

Study of Scale Formation in Oil Reservoir During Water Injection-A review

Amer Badr Bin Merdhah, *Universiti Teknologi Malaysia*
amer0227@yahoo.com

Abu Azam Mohd Yassin, *Universiti Teknologi Malaysia*
abuazam@fkkksa.utm.my

Scale deposition is one of the most important and serious problems which water injection systems are generally engaged in. Scale sometimes limits or blocks oil and gas production by plugging the oil-producing formation matrix or fractures and perforated intervals. Scale also deposited in down-hole pumps, tubing, casing flow-lines, heater treaters, tanks and other production equipment and facilities. Scale can occur at /or downstream of any point in the production system, at which super-saturation is generated. Super-saturation can be generated in single water by changing the pressure and temperature conditions or by mixing two incompatible waters. The most common oilfield scales deposited are calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate. This paper describes overview formation damage, scale deposition mechanisms and source of oil field scale, scale formation along the injection-water path in water-flood operations, scaling problems encountered in oil fields, solubility of scale, oilfield Scale types, scale control chemicals and laboratory investigations of scale in different media and procedures used to predict scale are presented.

Keywords: formation damage, scale deposition mechanisms, scaling problems, solubility of scale

1. Introduction

The injection of seawater into oilfield reservoirs to maintain reservoir pressure and improve secondary recovery is a well-established, mature, operation. Moreover, the degree of risk posed by deposition of mineral scales to the injection and production wells during such operations has been much studied. Scale deposition is one of the most serious oil field problems that inflict water injection systems primarily when two incompatible waters are involved. Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. Typical examples are sea water, with high concentration of SO_4^{2-} and formation waters, with high concentrations of Ca^{+2} , Ba^{+2} and Sr^{+2} . Mixing of these waters, therefore, could cause precipitation of CaSO_4 , BaSO_4 and/or SrSO_4 . There are other reasons why scale forms, and the amount and location of which are influenced by several factors. Yet, super-saturation is the most important reason behind mineral precipitation. A supersaturated is the primary cause of scale formation and occurs when a solution contains dissolved materials which are at higher concentrations than their equilibrium concentration. The degree of super-saturation, also known as the scaling index, is the driving force for the precipitation reaction and a high super-saturation, therefore, implies high possibilities for salt precipitation. Changes in temperature, pressure, pH, and $\text{CO}_2/\text{H}_2\text{S}$ partial pressure could also contribute in forming a scale (Mackay *et al*, 2003, Moghadasi *et al*, 2003a).

1.1 Common Oil Field Scales

The most common oil field scales are listed in Table 1, along with the primary variables that affect their solubility (Moghadasi *et al*, 2003a). These scales are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and Strontium sulfate (celestite) and calcium carbonate. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate. Lead and zinc sulfide scale has recently become a concern in a number of North Sea oil and gas fields (Collins and Jordan, 2001).

1.2 Scale Deposition

Scale deposition in surface and subsurface oil and gas production equipment has been recognized. Scale deposition is one of the most important and serious problems that inflict oil field water injection systems. Scale limits and sometimes blocks oil and gas production by plugging the oil-producing formation matrix or fractures and perforated intervals. It can also plug production lines and equipment and impair fluid flow. The consequence could be production-equipment failure, emergency shutdown, increased maintenance cost, and overall decrease in production efficiency. The failure of these equipments could result in safety dangers. In case of water injection systems, scale could plug the pores of the formation and results in injectivity decline with time (Todd and Yuan, 1992; Bayona, 1993; Asghari and Kharrat, 1995; Andersen *et al*, 2000; Paulo *et al*, 2001; Voloshin *et al*, 2003).

Scale deposition can occur from one type of water because of super-saturation with scale-forming salts attributable to changes in the physical conditions under which the water exists. Scale also can deposit when two incompatible waters are mixed and super-saturation is reached (Nassivera and Essel, 1979; Read and Ringen, 1982; Vetter, *et al.*, 1982; Todd and Yuan, 1992; Moghadasi *et al.*, 2003b; Moghadasi *et al.*, 2004).

Table 1: Most common oilfield scales

Name	Chemical Formula	Primary Variables
Calcium Carbonate	CaCO_3	Partial pressure of CO_2 , temperature, total dissolved salts, pH
Calcium Sulfate: Gypsum Hemihydrate Anhydrite	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ CaSO_4	Temperature, total dissolved salts, pressure
Barium Sulfate	BaSO_4	Temperature, pressure
Strontium Sulfate	SrSO_4	Temperature, pressure, total dissolved salts
Iron Compounds: Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferrous Hydroxide	FeCO_3 FeS $\text{Fe}(\text{OH})_2$ $\text{Fe}(\text{OH})_3$	Corrosion, dissolved gases, pH

1.3 Source of Oil Field Scale

The chief source of oil field scale is mixing of incompatible waters. Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. A typical example of incompatible waters are sea water with high concentration of SO_4^{2-} and low concentrations of Ca^{+2} , $\text{Ba}^{+2}/\text{Sr}^{+2}$, and formation waters with very low concentrations of SO_4^{2-} but high concentrations of Ca^{+2} , Ba^{+2} and Sr^{+2} . Mixing of these waters, therefore, causes precipitation of CaSO_4 , BaSO_4 , and/or SrSO_4 . Field produced water (disposal water) can also be incompatible with seawater. In cases where disposal water is mixed with seawater for re-injection, scale deposition is possible (Bayona, 1993; Andersen *et al.*, 2000; Bedrikovitsky *et al.*, 2001; Stalker *et al.*, 2003; Paulo *et al.*, 2001).

During the production, the water is drained to the surface and suffers from significant pressure drop and temperature variations. The successive pressure drops lead to release of the carbon dioxide with an increase in pH value of the produced water and precipitation of calcium carbonate (Mackay, 2003).

Zinc sulfide scale is more likely that the zinc ion source mixes with the hydrogen sulfide-rich source within the near well-bore or the production tubing during fluid extraction. Lead and zinc sulfide scales have recently become a concern in a number oil and gas fields. These deposits have occurred within the production tubing and topside process facilities (Collins and Jordan, 2003).

2. Scale Formation along the Injection-Water Path in Water-Flood Operations

At the injection wellhead, injection water temperature is usually much lower than reservoir temperature. When it travels down the injection well-string, the water cools the surrounding formations, and its temperature and pressure increase. If the water is saturated at surface conditions with salts whose solubility decreases with increasing temperatures (e.g. anhydrite), scale may form along the well-string.

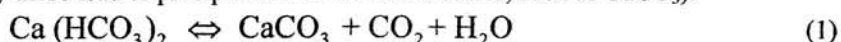
Scale precipitation from the injection water may happen behind the mixing zone as a consequence of temperature and pressure changes. This is particularly true of waters containing salts whose solubility decreases with increasing temperature and decreasing pressure. Forward of the mixing zone only reservoir brine (with oil) is present in the rock pores. Behind the mixing zone, only injected water in equilibrium at local temperature and pressure (with residual oil)

exists. In the mixing zone, precipitation of insoluble salts may occur due to the interaction, at local temperature and pressure, of chemical species contained in the injection water with chemical species present in the reservoir brine.

Nevertheless, at a different pressure, the remaining clear water moves ahead mix again with reservoir brine and scale precipitation may again take place. This cycle is repeated until the remaining clear water reaches a production well. Pressure and temperature decrease along the flow string up to the surface in the production well, and further changes in thermodynamic conditions occur in the surface equipment. This may again result in scale formation. Normally, these scales do the most damage in the well-bore when there are major falls in pressure but hardly any temperature changes (Khelil *et al*, 1979).

There are three principal mechanisms by which scales form in both offshore and onshore oil field system (Mackay, 2005; Jordan and Mackay, 2005):

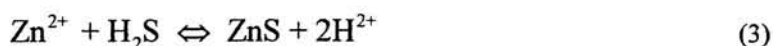
- a) Decrease in pressure and/or increase in temperature of a brine, goes to a reduction in the solubility of the salt (most commonly these lead to precipitation of carbonate scales, such as CaCO_3).



- b) Mixing of two incompatible brines (most commonly formation water rich in cations such as barium, calcium and/or strontium, mixing with sulfate rich seawater, goes to the precipitation of sulfate scales, such as BaSO_4).



Other fluid incompatibilities include sulfide scale where hydrogen sulfide gas mixes with iron, zinc or lead rich formation waters:



- c) brine evaporation, resulting in salt concentration increasing above the solubility limit and goes to salt precipitation (as may occur in HP/HT gas wells where a dry gas stream may mix with a low rate brine stream resulting in dehydration and most commonly the precipitation of NaCl).

3. The Scaling Problem in Oil Fields

Scaling deposition is one of the most important and serious problems which water injection systems are generally engaged in. Oil field scales costs are high due to intense oil and gas production decline, frequently pulling of down-hole equipment for replacement, re-perforation of the producing intervals, re-drilling of plugged oil wells, stimulation of plugged oil-bearing formations, and other remedial workovers through production and injection wells. As scale deposits around the well-bore, the porous media of formation becomes plugged and may be rendered impermeable to any fluids.

Many case histories of oil well scaling by calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate have been reported (Mitchell *et al*, 1980; Lindlof and Stoffer, 1983; Vetter *et al*, 1987; Shuler *et al*, 1991). Problems in connection to oil well scaling in the Russia where scale has seriously plugged wells and are similar to cases in North Sea fields have been reported (Mitcheli *et al*, 1980).

Oilfields scale problems have occurred because of water flooding in Saudi oil fields, Algeria, Indonesia in south Sumatra oilfields, and Egypt in el-Morgan oilfield where calcium and strontium sulfate scales have been found in surface and subsurface production equipment(El-Hattab,1982). The following is a brief explain of scaling cases reported in the literature.

Mitchell *et al*. (1980) described scale problems occurring in the forties field could be attributed two major factors:

- a) Commingling of forties formation and injection waters could precipitate both barium and strontium sulfates.
- b) Precipitation of calcium carbonate scale from formation water due to variations in pressure and temperature in production systems.

Todd and Yuan (1992) described barium sulfate scale occurrence was a severe production problem in North Sea oil operations. Barium sulfate is often accompanied by strontium sulfate to form a completely mixed scale called (Ba, Sr) SO_4 solid solution. Sulfate-anion-rich seawater injected into the reservoir formation subsequently mixed with formation water, which contains excessive barium and strontium.

Bayona (1993) reported two major problems with seawater injection in the north Uthmaniyah section of the Ghawar field in Saudi Arabia. The first is maintenance of acceptable water quality to prevent excessive losses of well injectivity and the second is control of plugging in the pores and corrosion at a reasonable level in the equipment due to which excessive losses of well injectivity occur. The only cause of these losses is the deposition of scales due to the presence of salts in the injection water.

Salman *et al.* (1999) conducted to predict the possibility of scale formation when seawater was injected into the northern Kuwaiti oilfields for reservoir pressure maintenance. Results indicated that the seawater was likely to be self-scaling with respect to calcium carbonate under production reservoir conditions could become a problem when the system underwent temperature and pressure changes.

Paulo *et al.* (2001) described Sulfate scale deposition is a common problem in the Alba field in the North Sea resulted from injected seawater mixing with aquifer brines. The problem is most severe in and around the injection and production well bores and can cause considerable disruption to hydrocarbon production after water breakthrough.

Moghadasi *et al.* (2003a) described scale formation in the Iranian oilfields has been recognized to be a major operational problem causing formation damage either at injection or producing wells. Scale contributes to equipment wear and corrosion and flow restrictions, thus resulting in a decrease in oil and gas production.

4. Solubility of Scales

"Solubility" is defined as the limiting amount of solute that can dissolve in a solvent under a given set of physical conditions. Factors that affect scale precipitation, deposition and crystal growth can be summarized as: supersaturation, temperature, pressure, ionic strength, evaporation, contact time and pH. Effective scale control should be one of the primary objectives of any efficient water injection and normal production operation in oil and gas fields. There are two solubilities of scales:

4.1 Calcium, Strontium, Barium Sulfates and Calcium Carbonate Solubilities

The solubility of calcium sulfate is an order of magnitude larger than that of strontium sulfate, with in turn is about one and one-half orders of magnitude larger than that of barium sulfate Figure 1. For example, Figure 1 indicates, that the solubility of strontium sulfate can be larger than 950 mg/l. This solubility, however, is true only when the solution is stoichiometrically balanced- i.e., when the number of strontium ions equals the number of sulfate ions. If an excess of either ion is introduced, the solubility is depressed markedly. This is known as the "common ion effect" (Lindlof and Stoffer 1983). The solubility reaches a maximum in highly concentrated brines.

According to Oddo *et al.* (1991), calcium carbonate solubility has an inverse relationship with temperature or stated more simply, CaCO_3 scale becomes more insoluble with increasing temperature and a solution at equilibrium with CaCO_3 will precipitate the solid as the temperature is increased. The tendency to form CaCO_3 also increases with increasing pH (as the solution becomes less acid). The decrease in total pressure around the pumps allows dissolved carbon dioxide to escape from solution as a gas causing an increase in pH with a subsequent increase in the tendency to form solid.

4.2 Zinc Sulfide, Lead Sulfide and Iron Sulfide Solubilities

Lead and zinc sulfide solubility is much lower even than iron sulfide, which is the common sulfide in oil field environments. For example in a 1M (mole/dm³) NaCl brine solution are presented in Figure 2 at pH = 5 the solubility of iron sulfide is 65 ppm, whereas lead and zinc sulfides are 0.002 ppm and 0.063 ppm respectively. Depending on the exact brine conditions, the solubility of zinc sulfide is between 30 and 100 times more soluble than lead sulfide. As with iron sulfide, the solubility of both lead and zinc sulfide increases with increasing solution pH (Collins and Jordan, 2001).

5. Scale Control Chemicals

In oil and gas well operations, water-insoluble scale is formed in tubing, casings, and associated equipment, as well as in the well bore and the formation itself, which carry, at least in part, water or brine waters. These waters can contain insoluble calcium, barium, strontium, magnesium, and iron salts.

Scale inhibitors are chemicals which delay, reduce or prevent scale formation when added in small amounts to normally scaling water. According to Bezemer and Bauer (1969), the most common classes of inhibitor chemicals are inorganic phosphates, organophosphorous compounds and organic polymers.

Polyphosphonocarboxylic acid (PPCA) and Diethylenetriaminepenta (methylenephosphonic acid) (DETPMP) are two common commercial scale inhibitors used in the oil and gas industry. Normally, PPCA is regarded as nucleation inhibitor and DETPMP as a growth inhibitor (Chen *et al.*, 2004).

Several combined scale removal and inhibition systems could be considered in order to meet these challenges. Hydrochloric acid (HCl) may be the most cost effective treatment to remove calcium carbonate, but corrosion control, system compatibility and inhibitor adsorption may all be difficult in a combined treatment. Conversely, scale dissolvers may offer better corrosion control and scale inhibitor compatibility when spent, but will be higher cost. Organic acids could offer a compromise which allows most of the system requirements to be met.

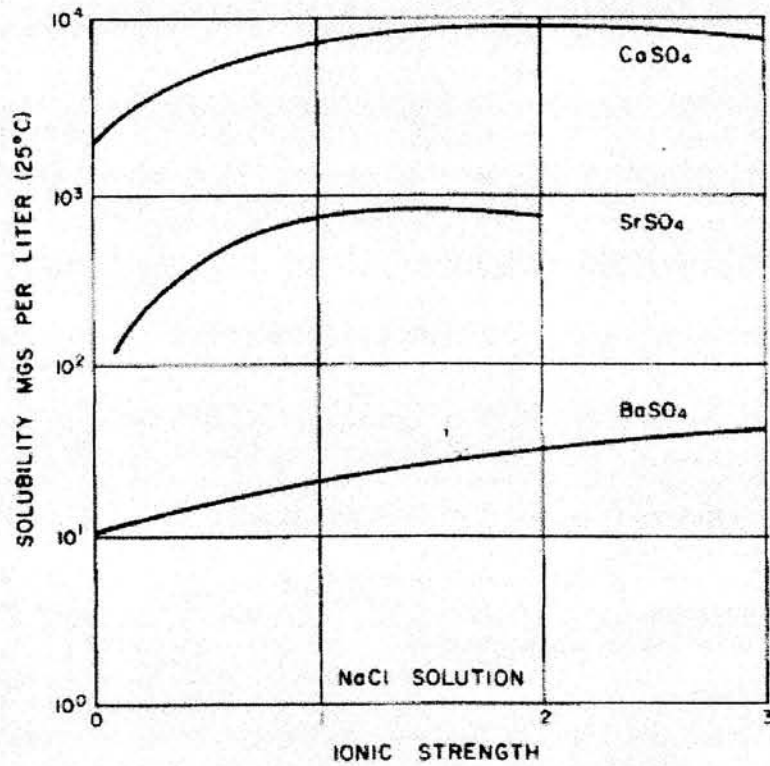


Figure 1: Relative solubilities of three sulfates in brine

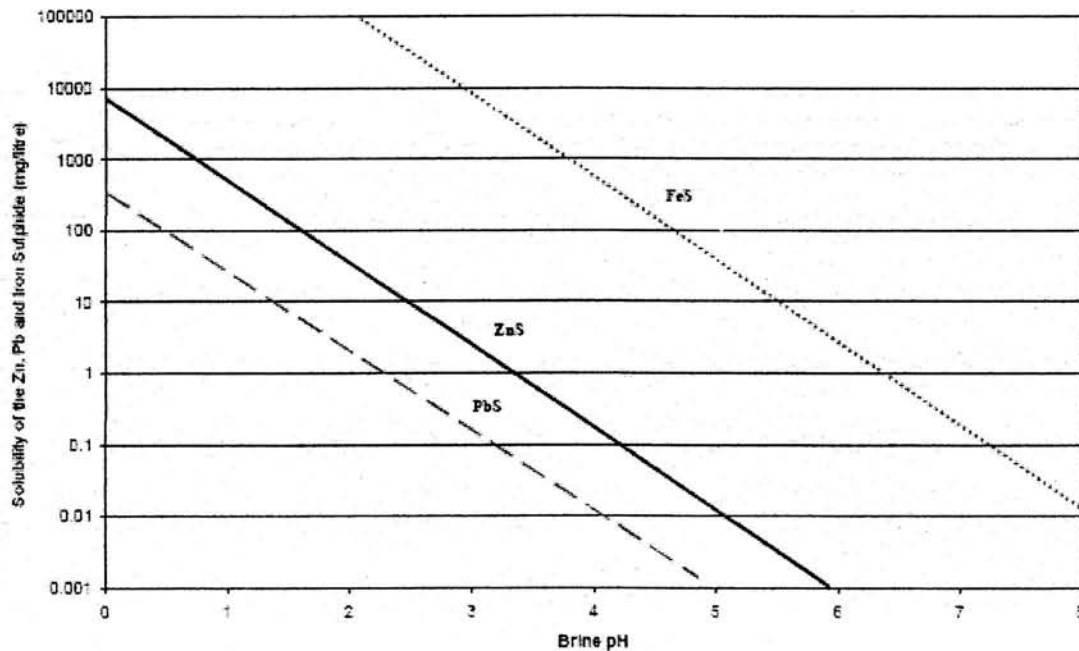


Figure 2: Comparison of zinc, lead and iron sulfide solubility in 1M NaCl brine at 25°C.

6. Laboratory Evaluation

Scale formation can be predicted by laboratory experiments. Several experimental studies have been conducted to determine the scaling potential in different oil-fields. In experimental studies, the extent of permeability damage

caused by flowing precipitates in cores and sand packs was investigated. Several investigators tested incompatible waters from oilfields in the North Sea (Mitchell *et al.*, 1980), the Middle East and El-Margon (El-Hattab, 1982) that produced barium, calcium and strontium precipitates. They reported that 15–20- μm -sized crystals blocked the pore throats in glass bead packs and in alumina cores, by size exclusion and bridging mechanisms. Crystals often grew perpendicular to the pore walls, and that some crystal aggregates also had the form of “books” and rosettes. Todd and Yuan (1992) also conducted laboratory investigations using North Sea reservoir brines that produced barium and strontium scales. Crystals depositing along and growing perpendicular to the pore surfaces caused most of the reduction in core permeability. They observed that doubling the super-saturation ratio of both barium and strontium produced an increase in the quantity of scale formed inside the pores and a change in the morphology of the crystals. Both changes increase the rate of permeability decline.

7. Modeling Development

Along with laboratory experiments, scale formation can be predicted by several models to determine the scaling potential in different oil-fields. Geochemical flow models were developed (Shen and Corsby, 1983; Yeboah *et al.*, 1993; Khatib, 1994) for both mineral dissolution and precipitation processes during convective transport. These models were based on the assumption of local thermodynamic equilibrium and negligible dispersion. They did not include solids migration, an assumption, which was severely limiting because many experimental studies demonstrated that precipitated solids could migrate within the porous matrix.

8. Summary

From the above survey of the literature, permeability decline caused by scale formation in the porous bed ranged from less than 30% to more than 90% of the initial permeability, depending on solution composition, initial permeability, temperature, flow rate and solution injection period. The pattern of permeability decline in a porous medium due to scaling injection was characterized by a steep initial decline which gradually slowed down to a lower. Several factors influencing scale formation had been examined. Increasing temperature, super-saturation and flow rate had a detrimental effect on the permeability reduction. Pressure had a slight effect on scale formation precipitation.

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