# CHAPTER II

# LITERATURE REVIEW

As to be mentioned earlier, the two majors types of retention/release mechanisms are adsorption/desorption and precipitation/dissolution. Most of the previous works in the area of squeeze treatments have been focused on the adsorption and subsequent desorption of scale inhibitors in a porous medium (Meyers et.al., 1985 and Shuler, 1993). More recently, precipitation treatments with inhibitors such as phosphonates and polyacrylic acids have been supplied in the field to enhance squeeze lifetimes (Jonasson, 1992 ; Yuan et.al., 1993 and Malandrio et.al., 1995).

Vetter (1972) tested three groups of scale inhibitors; polymers, esters of phosphoric acid and phosphonates in using with oilfield effluents. The effectiveness of precipitation was dependent upon temperature, supersaturation, and chemical composition. The important factors were the degree of supersaturation and the temperature. When the degree of supersaturation and the temperature increased, the effectiveness of the scale inhibitors were deteriorated significantly.

Meyers, Skillman, and Herring (1985) reported that a substantial number of wells in the Prudhoe Bay field were damaged by the deposition of calcium carbonate ($CaCO_3$) scale in the perforation tunnels and the near-welbore formation sandstone. Inhibitor squeeze treatments were employed to solve this scale damage and the capacity loss. The wells had monthly decline rates greater than 10 % . After applying the scale treatment, the production capacity could be maintained at the acceptable level more than 1 year. In some wells , treatment lives greater than 2 years were obtained. Several scale inhibitors were used for comparing the solubility, calcium tolerance, and adsorption suited in the Prudhoe Bay field. It was concluded that the adsorption/desorption data should be used to calculate the treatment life, the dosage of an inhibitor injected and the quantity of the overflush.

Lewis and Raju (1992) conducted a study on the squeeze treatment with the phosphonate, Aminotrimethylenephosphonic acid (ATMP), The reactivity of ATMP to precipitate with divalent cation species prevalent in typical brines, and secondly, the solubility of ATMP-cation precipitates was a function of pH, cation concentration, TDS and time. The matrix in Middle Eastern oil producing formations is typically limestone in nature. It was concluded that the ATMP molecules were entirely feasible to construct the adsorption bonds with the limestone formation matrix. This mechanism could function basically like a chromatographic process and , coupled with precipitation, could result in very long return lifetimes.

Yuan, Sorbie, and Todd (1993) simulated the complexity of squeeze model from many data of several wells in North Sea fields. The modelling had been carried out both for simple single sandbody squeezes and for inhibitor treatments in heterogeneous systems where there was free crossflow between strata. This study related to the field design criteria which should be applied to both "adsorption/desorption" and "precipitation/dissolution" scale inhibitor squeeze treatments. The results showed the significant effect of reservoir heterogeneity on inhibitor returns and, for such cases,that the placement strategy for inhibitor slug injection should be taken into consideration. The results also demonstrated the importance of selecting appropriate preflush and overflush volumes for creating the correct thermal conditions for in-situ inhibitor "precipitation".

Browning and Fogler (1993) studied the characteristics of the precipitates of calcium-phosphonate (HEDP). It was found that the composition of calcium/HEDP molar ratio of precipitate related to solubility limit, and precipitate morphology. The resulting precipitates were then further studied the precipitation/dissolution in a porous medium. The precipitation squeezè offerred longer squeeze lifetimes and more HEDP retention than adsorption squeeze. The results obtained from micromodel experiments showed that the CaHEDP precipitate placed in porous media was made up of long, fibrous particles preferentially situated in pore throats. The elution rate from the micromodel indicated that slow dissolution of apparently strong pore throat plugs dictated the long tailing region. Finally, multiple shut-in experiments mode in ceramic cores showed that while the amount of CaHEDP retention per shut-in did not increase with successive shut-ins, and enhanced return effect was observed with respect to the squeeze lifetime.

Kan, Oddo and Tomson (1994) studied physical properties of calcium-DTPMP precipitates. A combined dialysis and filtration method was used to prepare and characterize the solubility of a calcium phosphonate. The Ca-DTPMP precipitates were measured up to 2*m* ionic strength at temperature of 25 to 90 °C, and over a wide range of calcium and DTPMP concentrations. The stoichiometry of the solids, between 4 and 5.5 pH was $Ca_3H_4DTPMP$. The results of this study suggested that the solubility of phosphonates in most natural waters was controlled by a two-step mechanisms. The initial precipitate was stable unless fresh solution flowed over the solids, as occurred in many natural situations. When fresh solution flowed over the initially precipitated calcium phosphonate solid, a well-formed crystalline phase developed which was at least 2 orders of magnitude less soluble than the amorphous phase.

Many previous works mentioned above referred that squeeze treatment used for preventing downhole scale deposition was classified to two major types which were adsorption/desorption and precipitation/dissolution mechanisms. They were differed at the retention/release steps. In the past, the scale inhibitors were injected into the formation with a threshold concentration and based on the mechanism of adsorption and desorption. Thus, many previous works were focused on adsorption and subsequent desorption of scale inhibitors in a porous medium. The process of the adsorption/desorption treatment was revealed by development of equations explaining the treatment process (Shuler, 1993). At present, the mechanisms of the adsorption squeeze process were fully understood which differed from the precipitation squeeze process.

Recently, many research works were focused on the precipitation and dissolution mechanisms because of the longer squeeze lifetimes. The precipitation and dissolution process had more complex in understanding the actual mechanisms occurring in the formation. The precipitation treatments with inhibitors such as phosphonates and polyacrylic acids were implemented in the field to enhance squeeze lifetimes. These results were shown that this squeeze treatment offerred the longer squeeze lifetimes with no lasting formation damage effects for a long time.

Consequently, this study was focused on the precipitation and dissolution squeeze treatment. The precipitates (Calcium-Phosphonate) obtained from this work were characterized and further replaced into the micromodel and coreflood experiments represented as a porous medium or reservoir rock. The major aspect of this work was focused on the performance of phosphonate (ATMP) in porous media viewed by the specific apparatus (micromodel). The precipitation and dissolution of this precipitates were viewed through the stereo zoom unit. Finally, the squeeze treatment lifetimes were also determined with the elution curves.