CHAPTER II
LITERATURE SURVEY

In typical oil fields, gaseous hydrocarbons, which are the lightest constituents, occupy the topmost of the reservoirs, known as the gas cap. The next part underneath is commonly called the oil zone in which heavier liquid hydrocarbons are situated. Below the oil layer, it is the part being the porous rock formation containing brine called formation water. Most of oil and gas fields yield 10 to 20 barrels of brines for every barrel of oil (or gas equivalent). These brines are generally corrosive and contain carbonate and sulfate salts. Therefore, the appropriate scale treatment technique must be applied to inhibit the scale formation (Allen and Roberts, 1989).

2.1 Formation Waters

Formation waters are brines present in the sedimentary porous rock in the oil wells. Main constituents of the formation water are cations and anions that can bring about the scaling problem in any oil fields (Schechter, 1992).

2.1.1 Cations

The composition of the dissolved solids found in oil field water is dependent upon a number of factors: the composition of the water in the depositional environment of the sedimentary rock, subsequent changes by rock and water interaction during sediment compaction and migration, and changes by mixing with infiltration waters. Thus, there are many major cations in the oil field brines.

Calcium (Ca^{2+}) is generally present in the oil field waters, but its concentration is quite variable, ranging from less than 100 ppm (parts per million) to values in excess of 30,000 ppm. In general, waters associated with limestone ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and gypsum ($CaSO_4.2H_2O$) will contain more calcium than waters associated with sandstone. The presence of divalent cations such as calcium will be an important consideration in well treatment design.

Magnesium (Mg^{2+}) concentrations in oil field brines, like calcium concentrations, are dependent upon the origin of the waters and the rock and water

interaction. Perhaps the most important reaction affecting the magnesium content is the formation of dolomite.

The other cations often present in the oil field brines in lower concentrations are barium (Ba^{2+}), strontium (Sr^{2+}), and potassium (K^+). These alkali and alkali earth metals react similarly to calcium.

2.1.2 Anions

Water containing quantities of cations must necessarily contain similar quantities of anions so that the solution is electrically neutral. The major anion in most formation waters is chloride. It is also the predominate anion in seawater. Chloride ion does not readily form precipitates.

The next most substantial anion in many formation waters is bromide. As a general rule, formation water samples are more likely to be analyzed for carbonate or sulfate than for bromide. Thus, there is a lack of data for bromide concentrations. However, their concentrations range from less than 50 ppm to more than 6000 ppm.

Carbonates are always contained in the formation waters. The form of carbonates in the formation waters depends upon the pH and other factors including concentration of ions, temperature, etc.

Normally, seawater has about 900 ppm of sulfur as sulfate. The quantities of sulfates in the formation waters range from almost none to several thousand ppm which are likely to form the scale deposits with barium and strontium cations. The amount of sulfate ion present depends on many factors such as carbonates. Moreover, the formation waters may also contain phosphates, iodides, and other anions present in trace quantities (Schechter, 1992).

2.2 Scales

Scale is generally the precipitation of undesirable solids composing of several salts such as calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, and sodium chloride (Allen and Roberts, 1989). This scale is resulted from the reaction of divalent cation alkali such as calcium with carbonate or sulfate

minerals of the porous rock. Divalent cation alkalis mainly come from three sources: (1) the formation water, (2) brine overflush, and (3) dissolution of minerals in the formation as a result of the reservoir acidization (Browning and Fogler, 1993).

These undesirable solids are frequently led from the sudden changes in the produced fluid conditions such as pressure drop, temperature change, and pH change and/or the mixing of two incompatible fluids, the formation water and injected brines. When the pressure drop is occurred, the fluids will be pumped up more slowly than before. More enough time of the fluids flowing in the production system can bring the scale formation. Besides, the solubility of divalent salts varies considerably with pH, therefore pH value of the system is a very important parameter and can affect the composition and the amount of precipitates. Moreover, when temperature is changed, the scale formation occurred in different structure generates the difference in the solubility of scale. The scale normally contains different compositions due to different well conditions (Browning and Fogler, 1996).

The scale has been widely found in the oil production systems and commonly deposited in the matrix formation, wellbore, downhole pumps, tubing, casing, flowline heater, tanks and salt-containing water disposal, and waterflood system. Scale deposition generally forms as a result of crystallization and precipitation of minerals in the brine (Allen and Roberts, 1989). Continuous scale growth and deposition in properly untreated wells can ultimately cause the limit of the production efficiency of a reservoir and damage system equipment by blockage of the oil flow path.

For sulfate scales, they are often formed in the near wellbore region, perforations, and tail pipe assembly. These deposits can vary from almost pure calcium sulfate to complex mixture of alkali earth metal sulfates. In several cases, pure barium sulfate is found with traces of calcium and strontium sulfates. Barium sulfate deposits are usually caused by mingling of two incompatible waters, one containing soluble salts of barium and the other containing sulfate ions. Normally, barium sulfate scale increases with decreasing temperature as a result of decreasing barium sulfate solubility. Pressure drop may decrease the solubility of barium sulfate and then cause scaling. Moreover, the radioactive scale formation such as radium sulfate is very difficult to treat by any conventional chemical methods and causes

seriously environmental problems.   Therefore, it is of importance to control these scaling problems (Allen and Roberts, 1989 and Browning and Fogler, 1993).

Analysis of field brine can exhibit the scaling tendency.   Table 2.1 shows an example of barium sulfate scale caused by mixing of Bartlesville and Arbuckle brines from wells in the Boston Pool, Oklahoma.   Even though the quantities of the barium and sulfate ions are lower than the others, the barium sulfate scale deposited in the oil field potentially tends to cause a serious problem for oil production systems.

Table 2.1 Analysis of field brine and scale (Allen and Roberts, 1989).

Component	Brine Concentrations, mg/l		Composition in Scale	
	Bartlesville	Arbuckle	Component	Percentage
Sodium, Na^+	52,000	58,400	-	-
Calcium, Ca^{2+}	10,700	13,900	$CaCO_3$	0.65
Magnesium, Mg^{2+}	1,807	2,182	$MgCO_3$	8.12
Barium, Ba^{2+}	250	nil	$BaSO_4$	80.10
Sulfate, SO_4^{2-}	nil	194		
Chloride, Cl^-	104,750	120,750	-	-
Alkalinity, HCO_3^-	44	50		
			$SrCO_3$	4.45
			$SrSO_4$	3.60
			SiO_2	0.11
			Fe_2O_3	0.22
			Water	
			soluble	0.87
			Salts	1.02
			Oil	0.46
			Moisture	0.40
			Others	
			Total	100 %

2.3 Scale Treatments

Scale is usually classified by methods of treatment which can be divided into two categories, namely mechanical and chemical methods.

2.3.1 Mechanical Treatments

For perforated casing, reperforating is most effective method of bypassing perforations sealed with scale. Mechanical methods such as string shot, sonic tools, drilling, or reaming have been used to remove both soluble and insoluble scales from tubing, casing, or open hole. Moreover, scales may be removed from surface lines with scrapers or by reaming out. However, the disadvantage of this method is to face with an effluent disposal problem.

2.3.2 Chemical Treatments

For chemical method, chemically inert scales and chemically reactive scales are considered. Chemically inert scales are not soluble in chemicals. Chemically reactive scales may be further classified as (a) water soluble, (b) acid soluble, and (c) soluble in chemicals other than water and acid (Allen and Roberts, 1989).

2.3.2.1 Water-Soluble Scale

The most common water-soluble scale is sodium scale ($NaCl$) which can be readily dissolved with relatively fresh water. Acid should not be used to remove this scale. In addition, if gypsum scale is newly formed and porous, it may be dissolved by circulating water containing about 55,000 mg/l $NaCl$ pass through the scale. At 100°F, 55,000 mg/l $NaCl$ will dissolve three times as much gypsum as fresh water.

2.3.2.2 Acid-Soluble Scale

The most prevalence of all scale compounds, calcium carbonate ($CaCO_3$), is acid-soluble. Hydrochloric acid (HCl) or acetic acid can be used to effectively remove this scale. Acetic acid has special application downhole in pumping wells when it is desired to leave chrome-plated or high alloy rod pump in a well during acid treatment. Acetic acid will not damage chrome surfaces at

temperature below 200°F. However, hydrochloric acid will severely damage the chrome.

Acid-soluble scales also include iron carbonate ($FeCO_3$), iron sulfide (FeS), and iron oxide (Fe_2O_3). Hydrochloric acid is mixed with a sequestering agent to stabilize the ferric iron to prevent the precipitation of ferric hydroxide from spent acid solutions. Sequestering agents most commonly used include citric acid, acetic acid, mixtures of citric and acetic acid, EDTA (Ethylenediamine tetraacetic acid), and NTA (Nitrilotriacetic acid).

Scales are frequently coated with hydrocarbons, thus making it difficult for acid to contact and dissolve the scales. Surfactants can be added to all types of acid solutions to develop a better acid-to-scale contact. Surfactant selection for this use should be tested to determine that the surfactant will prevent acid-crude oil emulsions and will also leave water-wet rock surfaces.

2.3.2.3   Acid-Insoluble Scale

The only acid-insoluble scale which is chemically reactive is calcium sulfate or gypsum ($CaSO_4.2H_2O$). Calcium sulfate, though not reactive in acid, can be treated with chemical solutions which can convert calcium sulfate to an acid soluble compounds such as calcium carbonate ($CaCO_3$) and calcium hydroxide ($Ca(OH)_2$). The chemicals normally used for gypsum conversion are sodium carbonate (Na_2CO_3), ammonium bicarbonate (NH_4HCO_3), and potassium hydroxide (KOH). After converting gypsum, calcium carbonate or calcium hydroxide can then be removed by either hydrochloric acid or acetic acid. Furthermore, some compounds such as EDTA (Ethylenediamine tetraacetic acid) and DTPA (Diethylenetriamine pentaacetic acid) can dissolve gypsum without the necessity of conversion to calcium carbonate or calcium hydroxide. However, these compounds are not extensively used because of their high costs.

2.3.2.4   Chemically Inert Scale

The most common chemically inert scales are barium sulfate ($BaSO_4$) and strontium sulfate ($SrSO_4$). Barium sulfate scale on the formation face or in perforation systems may be removed by mechanical methods. Nevertheless, the best approach is to prevent the precipitation and deposition of these scales by using particular compounds known as scale inhibitors.

2.4 Scale Inhibitors

In general cases, the first warning of existence of a significant scale deposit is a decrease in well performance. Scale inhibitors are widely used to solve this scaling problem in many oil fields. The most important property of these scale inhibitors is the ability to prevent or to slow the nucleation and growth of the scale at very small concentrations in the order of a few ppm. This is known to be a minimum (threshold) concentration of the scale inhibitors. The release of scale inhibitors above a threshold concentration, therefore, can reduce the tendency for crystallization or completely prevent scale formation and growth by two pathways (Graham *et al.*, 1997):

(1) Nucleation inhibition: Disruption of thermodynamic stability of growing nucleons for homogeneous crystallization by endothermic adsorption of inhibitor species, causing dissolution of nucleated scale.

(2) Crystal growth retardation: Interference/blocking of the growth processes of the growing crystal for heterogeneous crystal growth by irreversible adsorption of inhibitor species at the active growth sites, resulting in their blockage.

The scale inhibitors are usually categorized into three main types: (1) phosphonates, (2) phosphonic acid esters, and (3) polymers such as polycarboxylic acid (Vetter, 1972). The most commonly used chemicals to inhibit the scale formation in the petroleum industry are phosphonates and polycarboxylic acid. Several organic phosphonates and polymers are now available to suppress the formation of a wide range of scales including calcium carbonate, calcium sulfate, calcium phosphate, barium sulfate and strontium sulfate. Many of these water-soluble liquid organic scale inhibitors are very suitable for squeeze treatment such as Aminotri(methylene phosphonic acid) (ATMP), Diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) for phosphonate types and several types of polycarboxylic acids such as Phosphinopolycarboxylic acid polymer (PPCA). In general oil field applications, phosphonate and polymeric scale inhibitors are usually applied in low pH solution whereas the reservoirs may have a pH in the range of approximately 4 to 7 or greater (Yuan *et al.*, 1993). Moreover, all of the scale

inhibitors have greater efficiency for the scale inhibition when they become more deprotonated (He *et al.*, 1996 and Xiao *et al.*, 2001).

2.5 Scale Inhibitions with Scale Inhibitors

There are two approaches that use the scale inhibitors to prevent the scaling problem, namely, continuous injection and squeeze treatment. The details of these methods can be described as follows:

2.5.1 Continuous Injection

The scale inhibitors are continuously injected with water flooding, which is typically used in secondary oil recovery. It is operated by injecting the water into the formation through the injection wells in order to move oil to the production wells, through narrow tubing toward the wellbore. This method can provide the most consistent amount of chemical during the scale treatment. However, the disadvantage of this method is an expensive installation cost of the necessary equipment that prohibits the prevalent use (Monsanto, 1996).

2.5.2 Squeeze Treatment

Nowadays, squeeze treatment technique is the most common and effective method widely used to prevent the scaling problem in the oil production system. The squeeze operation diagram can be shown in Figure 2.1. The squeeze treatment is a process, in which a slug of small volume of scale inhibitor solution is injected into the formation along with brine overflush under high pressure through the oil production well. Then, it is shut-in for approximately twenty-four hours in order to leave the scale inhibitor to maintain in the formation. During this shut-in period, the scale inhibitor will generally precipitate with the alkali cations contained in the formation water such as calcium and magnesium to form a water-soluble salt (Yuan *et al.*, 1993). Alternatively, the calcium could be injected with the scale inhibitor and subsequently precipitate in the formation.
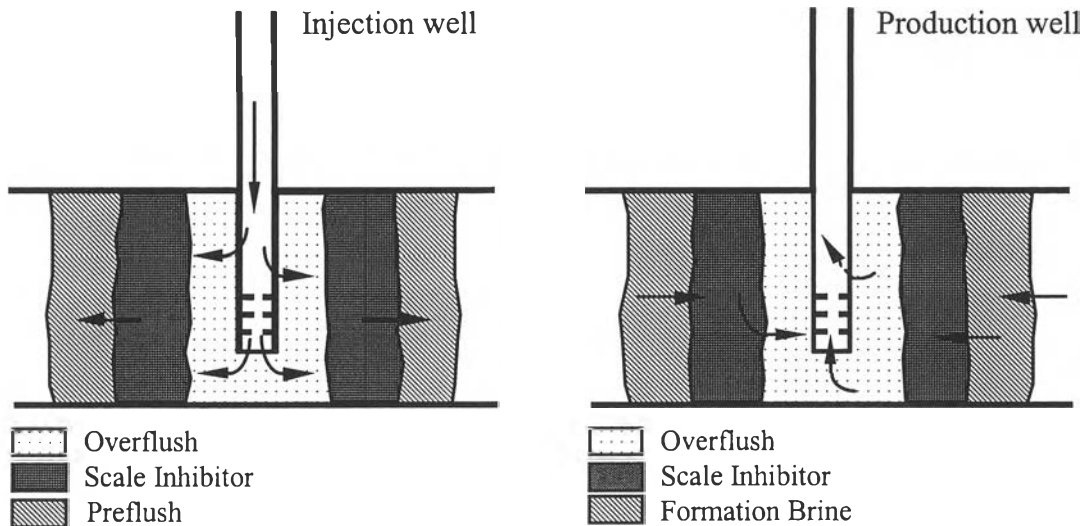
Figure 2.1 Procedure of squeeze treatment technique.

The procedure of squeeze treatment can be briefly explained as follows:

(1) <u>Preflush injection</u>: The purpose of this step is to prevent the formation of emulsion in the main inhibitor slug and to preferentially water-wet the near-well formation.

(2) <u>Scale inhibitor injection</u>: A solution of the threshold scale inhibitor dissolved in filtrated seawater and having a very low concentration in the ppm level is injected into the formation.

(3) <u>Overflush injection</u>: The suitable amounts of brine overflush are subsequently injected to force the scale inhibitor to a desired position.

(4) <u>Shut-in period</u>: The scale inhibitor is left in the formation for about a day. During this period, the inhibitor is retained in porous rock by one of the following three mechanisms:

(4.1) The inhibitor is adsorbed onto the surface of the reservoir rock.

(4.2) The inhibitor precipitates with available cations such as calcium in the formation to form soluble salt.

(4.3) The inhibitor is entrapped in small fractures in the formation.

(5) <u>Back production</u>: After shut-in period, the normal production is resumed. The scale inhibitor is slowly released back into the produced fluid through the production well. During the production period, the formation water will contain a proper concentration of the scale inhibitor, which can inhibit or slow the scale formation. Hence, it has high capability of achieving the scale treatment.

When the concentration of the scale inhibitor is decreased to below the level, which is effective for scale formation prevention, the oil production system has to be shut down and the reservoir must be resqueezed. Therefore, the effectiveness of the squeeze treatment is usually determined by the length of time, which the scale inhibitor is dissolved back into the produced fluid at a minimum effective concentration (C_{min}) or threshold concentration approximately 10 ppm, known as squeeze lifetime.

For an ideal treatment, the continuous release of the inhibitor should take place at C_{min} along the treatment period. However, in an actual treatment, large amounts of the scale inhibitor is immediately released back into the produced fluid at the initial period following by the quick drop below C_{min} of the scale inhibitor concentration, as shown by the elution curves in Figure 2.2. Therefore, it is of importance to design the squeeze treatment where the scale inhibitor must be gradually released from the porous rock, providing the desirably longest squeeze lifetime for scale inhibition (Browning and Fogler, 1993).
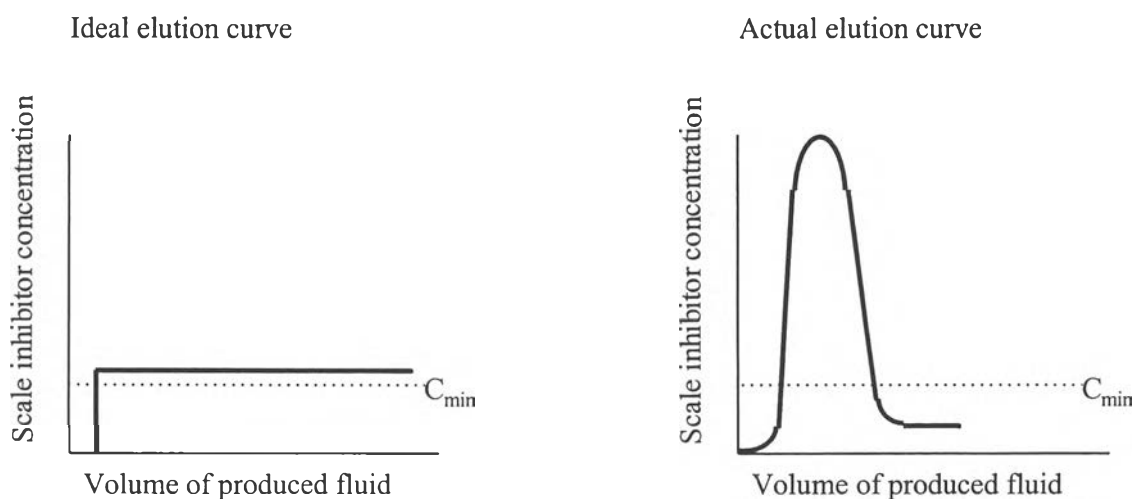

Figure 2.2 Comparison between an ideal and a typical elution curves (Browning and Fogler, 1993).

2.6   Related Works

The applications of the effective types of scale inhibitors in the precipitation squeeze treatment have been studied by Porous Media Group, the University of Michigan, Ann Arbor (Rerkpattanapipat, 1996 and Suwannamek, 1998). After this treatment in the oil fields, the scale inhibitors are released back into the produced fluid to lower or prevent the scale deposits. Related studies have been carried out on the use of the scale inhibitors to inhibit the scale formation, especially barium sulfate scale (Coveney *et al.*, 2000 and Xiao *et al.*, 2001). These scales are problematically difficult to remove once it is formed because of their low solubility even in acidization treatment, and subsequently cause considerable production losses (He *et al.*, 1996 and Xiao *et al.*, 2001).

Rerkpattanapipat (1996) studied the formation of Ca-ATMP precipitates and their precipitation and dissolution in porous media. It was found that two parameters that affect the type of precipitates are the pH value and Ca-ATMP molar ratio of the precipitating solution. The degree of supersaturation had little effect on the type of precipitates. The resulting Ca-ATMP precipitates were found to have different dissolution rates, which are dependent upon the precipitating conditions. Furthermore, during the elution period, the 3:1 Ca-ATMP precipitate elution curve exhibited a longer squeeze lifetime than 1:1 and 2:1 Ca-ATMP precipitates. Therefore, it is very suitable for scale treatment.

Suwannamek (1998) studied the dissolution of Ca-DTPMP precipitate in both batch synthesis and micromodel experiments. It was found that the Ca to DTPMP molar ratio in the precipitate increased with increasing pH of the precipitating solution and with temperature. The dissolution rate of the Ca-DTPMP precipitate increased with increasing solution pH of the elution fluid. The precipitate with a Ca to DTPMP molar ratio of 2:1 had the highest equilibrium solubility while the one with a molar ratio of 4.5:1 had the lowest solubility. Therefore, the 4.5:1 Ca-DTPMP precipitate gives the longest squeeze lifetime and is suitable for the inhibition of the barium sulfate scale formation.

Coveney *et al.* (2000) used the proposed energy minimization and molecular dynamic simulations to study scale inhibitor molecule which can bind the growing

faces of barium sulfate, resulting in a highly active inhibition of barium sulfate crystal growth. A macrocyclic aminomethylphosphonate was used to study the effect of scale inhibitor on the barium sulfate precipitation. The results showed that barium sulfate crystals were more spherical as the concentration of the scale inhibitor is increased. The reduction in sizes with increasing concentration suggested that the crystallization process is inhibited with nucleation becoming the dominant process.

Recently, Xiao et al. (2001) studied barium sulfate precipitation in the absence and in the presence of a polymeric scale inhibitor (PPCA). The induction period was used to evaluate barium sulfate nucleation. Various experimental conditions such as degree of supersaturation, ionic strength, temperature, and pH were investigated. The inhibition of barium sulfate nucleation in the presence of PPCA was correlated to those solution conditions. The experimental results revealed that only the deprotonated fraction and metal-complexed fraction of PPCA were effective to inhibit barium sulfate nucleation, while the protonated fraction had low capability of preventing barium sulfate nucleation. Nevertheless, the conditions used in Xiao's study were very high in barium concentration while this present work investigated the precipitation of barium sulfate over the conditions found in the fields and in the presence of scale inhibitors including ATMP, DTPMP, and PPCA.