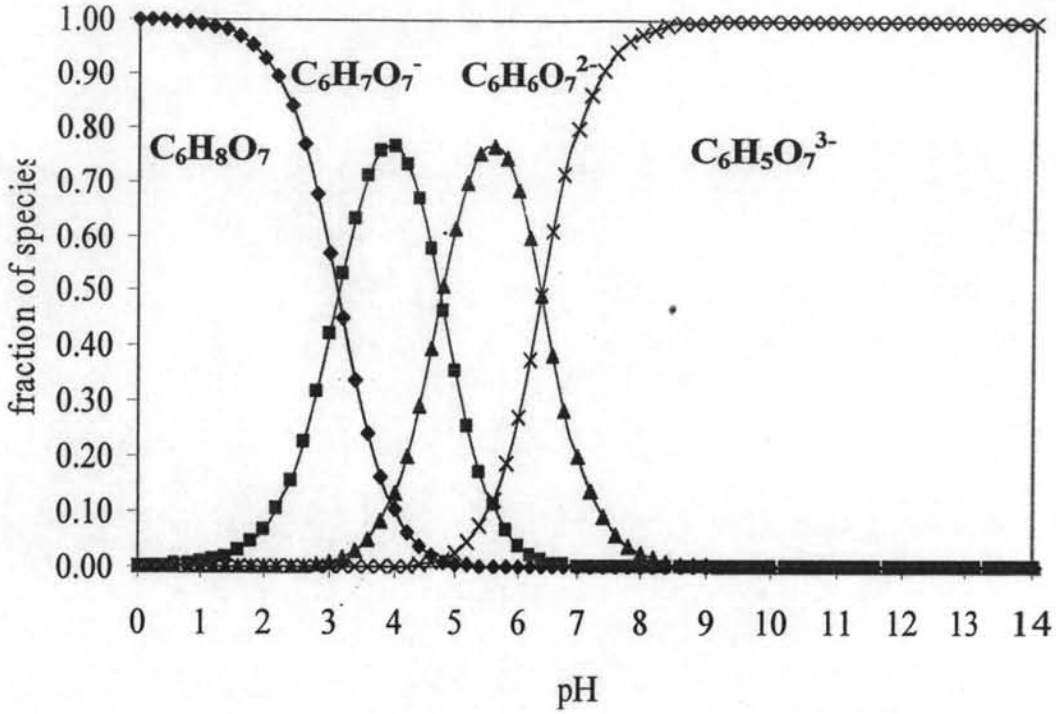


**Figure 2.3** Deprotonation of citric acid.