CHAPTER II

LITERATURE SURVEY

2.1 Scale

Most oil and gas fields produce 10 to 20 barrels of brine for every barrel of oil (or gas equivalent). These brines are generally corrosive and produce calcite or sulfate scale (Tomson et al., 1994). This scale is commonly deposited in the formation of matrix and fractures, wellbore, downhole pumps, tubing, casing, flowlines, heater treaters, tanks and salt water disposal and waterflood system. Scale deposits usually form as a result of crystallization and precipitation of minerals from water (Allen and Roberts, 1989).

The undesirable solids come from frequently pressure drops, temperature change, mixing of incompatible formation and injected brines. Scale usually blocks the oil and gas production by plugging the formation matrix, wellbore or production equipment. It has been found that scales are commonly composed of calcium carbonate ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), barium sulfate ($BaSO_4$) and sodium chloride ($NaCl$) (see Table 2.1) (Allen and Roberts, 1989). The sources of calcium ions are mainly from three places: 1) the formation water, 2) a brine over flush, or 3) calcium as a result of reservoir acidization (Browning and Fogler, 1993).

From the reaction of alkali with the carbonate or sulfate minerals of the rock, i.e. dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$) and magnesite ($MgCO_3$) through an exchange type reactions that can cause scale. The product becomes supersaturated with co-reacting species, resulting in scale crystallization.

Table 2.1   Analysis of brine and scale, Hobbs oil field, New Mexico (Allen and Roberts, 1989)

Analysis of brine	Scale after extraction of water and oil		
Chemical	mg/l	Type of scale	Percentage
Chloride, Cl^-	4,755	-	-
Sulfate, SO_4^{2-}	54	$CaSO_4$	1.8
Alkality, HCO_3^-	2,335	-	-
Calcium, Ca^{2+}	476	$CaCO_3$	95.5
Magnesium, Mg^+	291	-	-
Sodium, Na^+	2,150	-	-
Sulfide, S^{2-}	345	FeS_2	0.9
		Total	100

Although the solubilities of carbonate minerals could be lower than those of corresponding silicates or hydroxides, a continuous supply of fresh alkaline solution may be expected to result in a continuous release of carbonate ion from rock minerals into the solution (Baviere, 1991).

Another factor of scale formation is the change in fluid conditions such as pH and temperature. Because the solubilities of divalent salts and hydroxides varies considerably with pH, so pH value of the system is important. It can define the composition and the amount of precipitates. Moreover, from the solution acidity, it indicates the possible damage in the injection and production wells. When temperature is varied, scale formation occurred in different structure generates the solubility of scales.

2.2   Scale inhibitors

There are many types of chemicals available for scale prevention. These can be divided into 2 groups of chelating agents and threshold inhibitors. Chelating agents reduce the amount of available reacting species (Martell, 1992). Threshold inhibitors interact with the nucleated salt crystals and block the potential growth sites, resulting in completely preventing the growth of scale crystals (Gill, et al., 1995). The injection of threshold scale inhibitors in very low concentrations can slow down or completely prevent scale growth. The threshold scale inhibitors are usually classified into three groups: 1) phosphonates, 2) phosphoric acid ester, and 3) polymers, such as polyacrylic acid (Vetter, 1972). Phosphonates, for example, would be used to reduce the concentration of scale forming components in the formation fluids by either precipitating metal cations, or by reducing the rates of mineral dissolution in the formation from a crystal armoring mechanism (Jonasson, 1992).

Several organic phosphates are now available to inhibit the formation of calcium carbonate , calcium sulfate and barium sulfate. Many of these water-soluble liquid organic phosphates are suitable for squeeze treatments (Allen and Roberts, 1989). In field applications, phosphonate scale inhibitors are often applied in low pH solution whereas the reservoir may have a pH in the range of approximately 4 to 7 (Sorbie, et al., 1993).

Phosphonates and polymer - based inhibitors are the most useful inhibitors in the field because they can inhibit scale under varying conditions in different reservoirs. Also phosphonates can inhibit many different types of scale and it is easy to determine when a well has to be resqueezed. There are many chemicals in these types of inhibitors such as Aminotri (methylene phosphonic acid, ATMP), 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP), Ethylenediaminetetra (methylene phosphonic acid, EDTMP),

Hexamethylenediaminetetra (methylene phosphonic acid, HMDTMP) and Diethylenetriaminepenta (methylene phosphonic acid, DTPMPA).

At Prudhoe bay field, wells had monthly declining rates greater than 10% caused by the deposition of calcium carbonate ($CaCO_3$) scale in the perforation tunnels and the near wellbore formation sandstone. Five phosphonate inhibitors were studied, the results showed that DTPMPA was the best inhibitor to solve the problem of the Phudhoe field.

When temperatures in the reservoir are sufficiently high (exceeding 130°C), thermal degradation of the inhibitor will occur and result in a short squeeze life time (Jordan, et al., 1996). Usually, for use in a squeeze treatment, an inhibitor must :1) inhibit scale formation at a relative low concentration; 2) be stable at reservoir conditions; 3) be retained in the reservoir in sufficient quantity to provide a reasonable treatment life; 4) efficiently feed back into the produced brine at a concentration sufficient to inhibit scale and 5) be measurable quantitatively at low concentrations (Meyers, et al., 1985).

2.3 Squeeze treatment

Squeeze treatment is the most widely used method to prevent scaling problem in production systems. The threshold inhibitor is injected into the system near the wellbore formation where the inhibitor can be retained during the shut-in period. After a well is treated by injecting a phosphonate solution into the formation, the phosphonate ion concentration in the produced brine drops exponentially over the time (Kan, et al., 1994). Usually inhibitor levels off to low concentration of a few mg/L or less and remains at this concentration for million of brine production. The release of inhibitor is important to govern the squeeze lifetime. Many researchers divide the release

mechanism of inhibitors in a porous media into three parts, namely 1) adsorbed onto the surface of the porous media and desorbed back into produced fluids during production; 2) precipitate with available cations in the formation, the resulting precipitate dissolving back into the procuced fluid when production is resumed; and 3) entrapped in small fractures where inhibitors can slowly be released back into the production fluid.

Based on the precipitation/dissolution mechanism, the scale inhibitor reacts with cations and that leads to the formation of inhibitor precipitation. Cations can come from the formation water, brine overflush or dissolving from minerals in the formation. The main inhibitor retention mechanism within the porous medium is thought to be due to the formation of an insoluble inhibitor complex which may be in the form of an actual solid or gel-like immiscible liquid phase (Malandrino, et al., 1995). The precipitation squeeze processes are often accompanied by some degree of additional or enhanced adsorption of inhibitor molecules onto the rock surface (Yuan, et al., 1993). These precipitates can be in porous rock and the inhibitor is released to produced fluid during the production process.

For the aminotri(methylenephosphonic acid) (ATMP), two parameters that affected the molar composition of precipitates were the precipitating solution's pH and calcium/ATMP molar ratio. The 3:1 calcium/ATMP precipitate seems to be most ideally suited for actual squeeze treatments because it gives the longest squeeze lifetime (Rerkpattanapipat, 1996). In addition, the squeeze lifetime can be enhanced by adding extra calcium ion in to the elution fluid (Wattana, 1997).