CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Well Stimulation

Reservoir stimulation techniques can broadly be divided into two categories, fracturing and matrix acidizing. Fracturing creates new flow channels for the oil, while matrix acidizing is carried out to increase permeability in the near well bore region by either removing the damage in the existing pores (sandstone formations) or by creating new flow channels by dissolving certain components of the formation (carbonate formations). However, there are circumstances under which fracturing is rendered ineffective and matrix acidizing turns out to be a better option.

The common acidizing fluid for the dissolution of most of the aluminosilicates is a mixture of HCl and HF, called the mud acid. The percentages of the acids vary depending upon the mineralogy and permeability of the formations. For sandstones, recommendations developed by Mc. Leod in the 1980s are widely used, though they have undergone some modifications in the recent years (Crowe et al., 1992).

2.2 Zeolites

Zeolites are aluminosilicates with microporous crystalline structures. They are composed of silicon, aluminum and oxygen atoms. Each silicon and Aluminum atom is tetrahedrally coordinated to four oxygen atoms. Aluminum atoms carry a charge of -1 with them. To balance these charges, counterions of alkali and alkaline earth metals are attached in the zeolites. Different counterions would impart different structural properties. For example, the Type A zeolites, namely Type 3A, Type 4A and Type 5A, have Na^+, K^+ and Ca^{+2} as counterions and pore diameters of approximately 4Å, 3Å and 4.9Å respectively.

Zeolites have found numerous industrial applications in heterogeneous catalysis and separation technology owing to their specific structural and chemical properties. They can either be naturally occurring or synthesized.

2.3 Analcime

It is a naturally occurring zeolite, which can widely be found in US, Canada, Iceland, Italy, Switzerland and Nova Scotia. The Si/Al ratio in an ideal crystal of analcime is two. A unit cell can be depicted by the formula $Na_{16}[(AlO_2)_{16}(SiO_2)_{32}].16H_2O$. It is thought to dissolve in HCl according to the following stoichiometry (Hartman 2006),

$$Na_2OAl_2O_3.4SiO_2.2H_2O + 8HCl + 2H_2O \longrightarrow 2AlCl_3 + 4Si(OH)_4 + 2NaCl$$
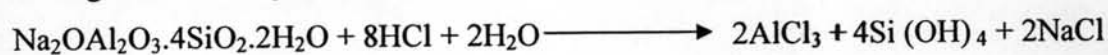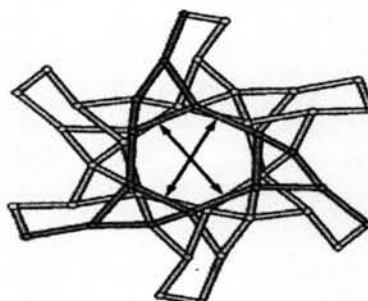
Analcime

$$D_{Pore} = 2.6 \text{ Å}$$
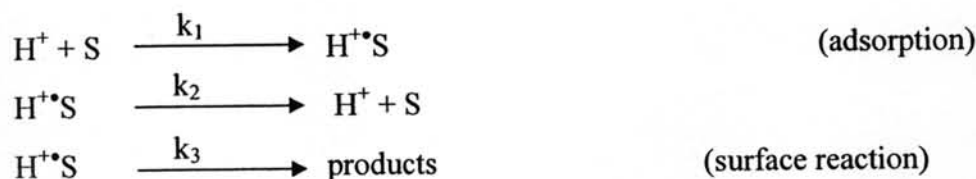
$$\frac{Si}{Al} = 2.0$$

Figure 2.1 Analcime structure

2.4 Analcime Dissolution Mechanism

Under low pH conditions, analcime dissolves in HCl according to the Langmuir-Hinshelwood rate law analogous to the Michaelis-Menten equation in enzymatic reactions (Hartman and Fogler, 2005). In their work, Hartman and Fogler have shown that, under analogous conditions, the dissolution rates of the zeolites Type Y

and Type A, also follow the Michaelis-Menten equation. A rate law of such a nature can be explained on the basis of an adsorption step in the dissolution step. If we consider S to be a site which is attacked by the H^+ ions- it could be either an Si---O bond or an Al----O bond- the steps of dissolution can be depicted as follows,

$$H^+ + S \xrightarrow{k_1} H^{+\bullet}S \qquad \text{(adsorption)}$$
$$H^{+\bullet}S \xrightarrow{k_2} H^+ + S$$
$$H^{+\bullet}S \xrightarrow{k_3} \text{products} \qquad \text{(surface reaction)}$$

Assuming the surface reaction to be rate limiting, the rate can be written as,

$$-r_d = \frac{V_{max}[H^+]}{(K_m + [H^+])},$$

Where,

$V_{max} = k_3 S_T$ is the maximum rate of dissolution, where S_T is the concentration of the sites at full coverage, and ,

$K_m = \dfrac{k_2 + k_3}{k_1}$ is the Michaelis-Menten constant.

2.5 Aluminum Facilitated Dissolution

Hartman and Fogler (2005, 2006) have argued that analcime dissolution in HCl is Aluminum facilitated and non stoichiometric, or that, the removal of Si from the framework is dependent on the Al removal. One of the evidences cited was that during the base case experiment (see Section 4.2), both Si and Al reach their plateaus simultaneously (Figure 4.9). This contention was substantiated with further experiments. In one such experiment, fresh analcime was added to the reaction mixture during the Si plateau region and prior to the decay of Si concentration. It is observed that both Si and Al reach their plateaus simultaneously again (Figure 2.2). A model based on the selective removal of Al from analcime framework was proposed later and undergirded with experimental evidence (Hartman and Fogler 2006). A selective rate removal parameter γ was introduced and it was defined as the ratio of measured

Si dissolution rate to the stoichiometric Si dissolution rate. Recall that analcime dissolution in HCl is non-stoichiometric.
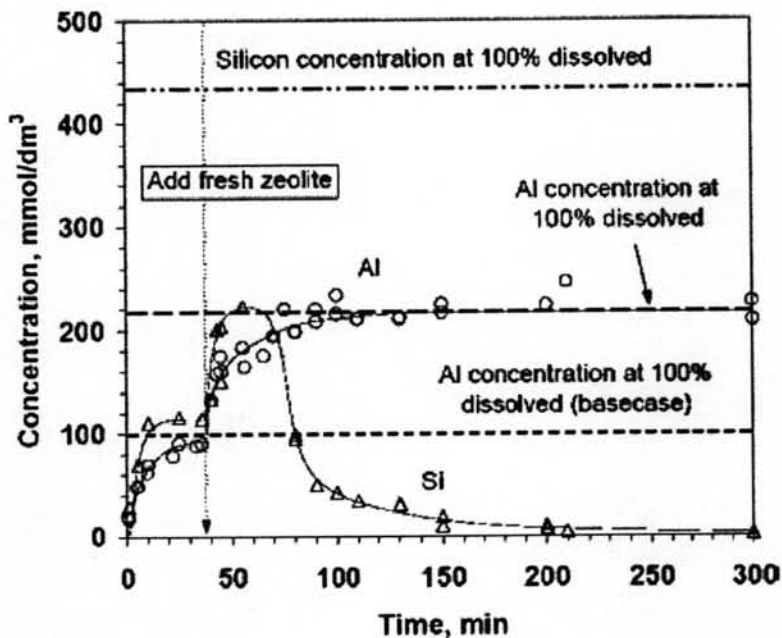
Figure 2.2 Addition of fresh analcime to base case experiment to elucidate Al facilitated dissolution of analcime.

2.6 Silica Precipitation

Studies on silica polymerization in near neutral solutions have been numerous, though the rate laws are ambiguous. Also, these studies are largely under homogeneous conditions and there have been rather a few investigations under highly acidic or heterogeneous conditions.

Iler (1979) has shown that monomeric $Si(OH)_4$ polymerization in supersaturated aqueous solutions can be divided into two broad steps:

1) Nucleation-condensation of the monomers to form particles of a "critical" size, and,

2) Growth of the particles to form gels or sols.

Under basic conditions without salts, particles grow without aggregation to form sols. The particles grow and flocculate to form volume spanning networks, or gels,

under acidic conditions, or in the presence of salts under basic conditions (Figure 2.2).
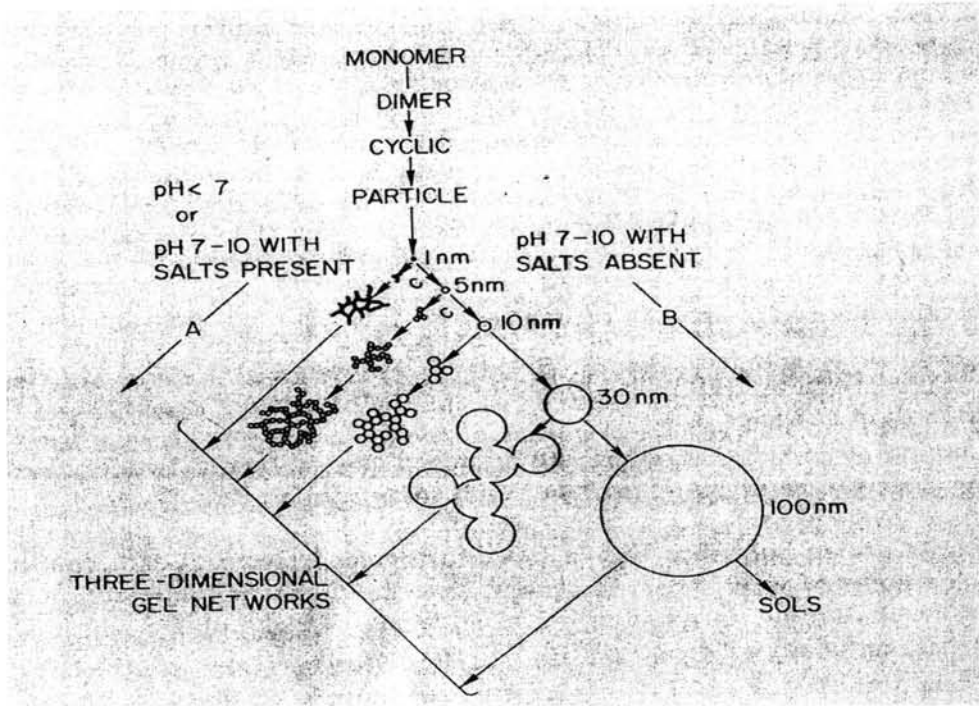

Figure 2.3 Polymerization behavior of silica (from "Chemistry of Silica"; Iler, 1979).

Contradictory reaction orders for nucleation and particle growth have been reported in literature. Rothbaum and Rhode (1979) suggested a rate law in which they combined the two steps. They proposed that the rate limiting step was the formation of a dimer which was the critical nucleus. So the nucleation was inherently assumed to be of second order. Particle growth was suggested to follow a fourth order rate law in their model. Icopini *et al.*, (2004) suggested that the critical nucleus was a cyclic tetramer, and the nucleation followed a fourth order rate law. Weres *et al.* (1981) also studied the particle growth, and suggested a fifth order rate law as opposed to the forth order model of Rothbaum and Rhode (1797). They also verified that presence of salt increases the precipitation rate. They have argued that this could be explained by either a specific catalytic effect by the anions, or the by the effect of hydration of the cations. Other researchers have explained this phenomenon on the

basis of the latter (Chan *et al.*, 1987, Marshall and Warakomski, 1980). These studies have concluded that, higher the degree of hydration of a cation, more it will reduce the solubility of silica, and hence, more it will increase the rate of precipitation. Chan *et al.*, (1987), have also established that the effect of salts is most significant on the induction time. The effect is relatively lesser on polymerization rate and none on the mechanism of polymerization. The priority of the cations in terms of decreasing effect is as follows:

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Li^+ > Na^+ > K^+$$
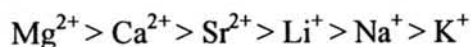
Effect of anions was also studied for the precipitation of silica on the surface of cationic micelles (Lin *et al.* 2000). The anions acted as mediating counterions to bring the $Si--- OH_2^+$ species to the surface of the micelles, where they polymerized to form mesoporous silica. In this system too, an induction period was observed, which decreased with the increasing binding strength of the counterion as,

$$NO_3^- > Br^- > Cl^- > F^- \sim SO_4^{2-}$$
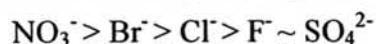
This is the well known binding strength Hofmeister series for cationic surfactants.

2.7 The Hofmeister Effect

In 1888, Hofmeister showed that the minimum amounts of different salts required to precipitate a particular protein from solution varied greatly. This was attributed to the altering of the water structure around the protein molecule, leading to salting-in or salting-out of the protein (Cacace *et al.*, 1997). The salting-out ions are categorized as water structure makers, or kosmotropes and the salting-in ions as water structure breakers, or chaotropes. It was later established that the effect of the anions was more pronounced than the cations (Leontidis, 2002). The order of salting-out effect of the anions in Hofmeister's experiments was found to be:

$$NO^{3-} < Br^- < F^- < SO_4^{2-}$$
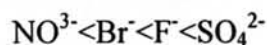
The series can however be reversed depending upon the pH of the solution and the nature of the solute. Recently it has been established however that only the salting out effects cannot completely explain the Hoffmeister effect and surface forces too

need to be considered (Leontidis, 2002). Hoffmeister series has however found to be followed in a number of situations dealing with surfactants and enzymes.

The Hofmeister effect has found great applications in colloidal science especially in the formation of mesoporous solids using surfactant templates, as evident from the work of Lin *et al.* (2000).