CHAPTER II
BACKGROUND AND LITERATURE REVIEW

Backgrounds on the topic of scale inhibition squeeze treatment and scale inhibition are provided in this chapter as efforts to familiarize readers with the important issues related to this thesis topic.
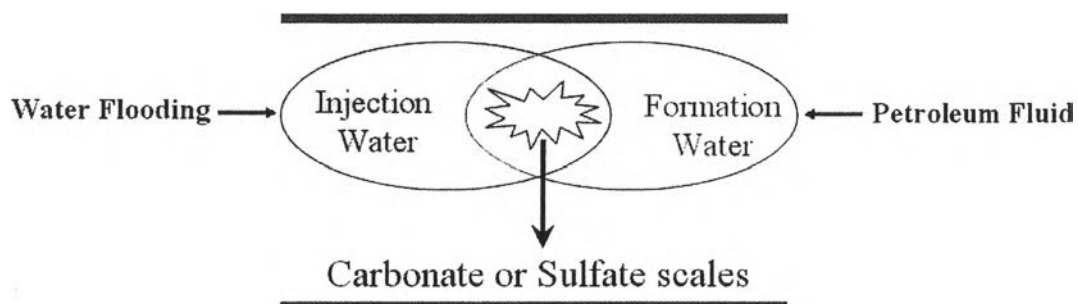
2.1 Scale Formation

Scale is the precipitation of undesirable solids composing of several salts such as calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, and sodium chloride (Allen and Robert, 1989). The scale is a serious problem which occurs in the oil/gas production systems and commonly deposits in near-wellbore matrix, injector well, production tubing and surface equipment (Crabtree, 1999). Scale formation in a production system occurs as a result of one of two mechanisms: (1) Mixing of two incompatible brines in the near wellbore formation; or (2) the sudden changes in produced fluid conditions such as pH, temperature or pressure. In each mechanism, the produced fluid becomes supersaturated, resulting in scale crystallization (Yoder, 1985).

The first mechanism is common in secondary recovery processes involving high salinity seawater mixing with formation water while the second mechanism often occurs in highly concentrated calcium waters. Formation waters are brines contained in the sedimentary porous rock in the oil wells. Main constituents of the formation water are cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), barium (Ba^{2+}), strontium (Sr^{2+}), and potassium (K^+) and anions such as chloride (Cl^-), carbonate (HCO_3^{2-}) and sulfate (SO_4^{2-}) that can bring about the scaling problem in any oilfield (Browning and Fogler, 1995).

Table 2.1 shows the composition of formation water and sea water from various oilfields. Table 2.2 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 (Allen and Robert, 1989).

Figure 2.1 Formation of scale as a result of mixing between injection water (sea water) and formation water.

For the second mechanism, scale occurs because of changes in the ionic composition, pH, pressure and temperature. A decrease in pressure and/or increase in temperature of brine reduce the solubility of dissolved solid causing the precipitation of carbonate scales such as $CaCO_3$. Sulfate scale forms when two incompatible brines are mixed. Commonly, formation water rich in cations such as barium, calcium and/or strontium mixes with sulfate-rich seawater leading to the precipitation of barium sulfate scale. Brine evaporation results in salt concentrations greater than the solubility limit and leads to salt precipitation for example the precipitation of NaCl. The barium sulfate is the least soluble, the hardest and the most difficult to remove of the oilfield scales. Therefore, barium sulfate precipitate is considered the most difficult to prevent (Mackay and Jordan, 2004).

Table 2.1 Composition of formation water and seawater from various oilfields (Frostman, 2002).

Properties/Source of Water	Formation Water Composition										Seawater Composition			Unit
	Rocky Mountian Fresh Water	Mid Western Salt Water	Permian and Mid Western (Low Ca)	Mid Continental Permain Rocky Mountain (High Ca)	Brent NW	Ninial Field, North Sea	Smith Well, Odem Field	"M", North Sea	""ST", North Sea	Statfjord Field	Ninial Field, North Sea	"M" & "ST" North Sea	Statfjord Field	
pH	8	7	7	6.5	NA	NA	NA	NA	NA	NA	NA	NA	NA	pH
HCO_3^-	1000	300	300	100	1255	1430	1170	496	2140	1100	142	124	150	ppm
SO_4^{2-}	50	2500	2500	800	1.4	14	14	11	5	NA	2712	2960	2800	ppm
Cl^-	5600	24200	81000	123000	17340	12660	30000	52360	68000	14.3	19354	19766	20310	ppm
Na^+	4000	13000	50000	60000	10875	8511	19100	29370	41900	8640	10500	10890	11150	ppm
Mg^{2+}	6	500	2600		24	25	146	504	102	70	1350	1368	1410	ppm
Ca^{2+}	32	2500	2500	13000	215	151	480	2809	779	300	400	428	435	ppm
Sr^{2+}	0.8	62	62	325	53	44	NA	574	269	50	8.1	8	7	ppm
Ba^{2+}	0	0.1	0.1	1	135	20	19	252	2180	60	0.03	NA	NA	ppm
K^+	NA	NA	NA	NA	258	160	NA	372	1700	190	380	460	420	ppm
HCO_3^-	16.4	4.9	4.9	1.6	20.6	23.4	19.2	8.1	35.1	18	2.3	2	2.5	mM
SO_4^{2-}	0.52	26	26	8.3	0.01	0.15	0.15	0.11	0.05	NA	28.3	30.8	29.2	mM
Cl^-	157.7	681.7	2281.7	3464.8	488.5	356.6	845.1	1474.9	1915.5	0.4	545.2	556.8	572.1	mM
Na^+	174.7	567.7	2183.4	2620.1	474.9	371.7	834.1	1282.5	1829.7	377.3	458.5	475.5	486.9	mM
Mg^{2+}	0.25	20.6	107		0.99	1.03	6.01	20.7	4.2	2.9	55.5	56.3	58	mM
Ca^{2+}	0.8	62.3	62.3	324.2	5.4	3.8	12	70	19.4	7.5	10	10.7	10.8	mM
Sr^{2+}	0.01	0.71	0.71	3.7	0.6	0.5	NA	6.6	3.1	0.57	0.09	0.09	0.08	mM
Ba^{2+}	0	0	0	0.01	0.98	0.15	0.14	1.8	15.9	0.44	0	NA	NA	mM
K^+	NA	NA	NA	NA	6.6	4.1	NA	9.5	43.5	4.9	9.7	11.8	10.7	mM
Ionic S.	243.1	866.1	2646.8	3722.3	593.5	482.9	962.4	1618.6	2137.4	295.2	704.9	726.9	742.1	mM

Table 2.2 Analysis of field brine and scale (Allen and Robert, 1989).

Chemical	Analysis of brines		Analysis of scale	
	mg/l			
	Bartlesville	Arbuckle	Scale type	Percent
Na^+	52,000	58,400	-	-
Ca^{2+}	10,700	13,900	$CaCO_3$	0.65
Mg^{2+}	1,807	2,182	$MgCO_3$	8.12
Ba^{2+}	250	nil	$BaSO_4$	80.10
SO_4^{2-}	nil	194		
Cl^-	104,750	120,750	-	-
HCO_3^-	44	50		
			$SrCO_3$	4.45
			$SrSO_4$	3.60
			SiO_2	0.11
			Fe_2O_3	0.22
			Water soluble	
			Salts	0.87
			Oil	1.02
			Moisture	0.46
			Total	99.60 %

2.2 Scale Treatments

Scale treatment is usually classified by methods of treatment into two categories, namely mechanical and chemical methods (Allen and Robert, 1989).

2.2.1 Mechanical Methods

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.

However, the disadvantage of this method is to face with an effluent disposal problem.

2.2.2 Chemical Methods

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 (Allen and Robert, 1989):

a.) Water-soluble scales

The most common water-soluble scale is sodium scale (NaCl) which can be dissolved with water.

b.) Acid-soluble scales

Hydrochloric acid (HCl) or acetic acid can be used to effectively remove calcium carbonate ($CaCO_3$). 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. Acid soluble scales also include iron carbonate ($FeCO_3$), iron sulfide (FeS), and iron oxide (Fe_2O_3). 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.

c.) Acid-insoluble scales

The only acid-insoluble scale which is chemically reactive is calcium sulfate or gypsum ($CaSO_4.2H_2O$). Calcium sulfate 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 ($Ca(OH)_2$). Calcium carbonate or calcium hydroxide can then be removed by either hydrochloric acid or acetic acid.

d.) Chemically inert scales

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.

2.3 Scale Inhibition

Scale inhibitors are widely used to control the scaling problem in many oilfields. The most important property of scale inhibitors is the ability to prevent or to slow the nucleation and growth of the scale at very small concentrations in the range of a few ppm. There is believed to be a minimum (threshold) concentration of the scale inhibitors. The release of threshold scale inhibitors in very low concentrations, therefore, can reduce the tendency for crystallization or completely prevent scale formation and growth by two pathways (Graham *et al.*, 2003):

a.) Nucleation inhibition

Disruption of thermodynamic stability of growing nucleons for homogeneous crystallization by endothermic adsorption of inhibitor species, causing dissolution of nucleated scale.

b.) 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.

2.4 Scale Inhibitors

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 Phosphinocarboxylic acid (PPCA). In general oil field applications, phosphonate and polymeric scale inhibitors are usually applied in low

solution pH 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; Xiao *et al.*, 2001).

## 2.5 Introduction of Scale Inhibitors into the Oil Reservoirs

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

2.5.1 Continuous Injection

Scale inhibitors are continuously injected with water flooding typically secondary oil recovery and 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 2.2. 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 alkaline cations contained in the formation water such as calcium and magnesium to form water soluble cations-inhibitor precipitate (Yuan *et al.*, 1993). Alternatively, the calcium could be injected with the scale inhibitor and subsequently precipitate in the formation.
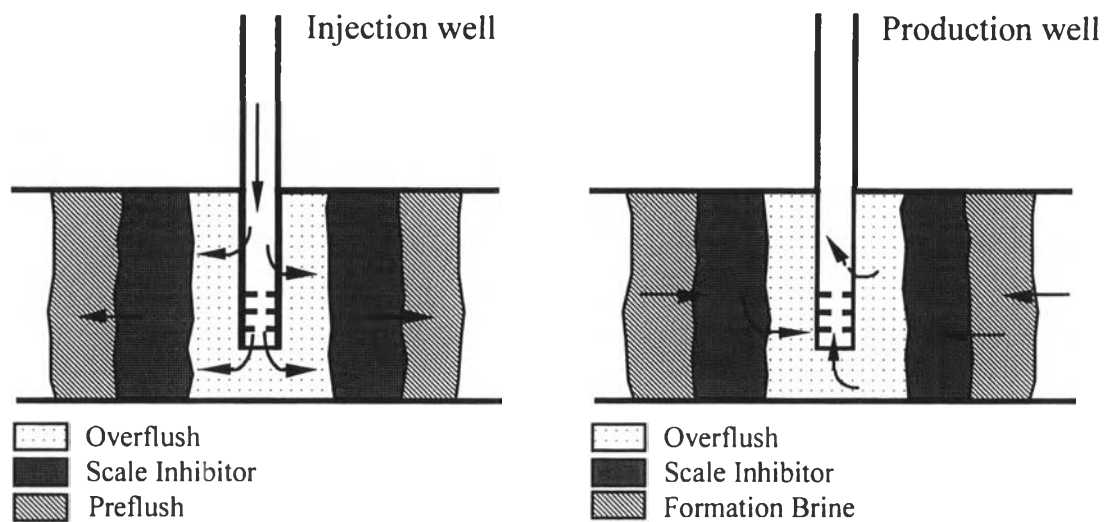
Figure 2.2 Procedure of squeeze treatment technique.

The procedure of squeeze treatment can be briefly explained as follows (Yuan *et al.*, 1993; Browning, 1996):

i.Preflush injection: 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.

ii.Scale inhibitor injection: A solution of the threshold scale inhibitor dissolved in filtrated seawater and having very low concentration in the ppm level is injected into the formation.

iii.Overflush injection: A suitable amount of brine overflush is subsequently injected to force the scale inhibitor to move to a desired position.

iv.Shut-in period: 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 (Yuan *et al.*, 1993):

-The inhibitor is adsorbed onto the surface of the reservoir rock.

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

-The inhibitor is entrapped in small fractures in the formation.

v.Back production: After shut-in period, the normal production is resumed. The scale inhibitor is slowly released back into the produced fluid through the production well at proper concentration, which can inhibit or slow the scale formation. Hence, it has high capability of achieving the scale treatment.

2.6 Squeeze Lifetime

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, 1996).

Ideal elution curve   Actual elution curve
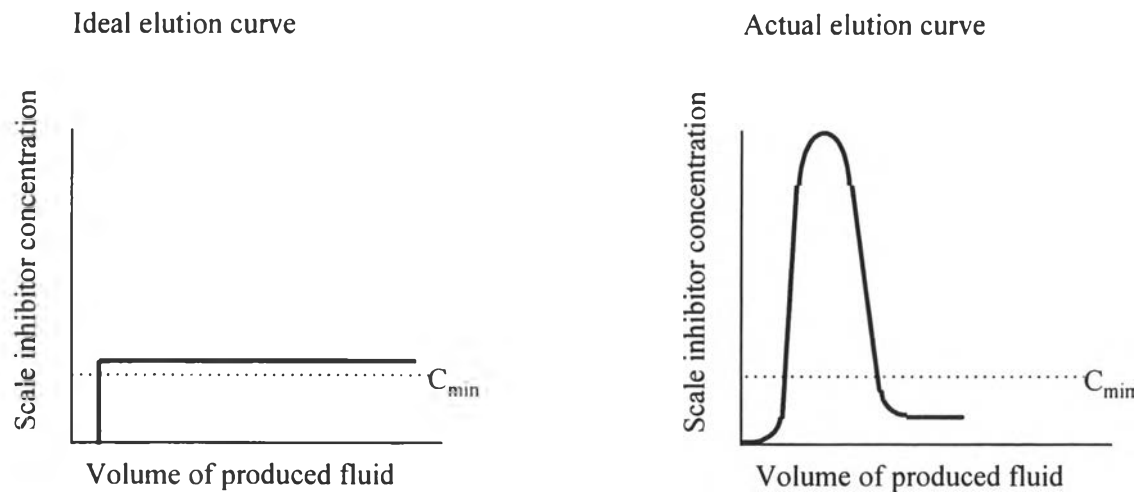
Figure 2.3 Comparison between an ideal and a typical elution curves (Browning, 1996).

2.7 Literature Reviews

Yuan *et al.* (1993) used the data from several wells in the North Sea fields to develop a complex simulation of squeeze treatment. This simulation was applied to both homogeneous and heterogeneous systems where there was free crossflow between strata. Their results showed that the placement method for an inhibitor slug injection should also be considered, and that selecting appropriate volumes of preflush and overflush fluids were important to create the correct thermal conditions in precipitation squeeze treatments.

Browing and Fogler (1995) studied the precipitation/dissolution mechanism and properties of Ca-HEDP (Calcium ion with 1-Hydroxylidene-1, 1-diphosphonic acid) precipitates in porous media. The results elucidated the fact that the Ca to HEDP molar ratio in the precipitates affects the solubility limit and precipitate morphologies. Their micromodel experimental results showed that the 1:1 Ca-HEDP precipitates formed in porous media were consisted of long fibrous spindles preferentially situated in pore throats resulting in a long tailing region of the elution curve. In addition, it was found that the lifetime of precipitation squeeze treatments were at a minimum, five times longer than that of adsorption squeeze treatments.

Browing (1996) were investigated the factors affecting the properties of Ca-HEDP precipitates. It was found that the degree of supersaturation had little effect on the precipitate properties, while the coupled effects of pH and the calcium to HEDP molar ratio in solution had a significant effect on the properties of the precipitates. The resulting precipitates having calcium to 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 dissolved at a slower rate than 1:1 Ca-HEDP precipitates.

Rerkpattanapipat *et al.* (1997) studied the precipitation and dissolution of the phosphonate scale inhibitor (ATMP) in porous media. It was found that three distinct precipitates were observed, these precipitated had Ca/ATMP molar ratios of 1:1, 2:1 and 3:1. The two most significant parameters affecting the type of precipitate were solution pH and Ca/ATMP molar ratio in the precipitating solution. The results from dissolution studies revealed that 3:1 Ca-ATMP precipitate provided the longest tail of the elution curves, which in turn offers the longest squeeze lifetime.

Suwannamek (1998) used DTPMP as a scale inhibitor, which contains five active phosphate groups. The results showed that the Ca to DTPMP molar ratio in the precipitates increased with increasing solution pH. Furthermore, an increase in the temperature also resulted in an increasing the molar ratio of Ca to DTPMP in the precipitates. In addition, a comparison of 2:1 calcium-inhibitor studies showed that the order of squeeze lifetime was that ATMP had the longest lifetime and that the lifetimes were in the order of HEDP< DTPMP< ATMP.

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 found to correlate to those solution conditions. The experimental results revealed that only the deprotonated fraction and metal-complexed fraction of PPCA are effective to inhibit barium sulfate nucleation, while the protonated fraction has low capability of

preventing barium sulfate nucleation. Nevertheless, this precipitation study of particle involved the effect of agitation on precipitation.

2.8 References

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