

CHAPTER II

LITERATURE SURVEY

2.1 Scale

Scale is generally the precipitation of undesirable solids. Continuous scale growth in untreated wells can limit the production efficiency of a reservoir and/or damage system equipment. Scale formation occurs due to the mixing of two incompatible brines resulting in the sudden changes in the produced fluid conditions, such as temperature, pressure and pH. In the different well conditions, scales will have different compositions (Browning and Fogler, 1996).

Sulphate formation is often found in the near wellbore region, perforations and tail pipe assembly. The cation compositions of these deposits may vary from almost pure calcium sulphate to complex mixtures of alkaline earth metal sulphates. In many cases, almost pure barium sulphate is formed with small quantities of strontium and traces of calcium sulphates. These formation are especially difficult to handle because of traces of radium sulphate giving rise to significant radioactivity and because of the difficulty in bringing about efficient scale removal by any conventional chemical methods (Burr and Howe, 1987).

Carbonate scales are always found in the upper part of production tubulars and in surface processes. Moreover, well pressure gradients may initiate carbonate formation in the lower hole in some wells (e.g. gas lift operation). Carbonate deposits containing siderite and interlayered wax deposits form in the upper hole (Burr and Howe, 1987).

2.2 Scale Inhibitors

Scale removal techniques can be divided into mechanical drilling and chemical dissolution or sequestration. The mechanical methods (i.e., drilling or jet cutting) may encounter with an effluent disposal problem. In addition, these mechanical techniques are so costly. Therefore, the petroleum industry preferentially uses scale inhibitors for preventing the scale formation (Burr and Howe, 1987).

The threshold scale inhibitors are widely used in oilfields. These scale inhibitors have an ability at very small amounts to keep large quantities of scalants in solution knowning as “the threshold effect”. The scale inhibitor will adsorb onto nucleated crystals and block the potential growth sites. The scale inhibitors are usually classified into three main groups: phosphonates, phosphoric acid esters, and polymers such as polyacrylic acid. Phosphonate inhibitors are commonly applied in the field today. Their advantages are as follows:

1. Phosphonate can inhibit scale formation at considerably low concentrations.
2. Phosphonates prevent scale in reservoirs effectively at different conditions because they are stable over a wide range of temperatures and pH values.
3. Phosphonates have been shown to inhibit many different types of scales, making them flexible from well to well (Nancollas, 1987).
4. The concentrations of phosphonates in the produced fluid is easily determined by the oxidation and colorimetric technique (Browning and Fogler, 1993). Consequently, it is easy to determine when a formation needs to be resqueezed.

2.3 Scale Treatment

There are two methods to prevent scale formation; namely continuous injection and squeeze treatment.

2.3.1. Continuous Injection

Continuous injection through narrow tubing leading to the wellbore provides the most consistent dosage of chemical, but installation of the necessary equipment is often prohibitively expensive (Monsanto, 1996).

2.3.2. Squeeze Treatment

Squeeze treatment method is most widely used to overcome scale precipitation. Figure 2.1 shows how to apply squeeze treatment. The advantages and disadvantages are shown in Table 2.1. The procedure of squeeze treatment is described briefly below:

1. Preflush Injection This step is to prevent the formation of emulsion in the main inhibitor slug and preferentially to water-wet the near-well formation.
2. Scale Inhibitor Injection A solution of a threshold inhibitor mixed with filtrated seawater having a very low inhibitor concentration (ppm, mg/l) is injected to the formation (Browning and Fogler, 1993).
3. Overflush Injection A suitable amount of brine overflush is used to push the inhibitor to a designed location.
4. Shut in Period The inhibitor is leaved to maximize inhibitor retention. During this period, the inhibitor is retained in the formation by one of three mechanisms: 1) the inhibitor is adsorbed onto the surface of the formation; 2) the inhibitor precipitates with available cations in the reservoir system; or 3) the inhibitor solution leaks into small fractures in the formation.

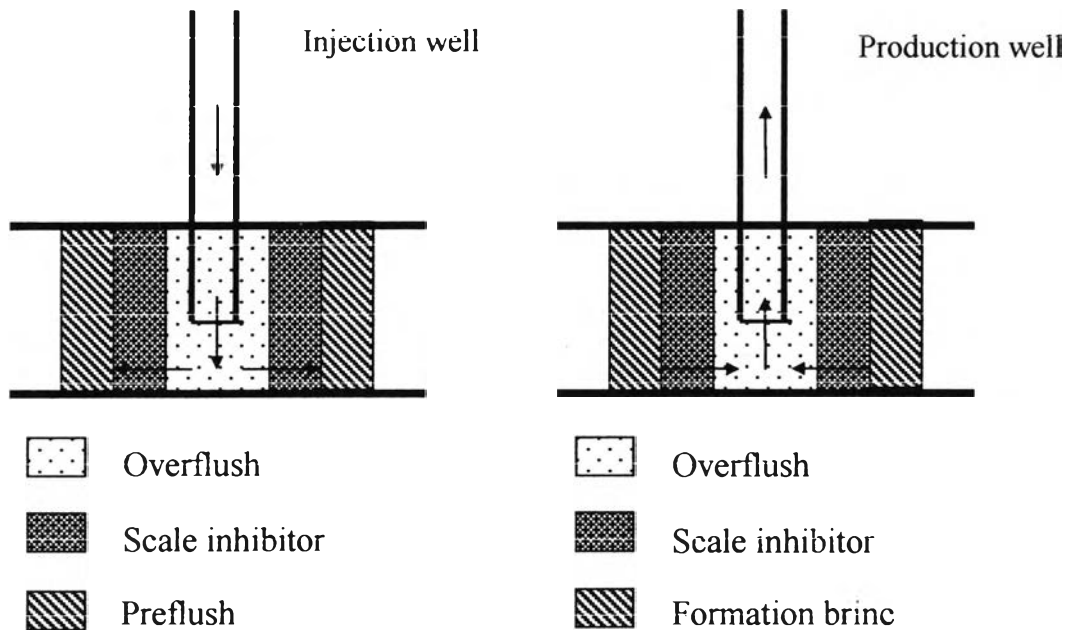


Figure 2.1 The procedure of squeeze treatment technique (Sorbie *et al.*, 1993).

5. Back Production When the production is resumed, the inhibitor is released back to produced fluid. The production can carry on until the concentration of the scale inhibitor is below the effective level. Therefore, the system will need the squeeze treatment again.

Table 2.1 Advantages and disadvantages of inhibitor squeeze treatment (Rerkpattanapipat, 1996).

Advantages	Disadvantages
1. Treat near well bore formation to prevent plugging during draw down.	1. A squeeze generally must be repeated from every two weeks to two years.
2. All steel surfaces at the well bottom are protected from scale.	2. The rule of thumb is that only about one-third of the added inhibitor is actually effective: one-third generally flows back with the first production and about one-third is never returned, although these ratio may improve upon repeated squeezes.
3. A squeeze can be done on old wells without pulling tubing.	3. There is virtually no control on the concentration of inhibitor which flows back with the brine.
4. During routine production, little maintenance is required and no on-site power is needed.	4. Performance on a new system is highly unpredictable.
5. Generally, a squeeze is a simple procedure for most service companies.	5. Once squeeze starts, it is not possible to change the concentration or the chemical, as it is with a treat string.
6. The potential lifetime of a squeeze is virtually unlimited, in theory.	6. There is real potential for formation damage.
7. Only periodic (about weekly) brine analysis is necessary to detect when to resqueeze.	7. It is difficult and expensive to treat corrosion due the difference chemical nature of corrosion inhibitors and the higher concentrations often needed.
	8. It is difficult to analyze for most scale inhibitors at the concentrations typically needed.

2.4 Retention/Release Mechanism

The effectiveness of squeeze treatment is usually judged by its lifetime, which the inhibitor released into the produced fluid is still above the effective concentration to inhibit scale from forming. This process is dictated by the retention/release mechanisms of inhibitors. There are two major retention/release mechanisms.

2.4.1 Adsorption/Desorption

The adsorption/desorption mechanism has been found to most likely occur in non-carbonate reservoirs with low cations concentrations and has been focused in many studies. The advantage of this mechanism is a release of inhibitor into the produced fluid with a minimal chance of formation damage. The adsorption of inhibitor is directly dependent on the properties and surface chemistry of the reservoirs system because they indicate amount of active adsorption sites that the inhibitor contacts.

The major factor that affects the adsorption/desorption process is the pH of the fluid contacting the formation surface. At higher pH values, The lower amount of inhibitor is adsorbed. Moreover, the inhibitor solution concentration, inhibitor type, molecular weight of inhibitor, temperature, mineral substrate, the brine strength and composition and the carbon dioxide saturation level in the solution also are variables that directly affect the amount of inhibitor adsorbed (Browning and Fogler, 1993).

2.4.2 Precipitation/Dissolution

The precipitation mechanism occurs when cations replace the hydrogens on the phosphonate group deprotonated (Browning and Fogler, 1995). Then, the precipitate subsequently releases back into the produced fluid.

The release of inhibitor from the precipitate is dependent upon a number of factors, including: 1) the dissolution rate of the precipitate from the reservoir; 2) the extent of external and internal precipitate migration; and 3) the pore plugging and changing flow patterns that occur during the elution process (Browning and Fogler, 1993).

2.5 Important Factors Affecting Precipitation

There are several important factors affecting precipitation as described below.

2.5.1 Types of Phosphonates

Different types of phosphonates used will result in different numbers of active phosphonate groups available for calcium attachment. For example, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) has two phosphate groups (PO_3H) so the maximum magnesium(or calcium)-to-HEDP molar ratio of the precipitate will be 2:1. If diethylenetriaminepenta (methylenephosphonic acid) (DTPMP) is used, the five calcium ions can attach to one molecule of DPMP (Browning and Fogler, 1995).

2.5.2 Degree of Supersaturation

The degree of supersaturation can affect how fast the initial nucleation and crystal growth occur. The type of nucleation (heterogeneous and homogeneous nucleation) will directly affect the precipitate properties such as the average particle size, the particle size distribution, the dissolution rate and the morphologies (Browning and Fogler, 1995 and Walton, 1967).

2.5.3 Solution pH

The ability of cation to precipitate with phosphonate is dependent upon the ability of the phosphonate molecules to deprotonate, leaving reaction site for the cation to bond. This deprotonation process, in turn, is highly dependent on the pH of the precipitating solution (Browning and Fogler, 1995).

2.5.4 Cation-to-Phosphonate Molar Ratio in Precipitating Solution

When the cation-to-phosphonate molar ratio in the precipitating solution increases, the higher number of cations will react with the phosphonate. This factor enhances the probability of obtaining higher calcium-to-phosphonate molar ratio in the resulting precipitates (Browning and Fogler, 1995).

2.6 **Related Works**

Nancollas and Sawada (1982) investigated the crystallization of calcite and aragonite at 70°C. In both cases, the rates of reaction were proportional to the square of the relative supersaturations and were surface-controlled. The growth rate of calcite decreased with increasing magnesium concentration. The presence of a low level of magnesium ion inhibited calcite growth with the formation of magnesian calcite while at higher magnesium concentrations, the spontaneous precipitation of aragonite took place. The growth rates of calcite and aragonite were markedly reduced by adding hydroxyethylidene-1, 1-diphosphonic acid (HEDP), a potential inhibitor. However, HEDP had little effect on the crystallization of vaterite, the least thermodynamically stable calcium carbonate polymorph.

Nancollas *et al.* (1985) found that the presence of relatively high concentrations of magnesium ion had no detectable effect on the rate of

dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) crystallization, and the same result was true at a lower supersaturation. In contrast, magnesium ion markedly retarded the rate of seed octacalcium phosphate ($\text{Ca}_8\text{H}(\text{PO}_4)_6 \cdot 2.5\text{H}_2\text{O}$, OCP). The retardation experiments using OCP seed crystals were all made at constant ionic strength and constant supersaturation with respect to OCP. Assuming a steady-state adsorption/desorption and the absence of interaction between growth sites, a Langmuir-type adsorption isotherm can be tested by plotting $R_0/(R_0-R)$ against $[\text{Mg}]^{-1}$ where R and R_0 are the rates of OCP crystallization in the presence and absence of magnesium ions, respectively. The linearity of the resulting plot suggests that the magnesium ions retard the rate of precipitation by adsorption at active growth sites on the crystal surface.

Meyers, Skillman, and Herring (1985) discovered that the deposition of calcium carbonate in the perforation tunnels and the near wellbore formation sandstone damaged a substantial number of wells in the Prudhoe Bay field. The wells had monthly decline rates greater than 10 %. After introduction of the inhibitor squeeze treatments, the production rate could be maintained at the acceptable level more than one year. Several scale inhibitors were used for comparing the solubility and calcium tolerance. The adsorption/desorption data were used to calculate lifetime of treatment, the amount of an inhibitor injected and quantities of overflush.

Browning and Fogler (1993) studied the precipitation/dissolution of calcium-1-hydroxyethylidene-1,1-diphosphonic acid (HDEP) in the porous medium and elucidated the important factors affecting the release of this precipitate. The results obtained from the experiments carried out in ceramic cores indicated that the precipitation/dissolution method offered longer squeeze lifetime and more HDEP retention than the adsorption/desorption method. The lifetime of the precipitation was five times greater than the adsorption squeeze lifetime in this experiment. Micromodel experiments

displayed that the Ca-HEDP precipitate placed in the porous media was made up of long fibrous particles preferentially formed in pore throats. The elution from the micromodel indicated that slow dissolution of apparently strong pore throat plugs was dictating the long tailing region. Finally, the results obtained from the multiple shut-in experiments performed in ceramic cores showed that while the quantities of Ca-HEDP retention per shut-in did not increase with successive shut-ins, an enhanced returns effect was observed with respect to the squeeze lifetime.

Kan *et al.* (1994) used a combined dialysis and filtration method to determine the solubility of calcium phosphonate. Diethylenetriamine-pentakis (methylenephosphonic acid), DTPMP having ten ionizable protons was used in their study. The solubility was measured up to 2m ionic strength at the temperature range from 25 to 90° C and over wide ranges of calcium and DTPMP concentrations. The stoichiometry of the precipitate was $\text{Ca}_3\text{H}_4\text{DTPMP}$ at the pH between 4 and 5.5. The results of this study suggest that the solubilities of phosphonates in most natural waters are basically controlled by a two-step mechanism. First, an amorphous calcium phosphonate can precipitate if the ion product exceeds the effective solubility product of amorphous calcium phosphonate. This initial precipitate is stable unless fresh solution flows over the solid as occurs in many natural situations. When fresh solution flows over the initially precipitated calcium phosphonate solid, a well-formed crystalline phase develops which is at least 2 orders of magnitude less soluble than the amorphous phase.

Browning and Fogler (1995) used 1-hydroxyethylidene-1, 1-diphosphonic acid (HDEP) as a phosphonate inhibitor. They found that the degree of supersaturation in the precipitating solution had a tiny effect on the properties of the Ca-HEDP precipitates. The Ca-HEDP precipitates formed at a low pH, and a low calcium:HEDP molar ratio had the calcium:HEDP molar

ratio of 1:1 and comprised long, fibrous spindles while the precipitates formed at a higher pH value and a higher calcium:HEDP molar ratio were powdery, spherical particles having the calcium:HEDP molar ratio of 2:1. The dissolution rate of the precipitates decreased when the calcium:HEDP molar ratio of precipitates increased. The fibrous particles of 1:1 calcium:HEDP precipitate preferentially situated in the throats. The resulting elution curve from micromodel experiment was classified into four regions: (1) the initial high HEDP concentration region; (2) the sharp declining region; (3) the gradually declining region; and (4) the long tail region dictated by the slow, axial dissolution of the compacted precipitate as a result of the severe mass transfer limitations from the precipitate interface to the free flowing elution fluid. The spherical particles of 2:1 calcium:HEDP precipitate existed in both the pores and pore throats. The resulting elution curve was divided into two distinct regions: (1) the initial sharp declining region and (2) the extensive long tailing being governed by the slow, hydrodynamic dissolution of the 2:1 precipitate.

Browning and Fogler (1996) found that the 1:1 calcium-HDEP precipitate was crystalline in nature while the 2:1 calcium-HDEP precipitate was amorphous rather than crystalline. The pH value which each distinct precipitate can form is called "critical" pH value. The critical pH value of the calcium to HEDP molar ratio of 1:1 was determined to be approximately 4.7. For the precipitate having a molar ratio of 10:1, the pH critical value was found to be approximately 3.9. The presence of calcium significantly altered the resulting titration curve by reducing the effective pK_a value of the third deprotonating hydrogen. The 1:1 precipitate released much faster than the 2:1 precipitate. The dissolution of the precipitate mixture containing both 1:1 and 2:1 calcium-HEDP ratios was carried out in the micromodel. The results showed that the resulting elution curve fell between those of the 1:1 and 2:1

precipitates because the fast initial release of the 1:1 precipitate was followed by the slow release of the 2:1 precipitate.

Rerkpattanapipat (1996) studied the formation of calcium with aminotri(methylenephosphonic acid) (ATMP) as a scale inhibitor. It was found that the precipitating pH and the calcium:ATMP molar ratio in the solution affected the type of precipitates. Moreover, the resulting Ca-ATMP precipitates had different dissolution rates which were dependent upon the conditions forming the precipitates.

Wattana (1997) studied HEDP and ATMP to form precipitates with calcium. It was found that the equilibrium solubility of each precipitate was a function of the pH of the solution. The precipitate formed at high pH conditions tended to have low solubilities. Furthermore, the presence of calcium cation in the elution fluid could suppress the solubility of 1:1 calcium-phosphonate precipitates and decreased their dissolution rates.

Jordan *et al.* (1997) carried out experimental studies using a series of a resin coated core floods conducted at 70°C and reservoir conditioned corefloods at 90 to 110°C. The same generic scale inhibitors were used for both adsorption and precipitation floods. They found that the precipitation of a typical scale inhibitor, either a polymeric or a phosphonate species, gave a longer squeeze lifetime at higher inhibitor concentrations than the adsorption. The results from the study of the outcrop precipitation core floods showed that the “hard” (lower solubility) precipitates gave longer lower concentration effluent profiles while the “soft” (higher solubility) inhibitor/calcium complexes gave shorter higher concentration of inhibitor in the effluent. Therefore, it is possible to regulate precipitation treatment to return at certain levels by the addition of different quantities of calcium (or other additive). The results obtained from the experiment of the reservoir conditioned precipitation core floods indicated that penta-phosphonate/calcium and hexa-phosphonate/calcium

solubilities were sensitive to the produced brine chemistry, principally the divalent cation concentrations of both calcium and magnesium. High concentrations of calcium decreased the solubility, resulting in a low concentration return curve of the inhibitor over an extended period of time. Moreover, the solubility of penta-phosphonate precipitate also declined with increasing temperature. The composition of produced brine affected the lifetime of precipitation squeeze.

Pokrovsky (1998) studied the precipitation of calcium and magnesium carbonates from homogeneous supersaturated solutions. The saturation degree with respect to CaCO_3 (s) (Ω_c) was defined as:

$$\Omega_c = \frac{IAP}{K_s^0} = \frac{\gamma_{\text{CO}_3^{2-}}^f [\text{CO}_3^{2-}] \gamma_{\text{Ca}^{2+}}^f [\text{Ca}^{2+}]}{K_s^0} \quad (2.1)$$

where IAP is the ion activity products of CaCO_3 in solution

K_{sp}^0 is the thermodynamic solubility products of calcite

γ_i^f is the activity coefficient of the free ion

At low degrees of supersaturations (e.g., $\Omega_c = 7-20$) and the $\text{Mg}^{2+}:\text{Ca}^{2+} \leq 5$ magnesium ions did not inhibit the rate of CaCO_3 nucleation. This finding is in contradiction with the common view that Mg is a retarding factor of CaCO_3 spontaneous precipitate from seawater. At a high Ω_c value, the dissolved magnesium inhibited CaCO_3 nucleation. Moreover, in a solution containing a small amount of magnesium ($\text{Mg}^{2+}:\text{Ca}^{2+} \leq 2.5:1$), the transformation proceeded to calcite. At a high activity of magnesium, the conversion of aragonite to calcite was completely retarded. The inhibiting effect of Mg^{2+} ions resulted from difficulties in its rapid dehydration relative to Ca^{2+} (aq) or from crystal poisoning by its adsorption onto the reactive site of CaCO_3 (s). This sequence of crystallization (supersaturated solution \rightarrow vaterite \rightarrow aragonite \rightarrow calcite) occurred

at a relative low supersaturation ($\Omega_c < 40$). At higher values of Ω_c (e.g., 50-200), the rate of transformation reaction (vaterite→calcite) was very fast and the chemical affinity of the system allowed a crystallization of calcite or the less-stable Mg-calcite. The saturation degree of magnesium carbonate, MgCO_3 (s), is the main parameter which controls the Mg content in the solid precipitate.

Raju (1998) found that water quality was of major importance in reservoir water flooding. It was concluded that seawater mixed with the formation brine that had a high calcium carbonate scaling potential could reduce the likelihood of scaling. This article outlined the chemistry of this process and how the water composition and scaling potential varied over the various stages from early production through water logging wells which required squeezing with scale inhibitors in the early production stages and might not require re-squeezing later.

Suwannamek (1998) studied the formation of calcium precipitates with diethylenetriaminepenta(methylenephosphonic acid)(DTPMPA). It was found that the Ca:DTPMPA precipitate molar ratio increased with increasing the solution pH. The setting temperature affected the precipitate molar ratio. The dissolution rate of Ca-DTPMPA precipitates increased with increasing the dissolving liquid pH. In comparison among three types of scale inhibitors for calcium-type scales, the order of squeeze lifetime was HEDP < DTPMPA < ATMP.

Liwsrisakul (1999) found that 1:1 Ca-HEDP precipitate transformed to the 2:1 Ca-HEDP precipitate in saturated solution and pH of 6 while 2:1 Ca-HEDP precipitate transformed to the 1:1 Ca-HEDP precipitate in saturated solution and pH of 2. The transformation rate of 1:1 to 2:1 Ca-HEDP precipitate was faster than the transformation rate of 2:1 to 1:1 Ca-HEDP precipitate. Differential reactor experiments showed that the initial dissolution rate of the 1:1 Ca-HEDP precipitate was faster than the rate of the 2:1 Ca-

HEDP precipitate. Moreover, the differential reactor experiments and micromodel experiments showed that excess of calcium in model formation water dissolved both 1:1 and 2:1 Ca-HEDP precipitates slower than less calcium in formation water. Therefore excess calcium in elution fluids can enhance a longer treatment lifetime.