

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Scales

Scales are any undesirable solids precipitating out from the liquid phase. The most common scales encountered in an oilfield consist of calcium carbonate, calcium sulfate, barium sulfate and strontium sulfate (Schalge, 1990). Primary factors affecting scale precipitation, deposition and crystal growth are supersaturation, mingling of two unlike waters having incompatible compounds in solution, change of temperature, change of pressure on solution, evaporation (affects concentration), agitation, long exposure time (crystal growth) and change of pH (Nancollas, 1987). Scale formation can occur almost anywhere, although the most troublesome areas are in the near wellbore formation or on the wellbore itself. Extensive scale buildup could severely limit the productivity of a well to the point where the well has to be cleaned or abandoned. In addition to operational problems, the formation of naturally occurring radioactive material (NORM) scales (i.e., radium sulfate) may offer environmental problems. Hence, controlling a scaling problem is so important. Carbonate scales can be easily dissolved by an acidization technique, on the other hand sulfate scales highly insoluble in acid solutions are removed by a mechanical technique such as drilling. However, one of the most effective methods used in oilfield to overcome this scaling problem is squeeze treatment performed by injecting a threshold scale inhibitor into a formation where they can control the formation of scales (Oddo and Tomson, 1990).

2.2 Squeeze Treatments

The advantages of treating oil wells by the squeeze treatment have been known for over fifty years (Oddo and Tomson, 1990; and Carlberg, 1987). Squeeze treatments are operated by placing scale inhibitors into the near wellbore formation where a portion of the inhibitors is potentially retained during the shut-in period via some retention mechanisms such as adsorption or precipitation. Once the production is resumed by flowing fluid through the formation, the scale inhibitors are released back into the produced fluid where they are able to prevent the formation of scales. The success of squeeze treatments is often based on its long squeeze lifetime. The squeeze lifetime is the time period that the concentration of scale inhibitor in the produced fluid is still above the minimum effective concentration for scale prevention.

The maximum lifetime could be achieved from an ideal squeeze treatment that the scale inhibitors placed into the formation are slowly released at or just above the minimum effective concentration (C_{min}). In this case, all of scale inhibitors are being utilized in scale inhibition at maximum efficiency and then provided the longest squeeze lifetime. However, in an actual squeeze treatment, most of scale inhibitors rapidly release back into the produced fluid during the initial resuming production. Therefore, the concentration of scale inhibitors sharply declines below the minimum effective concentration, which lends itself to the end of treatment lifetime. Figure 2.1 illustrates the concentration profiles of scale inhibitor released for ideal and actual squeeze treatment.

Once the scale inhibitors in the formation are exhausted or their concentrations in the produced fluid falls below the minimum effective concentrations, the wells have to be resqueezed. This situation is costly in terms of chemicals and production downtime.

Hence, it is imperative for oil producers to operate the squeeze treatments that maximize the squeeze lifetime.

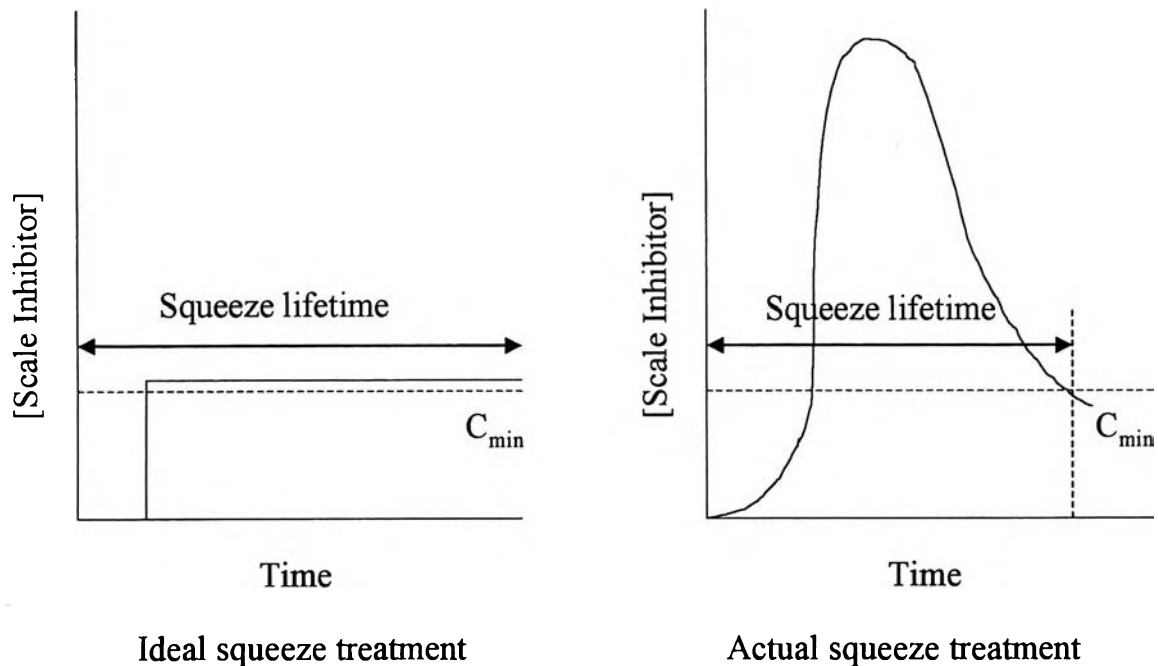


Figure 2.1 Comparison between an ideal elution curve and an actual elution curve (Browning and Fogler, 1993).

In order to design the efficient squeeze treatments and maximize the squeeze lifetime, it becomes extremely important to understand a fundamental of the inhibitor retention/release mechanisms which could aid in achieving this desired squeeze treatment process. The two major retention/release mechanisms that have been found to occur in a formation are:

1. Adsorption/Desorption mechanism
2. Precipitation/Dissolution mechanism

2.2.1 Adsorption/Desorption Mechanisms

This retention/release mechanism depends upon the adsorption/desorption characteristic of scale inhibitors with the reservoir rock.

The adsorption/desorption mechanism is advantageous because it provides an even release of scale inhibitors into the produced fluid with a minimal chance of formation damage (Oddo and Tomson, 1991). During shut-in period, scale inhibitors are adsorbed onto the formation surface then they are subsequently desorbed back into the produced fluid when production is resumed. The retention of scale inhibitors within the formation is mainly considered to be through a physical adsorption mechanism and the extent of the process is governed by an adsorption isotherm (Sorbie *et al.*, 1993). The amount of scale inhibitors adsorbed and the lifetime of an adsorption squeeze are dependent on the properties and surface chemistry of the reservoir system. Some of these reservoir properties include the pH of the fluid contacting the formation surface, the scale inhibitor-solution concentration and the carbon dioxide saturation level in the contact fluid (Przybylinski, 1989; and Myers *et al.*, 1985)

Many previous works have been focused on the adsorption and subsequent desorption of scale inhibitors that found to occur in noncarbonate reservoirs contacted by low-cation concentration waters (King and Warden, 1989). In addition, a previous study found that the phosphonates generally adsorb poorly onto sandstones and that the squeeze lifetime often ranges from 3 to 6 month (Carlberg, 1987). This lifetime is not favorable for oil producers, however the squeeze lifetime could be enhanced by injecting a polyquaternary amine along with the scale inhibitors into the formation (Shuler, 1991).

2.2.2 Precipitation/Dissolution Mechanisms

Precipitation process usually occur when the scale inhibitors react with divalent cations such as calcium or magnesium forming a precipitate salt of divalent cation-scale inhibitor precipitates retained in the formation during the shut-in period. After that, this precipitate salt is slowly dissolved back into the produced fluid when normal production is resumed. This

precipitation process is desirable in oilfield treatments because a large volume of scale inhibitors can be retained in the formation after injection and the dissolution kinetics are favorable in ensuring a slow release of scale inhibitors into the produced fluid resulting in a longer squeeze lifetime.

Calcium is one of the most divalent cations that easily forms the precipitates with scale inhibitors. A source of calcium ion results from one of three places which are the formation water, a brine overflush and reservoir acidization. In order to ensure that the precipitation will occur, the sufficient amounts of calcium ion and scale inhibitors are necessary to be presented in the reservoir. The release of scale inhibitors from a precipitation squeeze is dependent on a number of factors including the dissolution rate of the precipitate from the reservoir, the extent of external and internal precipitate migration and the pore plugging and changing flow patterns that occur during the elution process (Browning and Fogler, 1995).

The previous results have shown that squeeze lifetime has been known to last for up to 2 years in carbonate reservoir, which is significantly longer than those observed in adsorption squeeze treatment (Carlberg, 1987). However, one of the drawbacks of precipitation treatment has been its potential to induce the formation damage because of divalent cation-scale inhibitor precipitates as pseudoscale.

The difference in the precipitating conditions results in the different types and properties of the precipitates that, in turn, providing the difference in squeeze lifetime as well. Therefore, knowing the precipitating conditions that could form the desired precipitates would be a great tool for designing the efficient precipitation squeeze treatments. Four main parameters that potentially affect the precipitate's properties are types of scale inhibitor used, degree of supersaturation, the precipitating solution pH and cation to scale inhibitor molar ratio added in the precipitating solution (Browning and Fogler, 1995).

2.3 Scale Inhibitors

The scale inhibitors used to combat the scaling problem can be classified into three main groups which are phosphonates, phosphonic acid esters, and polymer such as polyacrylic acid (Vetter, 1972). Only small amount of scale inhibitor injected along with brines overflush into the formation can be capable to keep large quantities of scalants in the solution. This situation is called “threshold effect”. This effect causes the inhibition mechanism which is believed that threshold scale inhibitors interact with the nucleated scale crystals by disrupting the thermodynamic stability of the growing nucleons and interfering or blocking the growth processes of scale crystals (Gill *et al.*, 1985). The most effective scale inhibitors used today are the phosphonates because they have the ability to react with divalent cations in formation water via their active phosphate groups resulting in the formation of a precipitate salt and are stable over a wide ranges of the operating conditions. In addition to scale inhibition, phosphonates are effectively and widely utilized in many industrial processes such as dispersants, bleaching agents and corrosion inhibitors (Monsanto, 1986).

2.4 Related Works

Recently, precipitation squeeze treatment has increasingly been concerned in oilfield because it has been reported that this treatment offers the longer lifetime than adsorption squeeze treatment (Carlberg, 1987; and Browning and Fogler, 1993).

Lewis and Raju (1992) used Aminotrimethylene phosphonic acid (ATMP) as threshold scale inhibitor that had high reactivity to precipitate with divalent cation species prominent in typical brines and the solubility of ATMP-cation precipitates was a function of cation concentration, pH, TDS and time. It

was also found that the ATMP molecules were favorably adsorb on the limestone formation surface. This occurrence could basically be performed as a chromatographic process coupled with precipitation mechanism resulting in long squeeze lifetime.

Yuan *et al.* (1993) used numerous data from several wells in North Sea fields to simulate the complex squeeze model. This model had been operated in both homogeneous and heterogeneous systems where there was free crossflow between strata. The results showed that the placement method for inhibitor slug injection should be also considered. In addition, selecting appropriate preflush and overflush volumes was important step for creating the correct thermal conditions in the precipitation squeeze treatment.

Browning and Fogler (1993) studied the precipitation/dissolution mechanism of Ca-HEDP precipitates in porous medium and also its properties. The results were elucidated that the Ca to HEDP molar ratio in the precipitates affected the solubility limit and precipitate's morphologies. The results from micromodel showed that Ca-HEDP precipitates placed in porous media were made up of long fibrous particles preferentially situated in pore throats resulting in the long tailing region in the elution curve. In addition, it was found that the lifetime of precipitation squeeze treatment was five times greater than that of adsorption squeeze treatment.

Browning and Fogler (1995) investigated the precipitating factors affecting the properties of Ca-HEDP precipitates such as precipitating solution pH, the Ca to phosphonate molar ratio in the precipitating solution and the degree of supersaturation. It was observed that the degree of supersaturation had a little effect on the precipitate's properties, while the coupled effects of pH and Ca to HEDP molar ratio had a significant effect on the properties of the precipitates. In this work, the resulting precipitates having Ca/HEDP molar ratio of 1:1 and 2:1 were composed of fibrous spindles and spherical particles,

respectively. The results also revealed that the 2:1 Ca-HEDP precipitate provided the slower dissolution rate than the 1:1 Ca-HEDP precipitate.

Browning and Fogler (1996) determined the effect of precipitating conditions on the formation of Ca-HEDP precipitates. Two distinct precipitates were formed by varying the pH and Ca/HEDP molar ratio in precipitating solution. At the Ca/HEDP molar ratio of 1:1, the critical pH value was approximately 4.7 while at the molar ratio of 10:1, the critical pH value was about 3.9. However, the mixture of these both precipitates was obtained when the precipitating solution pH was not constant. The results from micromodel demonstrated that the 1:1 Ca/HEDP precipitate dissolved much faster than 2:1 Ca/HEDP precipitates.

Rerkpattanapipat (1996) used ATMP as a phosphonate scale inhibitor to study its precipitation and dissolution in porous media. It was found that three distinct precipitates having Ca/ATMP molar ratio of 1:1, 2:1 and 3:1 were observed. Two parameters affecting the precipitate's type were precipitating solution pH and Ca/ATMP molar ratio in precipitating solution. The results from dissolution study revealed that 3:1 Ca/ATMP precipitate provided the longest tail of the elution curves which in turn, offered the longest squeeze lifetime.

Wattana (1997) studied the dissolution kinetics of scale inhibitors in the presence of high concentration of calcium ion. Both HEDP and ATMP were used in this work. It was noticed that the solubility limit of the resulting precipitates was a function of precipitating solution pH and the presence of calcium ion in elution fluid could be able to enhance the squeeze lifetime.

Suwannamek (1998) used DTPMP containing five active phosphate groups as a scale inhibitor. The results demonstrated that the Ca/DTPMP molar ratio in the precipitates increased with increasing the precipitating solution pH. Furthermore, increasing the temperature also resulted in an increase of Ca/DTPMP molar ratio as well. In addition, the comparison among three types

of scale inhibitors showed that the order of squeeze lifetime was HEDP < DTPMP < ATMP.

Liwsrisakul (1999) studied the transformation of Ca-HEDP precipitates. It was observed that the transformation from 1:1 to 2:1 Ca-HEDP precipitate was faster than the transformation from 2:1 to 1:1 Ca-HEDP precipitate due to the high dissolution rate of 1:1 Ca-HEDP precipitate observed from the differential reactor.

Wattanasakwiboon (2000) investigated the precipitation between HEDP and magnesium ions under different precipitating conditions. It was found that the precipitating solution pH and the initial Mg/HEDP molar ratio in the precipitating solution affected the precipitate's properties which were the Mg/HEDP molar ratio in the precipitates, the morphologies and the equilibrium solubility. Four distinct Mg-HEDP precipitates having Mg/HEDP molar ratios of 1:2, 3:2 and 2:1 were observed.