CHAPTER II
LITERATURE SURVEY

The most effective method used to control scale formation in a reservoir is by injecting scale inhibitors into a formation. This method of preventing scale growth has been known since the late 1930's. Over the past few years, many studies on scale inhibitor precipitation have been carried out since inhibitor precipitation is generally regarded as one of the main mechanisms contributing to long term inhibitor retention. The process of injecting scale inhibitors into a formation is commonly referred to as the "squeeze technique". The advantages of treating oil wells by this squeeze technique have been known for over fifty years. The effectiveness of an inhibitor squeeze treatment is often measured by its lifetime. The most important factor affecting the squeeze lifetime is the retention and subsequent release mechanism of the inhibitor in the formation. The two major types of inhibitor retention/release mechanisms in a reservoir are adsorption/desorption and precipitation/dissolution (Browning and Fogler, 1993).

It has been shown that precipitation/dissolution squeezes offer longer lifetimes than adsorption/desorption squeezes. However, it is known very little about the mechanisms of the precipitation/dissolution squeeze process. For this reason, this thesis presented here had to concentrate on studying a precipitation/ dissolution squeeze treatment. More specifically, the focus will be on using model formation brine used in the field, to carry out a precipitation/dissolution squeeze. The important point was to optimize the squeeze treatment. Some background information are presented here.

2.1 Scaling

Scaling frequently occurs due to the mixing of two incompatible brines or due to changes of fluid conditions, such as pH, temperature, and pressure. These conditions are often met during the secondary oil recovery (Browning and Fogler, 1993). Scale formation will cause a reduction in the productivity of oil well. The type and amount of scale depend on many factors, such as pH, temperature, pressure and concentrations of ions in the formation water. Calcium carbonate is the prominent scale, which is widely found in the production systems.

2.2 Phosphonate Scale Inhibitors

In general cases, the first warning of existence of a significant scale deposit is a decline in well performance. A scale inhibitor is applied to solve this problem. One of the most common groups of inhibitors used to prevent scale in the petroleum industry is phosphonates. Phosphonate scale inhibitors are often used because of a number of advantages. Phosphonates are stable over a wide range of pH and temperature values, can inhibit many different types of scale, and have been proven to inhibit a wide range of scales including calcium carbonate, calcium sulfate, calcium phosphate, strontium sulfate, barium sulfate, and cobalt hydroxide. The effectiveness of scale inhibition is dependent upon the concentration of phosphonate used. Phosphonates have been shown to be effective in inhibiting scale at low concentrations. At higher phosphonate concentrations, the phosphonate has the ability to precipitate with cations (usually divalent cations) present in the formation water. The precipitation of phosphonate has two implications (Browning, 1996).

1.) The precipitate formed may act as a scale and cause formation damage. This is often referred to as secondary scale formation.

2.) This precipitate can be slowly dissolved back into the produced fluid in a manner that constitutes a precipitation treatment.

Hence, a cation-phosphonate precipitate is desired in a precipitation squeeze treatment.

2.3 Mechanisms of Phosphonate Precipitate Formation

The precipitated formation occurs in a supersaturated solution with precipitating agents at a set condition. The precipitating agents are usually divalent cations (such as calcium) and deprotonated phosphonates. First, the precipitating ions will form nuclei. The nucleation occurs when a cluster of cations and anions becomes large enough for spontaneous crystallization. The cluster where spontaneous crystal growth begins is referred to as the critical nucleus. Once nucleation occurs, the existing crystals begin to grow (Browning, 1996).

2.4 Mechanisms of Inhibitor Retention and Release in a Formation

In squeeze treatment, an inhibitor is injected into the formation for 24 hours and left in-situ. During this shut-in period, inhibitor is retained in the formation as a precipitate and then released into the produced fluid. The retention/release mechanisms of inhibitor play an important role by its lifetime for the success of a squeeze treatment (Browning, 1996). In this thesis, the type of retention/release mechanisms of inhibitor is precipitation/dissolution.

2.5 Precipitation/Dissolution Mechanism

Precipitation squeeze treatments have been carried out only in carbonate reservoirs. The precipitation occurs when the phosphonate scale inhibitor reacts with divalent cations (usually calcium from formation water) at a controlled condition. The cation-phosphonate precipitate is then dissolved

back into the produced fluid. Figure 2.1 shows the formation of precipitates with different ratios of calcium to phosphonates.

This thesis is a continuous work mainly relating to some parts of Browning (1996). Only 1-Hydroxyethylidene-1, 1-diphosphonic acid (HEDP) is considered as an inhibitor in the study because it has the simple structure and easy to study. Due to transformation kinetics of both 1:1 and 2:1 Ca^{2+}/HEDP precipitates molar ratio is one of the most interesting topics, this work is trying to clarify what will happen with 1:1 precipitates that are initially formed in the Ca^{2+}/HEDP supersaturated solution condition which favors the formation of a 2:1 precipitate. Analogously, transformation of 2:1 precipitates will be studied in the Ca^{2+}/HEDP supersaturated solution condition, which favor the formation of 1:1 precipitate.

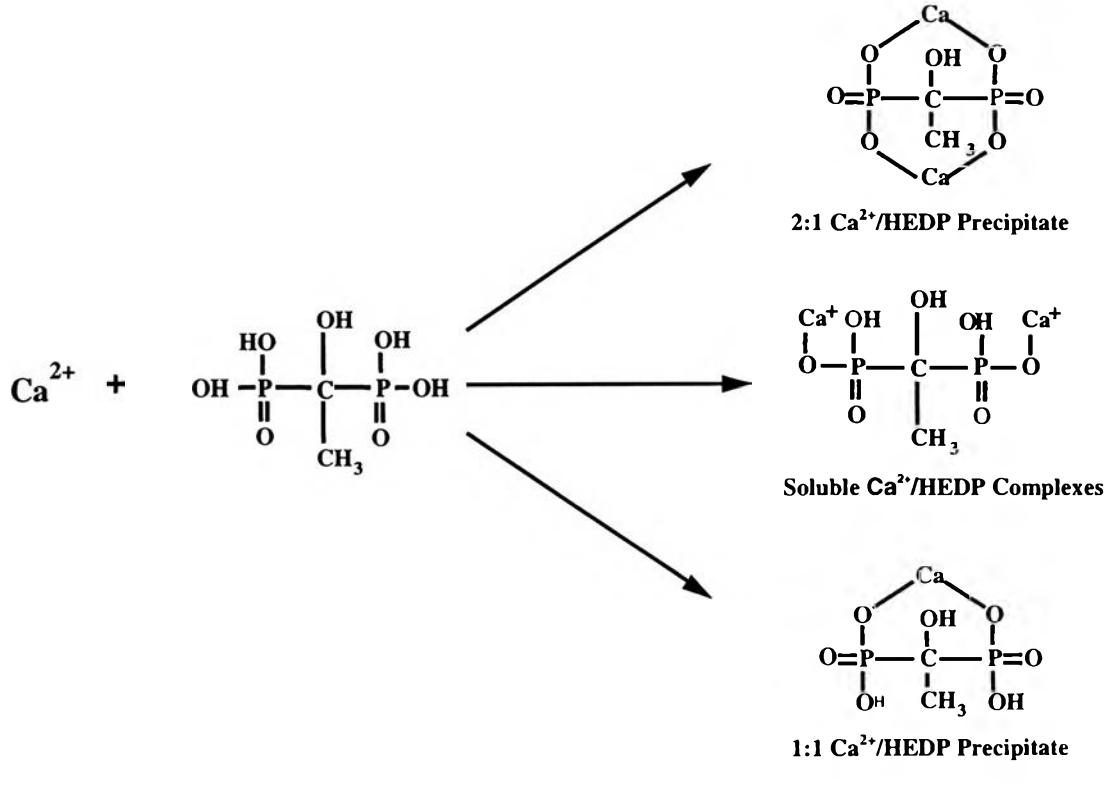

Figure 2.1 Reaction mechanism of calcium and a HEDP molecule (Browning, 1996)

However, not only transformation studies of these Ca^{2+}/HEDP precipitates will be of interest, but also the dissolution rate of the precipitate in a differential reactor will be another important part of this work. Furthermore, in order to extend the study to field conditions, model formation water is synthesized for studying the elution of the inhibitor (HEDP) from the Ca^{2+}/HEDP precipitates, which form in the pseudo two-dimensional porous medium (glass micromodel). The most vital of this part is the long tail curve that tells how much HEDP releases. That means the longer the tail of elution curve, the more enhancement the squeeze lifetime.

Rerkpattanapipat, P (1996) studied the precipitation and dissolution of calcium-phosphonate on inhibition of scale formation in porous media using the aminotri(methylenephosphonic acid) (ATMP). ATMP has three active phosphate groups which offer potential reacting sites with divalent cations. The 3:1 Ca^{2+}/ATMP precipitate seems to be the most suited for actual squeeze treatments because it gives the longest squeeze lifetime. Furthermore, the squeeze lifetime can be enhanced by adding excess calcium ion into the elution fluid (Wattana, 1997) For the diethylenetriaminepenta (methylenephosphonic acid, DTPMPA), five phosphate groups offer five active sites for calcium cation to react with. There were three parameters that affected the molar composition of precipitates : the solution's pH, Ca^{2+}/DTPMPA molar ratio and temperature. The 2:1 Ca^{2+}/DTPMPA precipitate had the highest equilibrium solubility in batch experiment. In addition, DTPMPA can release from 2:1 Ca^{2+}/DTPMPA precipitate faster than others in micromodel experiment.