

Studies on Scale Deposition in Oil Industries & Their Control

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Abstract

Scale formation is a vital issue in many industries leading to low operational efficiencies and economical losses. A good management strategy must be put in place to prevent the scale formation from building up or having further occurrence. Just as it has been acknowledged over the years that scale prevention is better than waiting until it forms and then taking remedial action. Many diverse expertise that could possibly be deployed by the oilfield operatives to decrease the risk of scale formation, control scale formation and to eliminate it if formed within down hole and topside oil/gas facilities are critically reviewed. With the important development and improvements in chemistry and fluid finish for effective scale inhibitions, oilfield scale can be distant from inside the tubular without risk to the steel tubing. In order to prevent scale in an as environmentally friendly way as possible, a good understanding of the chemical background for scale formation is necessary. There are fundamental differences between different scales that can lead to more scaling if the wrong choices are made. To avoid all extra costs related to scaling is unrealistic. But the costs can be minimized by thoroughly risk analyses and a focus on scale prevention. This paper presents a complete review on scale formations in oil industries and its potential impact during process.

Keywords: Scale deposition; Scale occurrence; Mineral Scales; Scale solubility

I. INTRODUCTION

The main scale deposits of composition samples is made up of organic, inorganic and crystal water [1].

An Accumulation of undesirable deposits on equipment surfaces is a phenomenon that occurs in practically all processes in which untreated water is heated. The deposits commonly met may be categorized into the subsequent five groups: (a) The mineral scales (e.g. CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4 , CaF_2 , SiO_2), (b) The suspended matter (e.g. mud or silt), (c) The corrosion products (i.e., Fe_2O_3 , Fe_3O_4 , ZnO , CuO), (d) The microbiological, and (e) metal-inhibitor salts. The deposition of these materials, especially on heat exchanger surfaces in cooling, boiler, geothermal, and distillation systems, can cause a number of operational problems such as plugging of pipes and pumps, inefficient water treatment chemical usage, increased operation costs, lost production due to system downtime, and ultimately heat exchanger failure. For operating industrial water systems greater water conservation has been a driver at higher cycles of concentrations, thus the growing potential of deposit buildup on heat exchanger surfaces. The Operating industrial water systems under stressed conditions burdens a better considerate of the system (feed and recirculation) water chemistry as well as the growth of new & innovative agents for controlling scale/deposit, corrosion.

A scale deposit may occurs as single mineral phases, but more commonly it is a combination of different elements, which can occur when a solution becomes saturated, mostly due to changes in temperature during the injection operations, changes in pH values or if two different chemicals which will be precipitated are brought together. There are several mineral ions usually dissolved at produced water, these include calcium (Ca^{2+}), barium (Ba^{2+}), strontium (Sr^{2+}) cations and carbonates (CO_3^{2-}), sulfate (SO_4^{2-}) anions [2].

The development of inorganic, sparingly soluble salts from aqueous brines during oil and gas production is known as 'scale' and it is one of the major flow assurance problems. Scale forms and deposits under supersaturated conditions, formation water from the bottom hole and the injected seawater takes place wherever the mixing of the incompatible types of water. The deposited scale adheres on the surfaces of the producing well tubing and also on parts of water handling equipment which accumulates over time and leads to the existence of problems in reservoirs, pumps, valves and topside facilities. Since, the deposition/ adhesion takes place a decrease in the performance of heat transfer equipment such as boilers and heat exchangers occurs, as well as in flow rates. These problematic conditions are found not only in the oil fields but also in the distillation plants. The rapid increase of the mineral deposits leads to inevitable damage of the equipment parts. As a consequence, suspension of oil operations is necessary for recovery or replacement of damaged parts. In the oil field these interruptions are accompanied by extremely high costs.

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 studied. Scale formation in surface and subsurface oil and gas production equipment has

been recognized to be a major operational problem. It has been recognized as a major cause of formation damage either in injection or producing wells. Scale contributes to equipment wear, corrosion and flow restriction resulting in a decrease in oil and gas production. Experience in the oil industry has indicated that many oil wells have suffered from flow restriction because of scale deposition within the oil producing formation matrix and the downhole equipment, generally in primary, secondary and tertiary oil recovery operation as well as scale deposits in the surface production equipment. There are other reasons that scale forms, amount and location are influenced by several factors. And the most important reason behind mineral precipitation is supersaturation.

A supersaturated condition is the primary cause of scale formation. It occurs when a solution contains dissolved materials are at higher concentrations than their equilibrium concentration. The degree of supersaturation, also known as the scaling index, is the driving force for the precipitation reaction. A high supersaturation condition, therefore, implies higher possibilities for salt precipitation. Scale can occur at/or downstream at any point in the production system, where supersaturation is generated. Supersaturation can be produced in single water by changing pressure and temperature conditions or can be produced by mixing two incompatible Waters. Changes in temperature, pressure, pH, and $\text{CO}_2/\text{H}_2\text{S}$ partial pressure could also contribute to scale formation [1].

A. Scale Deposition

In the oilfield, scale can cause many problems. Scale problems exist through all phases of oil and gas production. This can occur from the time fluids begin to enter production well bore until the water is disposed of or injected into a subterranean zone. Scale deposits are detrimental because they restrict flow of liquids and gases through oilfield systems. Oilfield deposits can be classified into two general categories: organic and inorganic. Inorganic deposits are generally associated with water formed scales such as calcium carbonate, calcium sulfate and barium sulfate. Inorganic deposits such as iron sulfide and iron carbonate may be corrosion by products, or they may be the result of scale deposition. Deposits such as clays, sand, shales etc. can be part of the formation rock.

On the other hand, Organic deposits are usually soluble in oil or hydrocarbon based solvents such as xylene, toluene, kerosene, etc. Generally, organic deposits are associated with crude oil, paraffin, asphaltenes and other materials that occur or precipitate from crude oil handling. Deposits such as corrosion inhibitor “gunk” are organic, but may not be soluble in solvents. Some organic deposits such as precipitated scale inhibitor or corrosion inhibitor are not soluble in hydrocarbons, but are classified as organic because of their chemical make-up.

B. Source of Oil Field Scale

The chief source of oilfield scale is a mixture of incompatible waters. Scale deposition can occur from one type of water because of supersaturation 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 supersaturation is reached [3].

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} , $\text{Ba}^{+2}/\text{Sr}^{+2}$. 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 such cases where disposal water is mixed with seawater for re-injection, scale deposition is possible [4]. 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. Zinc sulfide scale is more likely when zinc ion source mixes with the hydrogen sulfide-rich source within the near wellbore or the production tubing during fluid extraction. Lead and zinc sulfide scales have recently become a concern in a number of oil and gas fields. These deposits have occurred within the production tubing and topside process facilities [2].

C. The Scaling Problem in Oil Fields

Scaling deposition is one of the most serious problems where water injection systems are engaged in. Generally, scale deposited in downhole pumps, tubing, casing flow lines, heater treaters, tanks, and other production equipment and facilities. Scale formation is a major problem in the oil industry. It may occur in downhole or in surface facilities. The formations of these scales plug production lines, equipment and impair fluid flow. Their consequence could be production equipment failure, emergency shutdown, increased maintenance cost, and an overall decrease in production efficiency. The failure of production equipment and instruments could be resulted in safety hazards. According to Bertero (1998), one of main problems encountered in water flooding projects is scale formation caused by chemical incompatibility between potential injection waters and reservoir brine [5]. Chemical compatibility evaluation through laboratory experiments on cores at reservoir conditions is of limited value because only first-contact phenomena are reproduced. For a scale layer to be built up, the supersaturated formation water should contact the walls of the production equipment. The tendency for scale to be deposited, therefore, will be low, if the crude has a low water cut and if the water is finely dispersed in the oil. The rate of scale deposition is approximately proportional to the rate of free water production. Depending upon where the formation water becomes supersaturated, scale may be deposited in both flow line and tubing. In some cases, it may be deposited even in the perforations and in the formation near the wellbore.

The formation of inorganic mineral scale within onshore and offshore production facilities around the world is a relatively common problem. Scale can form from a single produced connate or aquifer water due to changes in temperature and pressure, or when two incompatible waters mix. An example of the latter would be seawater support of a reservoir where the formation water is rich in cations (Ba, Sr, and Ca) and the injection water is rich in anions (SO₄). The production of such fluids results in the formation of inorganic scale deposits. Types of scale and their solubility is a function of the water chemistry and physical production environment. Oilfield scales cost high due to intense oil and gas production decline, frequently pulling of downhole 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 wellbore, the porous media of formation becomes plugged and may be rendered impermeable to any fluids.

The production problems are caused by mineral scale in oil production operations have been known. Among the most onerous of all scaling problems is that of sulfate scales, particularly barium sulfate scale. This is a difficult scaling problem because of the low solubility of barium sulfate in most fluids and the commensurate low reactivity of most acids with barium sulfate scale. Deposition of barium sulfate into a continuous scale surface on production tubular exposes very little surface area for treatment by chemicals, and therefore this scale is almost impossible to remove once it is deposited. The most popular approach to address the barium sulfate scale problem has been retarded or prevented the formation of this scale in the first place [6].

Many case histories of oil well scaling by calcium carbonate, calcium sulfate, strontium sulfate, and barium sulfate have been reported [7]. 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. Oilfields scale problems 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. The following is a brief explanation about scaling cases reported which was mentioned in the Bezemer and Bauer (1969) literature [8], they indicated main difficulties encountered in the South Sumatran fields (Indonesia) due to the deposition of calcium carbonate scale have been restriction of flow through tubing and flow lines, wear and abrasion of plungers and liners, and stuck plungers or wellhead valves, so far, the only methods of combating the scale problem have been routine acidizing and well pulling. As for the pumping wells, it was estimated that some 50 percent of the total well pulling effort was directly attributable to scale deposition. Describing scale problems that occur in the Forties field can be attributed into two major factors [8]:

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

Furthermore, they mentioned that, barium sulfate scale formation was a major problem could occur readily in the wellbores of the Forties field when produced water containing a high barium ion concentration mixed with injection seawater of a high sulfate ion concentration. Barium sulfate scale has been found in the topsides equipment, production header and water handling plant.

In addition, they found downhole, deposited on the production tubing and liner resulting in reducing bore sizes and associated loss of production. Typically scale of formation begins with the onset of sea water breakthrough into a wellbore and can lead to very rapid production declines. Todd (1992) described barium sulfate scale occurrence was a severe production problem in North Sea oil operations [9]. Barium sulfate is often accompanied by strontium sulfate to form a completely mixed scale called (Ba, Sr) SO₄ 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 [4]. The first problem is that maintenance of acceptable water quality to prevent excessive losses of well injectivity. The second problem is that controlling 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. Moreover, water injectivity loss in the Siri field in Iran from an initial injection rate of 9100 bbl/day to 2200 bbl/day within six years of injection [10]. Field and laboratory data indicated that loss of injectivity was the result of permeability reduction caused by fine particles migration and deposition in the rock pores. Salman et al., conducted a study in order to predict the possibility of scale formation when seawater was injected into the northern Kuwaiti oilfields for reservoir pressure maintenance [11]. Results indicated that the seawater was likely to be self-scaling with respect to calcium carbonate under production reservoir conditions but could become a problem when the system underwent temperature and pressure changes.

Paulo et al., in 2001, described that Sulfate scale deposition is a common problem in the Alba field in the North Sea resulted from injected seawater mixing with aquifer brines [12]. The problem is that most severe in and around the injection and production well bores and can cause considerable disruption to hydrocarbon production after water breakthrough. Voloshin et al., presented an overview of scale problems encountered in Western Siberian oilfields where formation pressure was maintained by injecting water (Senoman, fresh and Podtovarnaya water) and electric submersible pumps (ESPs) and rod pumps were used to lift reservoir fluids to surface [13]. Moreover, scale was one of the main reasons for ESPs failure, which were widely used in the West Siberian oil fields. Investigation showed that carbonate deposit (calcite) was the main culprit, along with mechanical impurities. Iron deposits were present too. In 2003, many thousands of wells compromised by scale in Western Siberian oilfields.

Moghadasli et al., described scale formation in the Iranian oilfields has been recognized to be major operational problem causing formation damage either at injection or producing wells [14]. Scale contributes to equipment wear and corrosion and flow restrictions, thus resulting in a decrease in oil and gas production. Strachan et al., in 2004, reported that barium sulfate scale

was a major problem in the BP Magnus field, even at low water cuts (<1%) [15]. In the late 1990's, BP Magnus adopted a policy of executing pre-emptive scale squeeze treatments on newly completed wells to prevent scale deposition and maintain well productivity in water breakthrough.

D. An Overview of Formation Damage

Formation damage occurs during the life of many wells. The well performance can be lost because of formation damage as mentioned in several review articles. Fines migration, inorganic scale, emulsion blockage, asphaltene, and other organic deposition are a few mechanisms that can cause formation damage [16]. The success of oil recovery is strongly influenced by whether the reservoir permeability can be kept intact or even improved. Permeability changes in petroleum reservoirs have received a great deal of concern by the oil and gas industry. This problem is termed as formation damage. It can occur during almost any stage of petroleum exploration and production operations.

Formation damage in scaled-up production wells caused by incompatibility of injected and formation waters have long been known. Permeability decline due to precipitate of salts. Among the most onerous of all scaling species is that of sulfates, particularly barium and strontium sulfates [17]. Due to the extensive use of water injection for oil displacement and pressure maintenance in the oilfield, many reservoirs experience the problem of scale deposition when injection water begins to breakthrough. In most cases, the scaled-up wells are caused by the formation of sulfate and carbonate scales of calcium and strontium. Because of their proportionate hardness and low solubility, there are restricted processes available for their removal and preventive measures such as the squeeze inhibitor treatment must be taken. It is therefore important to gain a proper understanding of the kinetics of scale formation and its detrimental effects on formation damage under both inhibited and uninhibited conditions. According to Moghadasi et al., (2004), formation damage is a general terminology referring to the impairment of the permeability of petroleum bearing formations by various adverse processes [14]. Formation damage is an undesirable operational and economic problem that can happen during the several phases of oil and gas recovery from subsurface reservoirs involving drilling, production, hydraulic fracturing and work over operations. Formation damage is a costly headache to the oil and gas industry. The fundamental processes causing damage in petroleum bearing formations are: hydrodynamic, physico-chemical, chemical, thermal, and mechanical.

Two phenomena can change the permeability of the rock starting with change of porosity. This phenomenon is due to the swelling of clay minerals or deposition of solids in the pore body. The other is the plugging of pore throats. The narrow passages govern the ease of fluid flow through porous media. If they are blocked, the permeability of the porous rock will be low even though the pore space remains large. Either organic or inorganic matter may cause the plugging of pore throats. The organic induced damage is due to the formation of high viscosity hydrocarbon scale when temperature and pressure conditions in the reservoirs are changed. The inorganic damage involves release and capture of particulate including in-situ fines and precipitates from chemical reactions. The mechanisms that trigger the formation damage can be categorized into three major processes [18]:

1) Hydrodynamic

A mechanical force mobilizes loosely attached fine particles from the pore surface by exerting a pressure gradient during fluid flow. The movement of many different types of fines including clay minerals, quartz, amorphous silica, feldspars, and carbonates may cause mechanical fine migration damage.

2) Physicochemical

This mechanism is caused by the water sensitivity clays. Clays exist in equilibrium with the formation brines until the ionic composition and concentration of the brine is altered. Permeability declines because the swollen clay occupies more of the pore space, but more often occurs because of fines released by the swelling.

3) Geochemical

The injected fluid may not be compatible with the native pore fluid during treatment of reservoirs or water flooding. This incompatibility results in chemical none equilibrium in the porous system. Ions in the source water may react with ions in the reservoir fluids to form solid precipitates downstream in the porous system to plug pore throats or to deposit onto pore wall resulting in porosity reduction. Mineral scale formation and deposition on downhole and surface equipment is a major source of cost and reduce production to the oil industry. Solid scale formation mainly results from changes in physical-chemical properties of fluids (i.e., pH, partial pressure of CO₂, temperature, and pressure) during production or from chemical incompatibility between injected and formation waters. Precipitation of mineral scales causes many problems in oil and gas production operations: formation damage, production losses, increased workovers in producers and injectors, poor injection water quality, and equipment failures due to under-deposit corrosion. The most common mineral scales are sulfate and carbonate based minerals. However, scale problems are not limited to these minerals and there have recently been reports of unusual scale types such as zinc and lead sulfides.

The formation of mineral scale in production facilities is a relatively common problem in the oil industry. Most scale forms either by pressure and temperature changes that favor salt precipitation from formation waters, or when incompatible waters mix during pressure maintenance or water flood strategies. Scale prevention is achieved by performing squeeze treatments in which chemical scale inhibitors are injected in the producers near wellbore.

Mechanisms by which a precipitate reduces permeability include solids depositing on the pore walls because of attractive forces between the particles and the surface of the pore, a single particle blocking a pore throat, and several particles bridging across a pore throat. The characteristics of the precipitate influence the extent of formation damage. Such conditions as a large

degree of supersaturation, the presence of impurities, a change in temperature, and the rate of mixing control the quantity and morphology of the precipitating crystals [19].

In the North Sea, the universal use of sea water injection as the primary oil recovery mechanism and for pressure maintenance means that problems with sulfate scale deposition, mainly barium and strontium, are likely to be present at some stage during the production life of the field [20]. Formation damage studies are executed for understanding of these processes via laboratory and field testing, development of mathematical models via the description of fundamental mechanisms and processes. Mineral scale formation is one of the main mechanisms of formation damage. Moreover, the formation of mineral scale associated with the production of hydrocarbons has always been a concern in oilfield operation. Depending on the nature of the scale and on the fluid composition, the deposition can occur inside the reservoir which causes formation damage [21], or in the production facilities where blockage can cause severe operational problems. Furthermore, the two main types of scale which are commonly found in the oilfield are carbonate and sulfate scales. Whilst the formation of carbonate scale is associated with the pressure and pH changes of the production fluid, the occurrence of sulfate scale is mainly due to the mixing of incompatible brines, i.e. formation water and injection water. According to Bagci et al., (2000) [22], formation damage is a well-known phenomenon in many water flooding operations. This damage depends on many factors, such as the quality of the injected water and rock mineralogical composition.

Movement of particles in reservoirs has long been recognized to cause formation damage. Nevertheless, during drilling and production operations, these fine particles could have been incorporated in the formation during geological deposition or can be introduced into the formation. Investigations and diagnosis of specific problems indicate that the reasons are usually associated with either the physical movement of fine particles, chemical reactions, or a combination of both. In addition, formation damage could be happen from the fine particles introduced with the injection water.

E. Occurrence of Formation Damage

During petroleum exploration and production, when fluids are introduced into a porous rock, its original purpose is to increase the recovery of hydrocarbon. However, because the incompatibility between injected and native fluids, change of reservoir rock properties can often be expected. During various oil exploitation activities, the following sections describe the potential causes of formation damage.

1) Drilling

During drilling, higher pressure is required in the wellbore to control the formation being penetrated, the pressure differential will result in invasion of mud solids and mud filtrate into reservoir rock near wellbore. Solid invasion is strongly influenced by particle size and pore throat size distribution.

2) Production

During the oil and gas production, the temperature and pressure in reservoirs are constantly altering. Organic scale such as asphaltenes and paraffin waxes may deposit outside of the crude oil to plug the formation. Inorganic salts such as calcium carbonate and barium sulfate may also precipitate out of the aqueous phase to block flow paths. The great pressure gradient near the wellbore often is capable of mobilizing fines residing on the surface of pore wall around the producing wells to cause fines migration.

3) Water Flooding

Combination of the injected water with the indigenous reservoir fluids is an important factor that influences the success of a water flooding program. The ions contained in the injected fluid may react with the ions in the native fluid to insoluble precipitates.

4) Stimulation

Most stimulation operations involve chemical treatments. Reactions of different kinds occur when chemicals are introduced into formations. Some of the reactions have adverse effects on formation permeability.

F. Water Flooding

Water injection to improve oil recovery is a long-standing practice in the oil industry. Pressure maintenance by water injection in some reservoirs may be considered satisfactory for oil recovery. The main objective of water flooding is to place water into a rock formation at desired rate and pressure with minimal expense and trouble. This objective, however, could not be achieved unless water has certain characteristics. The water, therefore, should be treated and conditioned before injection. This treatment should solve problems associated with the individual injection waters, including suspended matter, Corrosivity of water scale deposition, and microbiological fouling and corrosion.

Pressure maintenance by sea water injection is planned for major North Sea oil reservoir. Sea water is proposed to be injected, where possible, into water saturated formations underlying the reservoir. Analyses of the water composition indicate that scale formation may occur by two possible mechanisms. First mechanism, changing pH and temperature conditions for sea water may precipitate insoluble salts. The second mechanism is that the mixing of sea water and formation water may cause precipitation of solids. Both mechanisms could result in damage to the near wellbore formation [23]. The main difficult problems in designing a proper water flood operation as the following [24]:

1) The predetermination of chemical incompatibilities of waters used in the flood.

- 2) The forecast of these incompatibility effects on future field operations. This forecast should cover the type, extent, and location of all future damages resulting from chemical incompatibility problems.

The chemical incompatibility of injected seawater and formation water has prompted deposition of barium and strontium sulfate scales in producing wells of the Namorado field. The precipitation squeeze process was chosen as a means of preventing scale formation in this field [25]. Sea water and formation water can become mixed during water injection both around an injection well, and also after breakthrough of injection water into production wells. Injection wells will mainly form scale in the pores of the formation rock. Production wells may form scales both within the formation and in the well tubular and process equipment. The selection of the injection water is a critical factor when water flood operations are planned. The most obvious (and the cheapest) source of water is the sea water in offshore oilfields; in onshore fields, waters from shallow aquifers are normally used for injection. River water is used only when no other source is available due to the high content of suspended matter and microorganisms usually present. In all cases, the prior condition for good injection water is that it must not impair well injectivity and reservoir fluid characteristics. Injection water must be free of suspended particles, organic matter, oxygen, and acid gases (CO₂ and H₂S) before it is pumped into the injection wells [5].

II. 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. As the water enters the reservoir, three main phenomena occur:

- 1) Along the water flow path, temperature increases due to heat exchange with the reservoir rock and fluids.
- 2) Pressure decreases along the flow path.
- 3) Injection water mixes with reservoir brine.

Scale precipitation from the injection water may happen behind the mixing zone as a consequence of temperature and pressure changes. This is particularly true for waters containing salts whose solubility decreases with increasing temperature and decreasing pressure. Reservoir brine is present in forward position to the mixing zone 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. The remaining clear water moves ahead and mixes with reservoir brine at different pressure, due to which scale precipitation take place again. 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 wellbore when there are major falls in pressure but hardly any temperature changes [26]. Figure gives some indication of which changes occur at which part of an oilfield. Seawater injection is common in North Sea field developments.

The often layered nature of the reservoir results in early water breakthrough. The chemical incompatibility between injected seawater and formation water makes BaSO₄ and related scale deposition possible at various producing wells and facilities in North Sea operations. Injected water may also mix with formation water in the near wellbore area, causing possible resistance to flow. The presence of strontium and barium ions in some formation water necessitates the examination of the possible formation damage resulting from solid solution formation of barium sulfate and strontium sulfate [9].

A. Where Does Oilfield Scale Form?

The scaling reaction depends on there being adequate concentrations of sulfate ions in the injected seawater, and barium, strontium, and calcium divalent cations in the formation brine to generate sulfate scale or on there being enough bicarbonate and calcium ions to generate carbonate scale. Therefore, scale precipitation may occur wherever there is mixing of incompatible brines, or there are changes in the physical condition such as pressure decline. An overview of all the possible scale formation environments for seawater, aquifer, natural depletion and produced water re-injection is presented [27]:

- 1) Prior to injection, for example if seawater injection is supplement by produced water re-injection (PWRI).
- 2) Around the injection well, as injection brine enters the reservoir, contacting formation brine.
- 3) Deep in formation, due to displacement of formation brine by injected brine, or due to meeting flow paths.
- 4) As injection brine and formation brine converge towards the production well, but beyond the radius of a squeeze treatment.
- 5) As injection brine and formation brine converge towards the production well, and within the radius of a squeeze treatment.
- 6) In the completed interval of a production well, as one brine enters the completion, while other brine is following up the tubing from a lower section, or as fluid pressure decreases.
- 7) At the junction of a multilateral well, where one branch is producing single brine and the other branch is producing incompatible brine.
- 8) At a subsea manifold, where one well is producing single brine and another well is producing different brine.
- 9) At the surface facilities, where one production stream is flowing one brine and another production stream is flowing another brine.

- 10) During aquifer water production and processing for re-injection could lead to scale formation within self-scaling brine or mixing with incompatible formation brine.
- 11) During pressure reduction and/or an increase in temperature within any downhole tube or surface processing equipment, leading to the evolution of CO₂ and to the generation of carbonate and sulfide scale if the suitable ions are present. Temperature reductions could lead to the formation of halite scales if the brine was close to saturation under reservoir conditions.

Oilfield scales are inorganic crystalline deposits that form as a result of the precipitation of solids from brines present in the reservoir and production flow system. The precipitation of these solids occurs as the result of changes in the ionic composition, pH, pressure, and temperature of the brine. There are three principal mechanisms by which scales form in both offshore and onshore oil field system [28].

B. Common Oilfield Scales

The most common oilfield scales are listed in Table 1, which have different solubility (Moghadasi et al., 2003) [29]. These scales are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and strontium sulfate and calcium carbonate. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate.

Table – 1
The most common oilfield scales

Name	Chemical formula
Calcium Carbonate	CaCO ₃
Calcium Sulfate Gypsum Hemihydrates Anhydrite	CaSO ₄ .2H ₂ O CaSO ₄ .1/2H ₂ O CaSO ₄
Barium Sulfate	BaSO ₄
Strontium Sulfate	SrSO ₄
Iron Compounds Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferrous Hydroxide	FeCO ₃ FeS Fe(OH) ₂ Fe(OH) ₃

C. Natural Occurring Radioactive Material (Norm) Scale

Some oilfield scales contain naturally occurring radioactive materials. The oil industry refers to these scales as NORM. Usually the radioactivity in these scales is very low and not dangerous. Radioactivity of NORM scale is usually caused from the radioactive isotopes Radium 226 and Radium 228 being co-precipitated with an oilfield scale. Radium is similar chemically to barium and strontium; therefore, it readily precipitates with them, causing the resulting scale to be classified as NORM. Scale deposits such as calcium carbonate, calcium sulfate can infrequently be classified as NORM scale.

D. Exotic Scales Are Generally Associated with Deep Hot Wells

Many gas wells have molten sulfur in the reservoir (sulfur's melt point ≈ 220 degrees F), and as the fluids cool from being produced, elemental sulfur can deposit in the tubing or other equipment. Zinc sulfide deposits can be the result of a naturally occurring scale, or they can be caused from "heavy" well completion fluids. These "heavy" completion fluids use zinc chloride or zinc bromide as weighting agents. The zinc in these fluids can react with hydrogen sulfide to form zinc sulfide which is not soluble in hydrochloric acid. Elemental lead and mercury deposits are sometimes encountered. Mercury and lead can react with hydrogen sulfide to form lead sulfide and mercury sulfide deposits. Dissolved lead and mercury can be encountered in the produced water of deep hot gas wells. The soluble lead and mercury can precipitate as lead sulfide when produced water is mixed with water from another zone.

E. Types of Mineral Scales

Common oilfield scale deposits can be classified into pH independent and pH sensitive scales. The scaling tendency of sulfates (calcium sulfate, barite and celestite) and halite scales are not a strong function of brine pH. The carbonates (calcite, dolomite and siderite) and sulfide scales are acid soluble and their scaling tendencies are strongly influenced by the brine pH. For pH sensitive scales, the scale prediction is more complicated since issues that control the brine pH also affect their scaling tendencies [30].

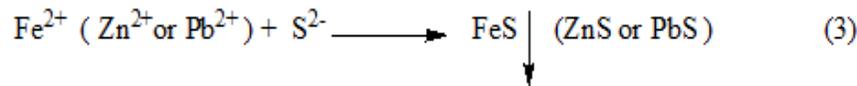
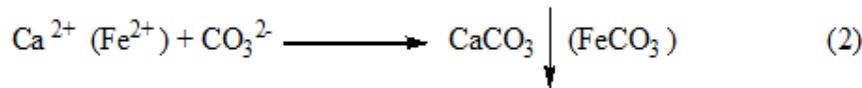
1) pH independent scale

These are sulfate compounds of barium, strontium, or calcium. The sulfate ion (SO₄²⁻) normally found in the seawater reacts with Ba²⁺ Sr²⁺ and/or Ca²⁺, ions, which are naturally found in the formation water depending on the geological history of the oil fields. These compounds are also mildly soluble in water and as a result they subsequently precipitate out and form solid solutions



2) pH dependent scale

The carbonates (calcite, dolomite and siderite) and sulfide scales are acid soluble. Their formations are as shown in the equation below.



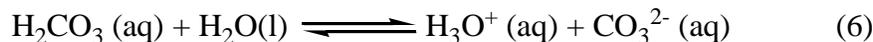
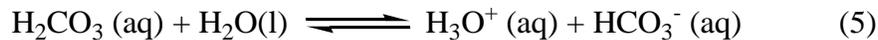
III. MECHANISM OF SCALE DEPOSITION

A. Calcium scale mechanism

Scale can form by various reasons depending on a number of factors. A simple equilibrium approach is used to explain how different parameters impact solubility and thus scale formation. To limit the extent of this report, we focus on the formation of calcium carbonate. The reactions that lead to formation of solid calcium carbonate are as follows [31]. First carbon dioxide reacts with water to produce carbonic acid as seen by reaction 4.



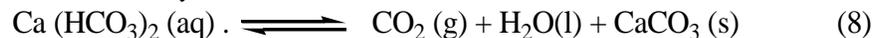
This carbonic acid will continue to dissociate hydrogen, creating new deprotonated species of carbonic acid, as seen in reaction 5 and 6.



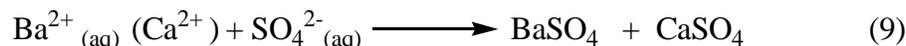
In the water mixture there will be a mixture of the species H_2CO_3 , HCO_3^- and CO_3^{2-} . Finally, in the presence of calcium and carbonic acid, calcium carbonate will precipitate out as seen by reaction 7.



Since, produced water usually contains a carbonic acid and calcium ions, a recombination of these reactions will give a better representation of the situation, as seen by reaction 8.

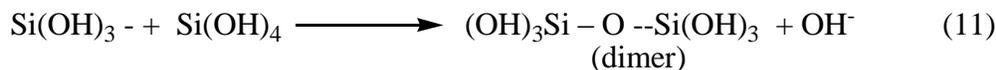
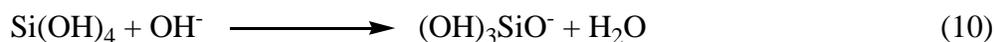


Calcium and carbonic acid together in liquid form will be in equilibrium with water, solid calcium carbonate and CO_2 gas. Scale deposits from incompatible mixing occurs when two incompatible waters like injected seawater in to reservoir during water flooding enhanced recovery operations and formation water gets mixed down hole. The produced water then gets over saturated with scale components. This happens because seawater has a high content of sulfate (SO_4^{2-}) and formation water is rich in ions such as calcium (Ca^{2+}) and barium (Ba^{2+}). Mixing of these two waters leads to precipitation of sulfate scales, such as CaSO_4 and BaSO_4 shown in reaction 9. The scaling tendency of the fluid mixture changes with time depending on the ratio of seawater and formation water.



B. Silicon Scale Mechanism

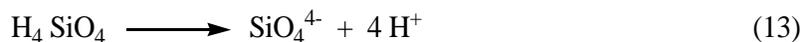
The prospect of silica scaling increases once the dissolved silica levels in the system exceeds the amorphous silica solubility limit (120-140 mg/l) at normal temperature. Polyvalent metal ions present in feed water streams can complex silica and catalyze the precipitation. The composition and the amount of a silica deposit as well as the rate at which it forms is dependent on pH, temperature, the ration and concentration of calcium and magnesium and the concentration of other polyvalent ions in the fed water. It has already founded that polymerized colloidal silica in the presence of polyvalent metal ions forms flocculated silica. The magnesium silicate is highly PH dependent. Below pH 7, magnesium silicate precipitation does not take place because silica is present primarily in unionized form. As the solution pH is increased (above pH 9), magnesium silicate is very likely to form. Additionally, the magnesium silicate is very complicated due to numerous forms of diverse compositions that could possibly precipitate depending on the water chemistry (Mg, SiO_2 , pH, temperature, etc.). Silicic acid reactions show very high sensitivity to pH and tend to be accelerated by the presence of hydroxide forming metals e.g., Fe^{2+} , Mg^{2+} or Al_3^+ . Though believed to be a very complex mechanism, silica polymerization is believed to follow the base catalyzed reaction showed below [32].



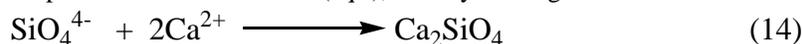
Deep water oil and gas production involves hydrocarbons, produced water (brine), carbon dioxide (CO₂), hydrogen sulfide (H₂S), and other chemicals. Under high pressure sand temperatures, brine can form acidic mixtures that cause general corrosion and pitting of pipe sand solid mineral deposits (scale) that inhibit flow in a well. Another unforeseen situation is that the temperature of ultra-deep water is high enough for water to dissolve sand (SiO₂) forming volatile orthosilicic acid, which in itself is an interesting problem.



The pressure drop experience by the fluid during transportation from reservoir to topside, with subsequent increase in pH, can lead to dissociation of orthosilicic acid shown below.



The dissociated orthosilicate anion, SiO₄⁴⁻ at the oil brine interface reacts with either Ca²⁺ or Na⁺ cation or both in the brine to form stable silicate mineral deposits of different classes (eqs.), thereby causing flow assurance issues at the surface facilities.



C. Natural Occurrence of Silicon

The greatest silica values are typically found in well water supplies, with wells in the California Central Valley being the most notorious in the United States, showing levels in the range of 20 to 60 milligrams per liter (mg/L). Since, most of silica found in well waters is a result of dissolving silica-containing rock, well water will contain reactive silica. Surface waters, on the other hand, will tend to contain more colloidal forms of silica, although the typical surface water will still contain more reactive than colloidal forms of silica [3]. The chemistry of silica in surface water supplies is very complex since biological activity tends to come into play. Diatoms, a species of algae, assimilate reactive silica in the dissolved form, using this material to create a protective shell made of silicon dioxide crystals. As these algal cells decompose, the silica is once again released into the environment as reactive silica, creating a complex ecological balance between dissolved silica and silicon dioxide structures [4].

D. Solubility of Scale Formation

Solubility is defined as the limiting amount of solute that can dissolve in a solvent under a given set of physical conditions. When a sufficiently large amount of solute is maintained in contact with a limited amount of solvent, dissolution occurs continuously until the solution reaches a state when the reverse process becomes equally important. This reverse process is the return of dissolved species (atoms, ions, or molecules) to the dissolved state, a process called precipitation.

Dissolution and precipitation occur continuously at the same rate, the amount of dissolved solute present in a given amount of solvent remains constant with time. The process is one of dynamic equilibrium and the solution in this state of equilibrium is known as a saturated solution. The concentration of the saturated solution is referred to as the solubility of the solute in the given solvent. Thus, solubility of a solute is defined as its maximum concentration which can exist in solution under a given set of conditions of temperature, pressure and concentration of other species in the solution. A solution that contains less solute than required for saturation is called an unsaturated solution. A solution, whose concentration is higher than that of saturated solution due to any reason, such as change in other species concentration, temperature, etc., is said to be supersaturated. When the temperature or concentration of a solvent is increased, the solubility may increase, decrease, or remain constant depending on the nature of the system. For example, if the dissolution process is exothermic, the solubility decreases with increased temperature; if endothermic, the solubility increases with temperature. Both unsaturated and saturated solutions are stable and can be stored indefinitely whereas supersaturated solutions are generally unstable. However, in some cases, supersaturated solutions can be stored for a long time without exhibiting any change and the period for which a supersaturated solution can be stored depends on the degree of departure of such a solution from the saturated concentration and on the nature of the substances in the solution.

1) Solubility product

A salt is a neutral substance formed by combining positive and negative ions. When a salt is dissolved in a solvent, for most cases water, the salt will separate into its constituent ions, so called solute molecules. These ions will interact in various degrees

with the solvent; we say they have different ionic activity. The product of the salt's ion activities gives the solubility product, K_{sp} . If the solution (of solvent and solute) is close to an ideal solution, one can substitute ionic activity with the concentration of each ion. The solubility product is a measure of how many moles of ions per unit volume of solvent there can be a system before a salt precipitates out. K_{sp} can vary with solvent, but water is often used as reference. A low K_{sp} value means that little salt will be dissolved in water and this salt will be referred to sparingly soluble salts. When a salt is dissolved in water, the resulting solution can be acidic, neutral or basic. The negative ion can work as a base or the positive ion as an acid. If either of them have such properties, the result is a neutral solution. This also implies that solvent's pH impacts the solubility product. In the case of calcium carbonate, the carbonate ion can attract a proton from water, resulting in a basic solution. When reducing the pH by adding additional acid, the equilibrium will be shifted favoring dissolution of calcium carbonate into carbon dioxide (CO_2) and calcium ions. There follows a brief description of each solubility.

2) Calcium, Strontium, Barium Sulfates, and Calcium Carbonate Solubility's

The chemical species of interest to us are present in aqueous solutions as ions. Certain combinations of these ions lead to compounds, which have very little solubility in water. The water has a limited capacity for maintaining those compounds in solution and once this capacity (i.e. solubility) is exceeded, the water becomes supersaturated; and the compounds precipitate from solution as solids. The solubility's of typical oilfield scales are given in Figure 1. Although the solubility curves (Figure 1) of these crystalline forms versus temperature show that above about $40^\circ C$ ($104^\circ F$), anhydrite is the chemically stable form, it is known from experience that gypsum is the form most likely to precipitate up to a temperature of about $100^\circ C$ ($212^\circ F$). Above this temperature, hemihydrates become less soluble than gypsum and will normally be the form precipitated. This, in turn, can dehydrate to form a scale at temperatures below $100^\circ C$ and hemihydrates forms above this temperature. Therefore, precipitation of solid materials, which may form scale, will occur if:

- 1) The water contains ions, which are capable of forming compounds of limited solubility.
- 2) There is a change in the physical conditions or water composition, lowering the solubility.

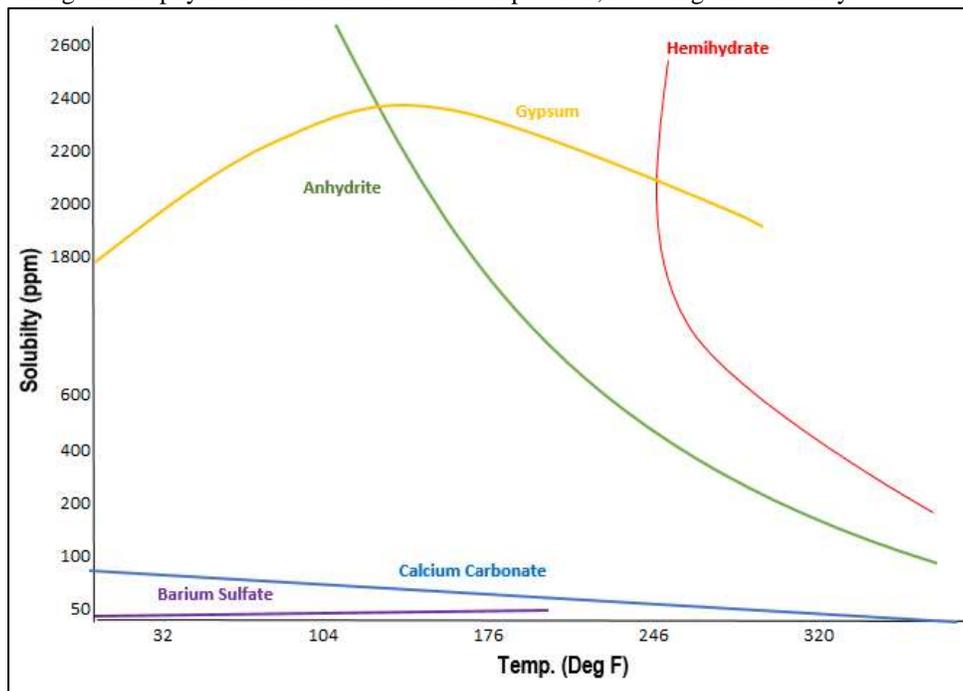


Fig. 1: Solubility's of common scales (Connell, 1983)

E. Factors That Affect Scale Precipitation, Deposition and Crystal Growth

Factors that affect scale precipitation, deposition and crystal growth can be summarized as: super saturation, 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 follows a brief description of some factors.

1) Effect of Super Saturation

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 supersaturation, also known as the scaling index, is the driving force for the precipitation reaction and a high supersaturation, therefore, implies high possibilities for salt precipitation. Since, the solubility of the sulfates of calcium, strontium, and barium can all be estimated, the amount of supersaturation of each can be predicted for any given system of different waters. Caution, however, must be exercised when working with estimated values of solubility and supersaturation. Many different variables, including temperature, pressure, other ions, pH, turbulence, rate of kinetics of precipitation, and

seeding or nucleation all have an effect on the behavior of mixtures of incompatible waters. Some of these variables are beyond the scope of definition in an oilfield situation. They introduce unknown factors that make any estimate of solubility, supersaturation, and the likelihood of precipitation and scaling uncertain. According to Lindlof and Stoffer, 1983 [33], strontium sulfate solubility is decreased by the common ion effect; the supersaturation becomes a disproportionately higher percentage of total strontium sulfates in the solution. The supersaturation represents the amount of strontium sulfate present in excess of the solubility and thus represents the amount available for precipitation from solution and possible scaling. The supersaturation exists in a metastable state and, as such, the manner in which it exists in solution or comes out of solution by crystallization and precipitation is entirely unpredictable.

2) Effect of Temperature

Heating the reservoir water tends to precipitate calcium sulfate, since it can be seen from Figure 1 that calcium sulfate is less soluble at higher temperatures. Calcium sulfate is often observed on the fire tubes of heater theaters. Calcium carbonate also tends to precipitate more at decrease in solubility at higher temperatures. Although this increase can be several-fold, solubility still remains at a low level. Contrary to the behavior of most materials, calcium carbonate becomes less soluble as temperature increases. The hot water is more likely the CaCO_3 precipitation. Hence, water, which is non-scaling at the surface, may result in scale formation in the injection well if the downhole temperature is sufficiently high. According to Oddo [17], 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. Landolt-bornstien in a study by Moghadasi et al., (2003), showed the effect of temperature on solubility of calcium sulfate [29]. Gypsum solubility increases with temperature up to about 40°C , and then decreases with temperature. Note that above about 40°C , anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of calcium sulfate in deeper, hotter wells.

Actually, the temperature at which the scale changes from gypsum to anhydrite or hemihydrates is a function of many factors, including pressure, dissolved solids concentration, flow conditions and the speed at which different forms of calcium sulfate can precipitate out from solution. Prediction which form of calcium sulfate will precipitate under a given set of conditions is very difficult. Even though an anhydrite precipitate might be expected above 40°C in preference to gypsum due to its lower solubility, gypsum may be found at temperature up to 100°C . It is often difficult to precipitate anhydrite directly from solution, but with the passage of time, gypsum can dehydrate to form anhydrite. Above 100°C , anhydrite will precipitate out directly in a stirred or flowing system. Calcium sulfate is one of several soluble salts commonly deposited from oil field waters. That deposition is the result of a supersaturated condition approaching equilibrium by precipitating some of its dissolved salt burden. Precipitation continues until stability has been achieved. Barium sulfate solubility increased with temperature increase, with increase ionic strength of brine, and with pressure. Barium sulfate precipitation was affected most strongly by temperature. Jacques and Bourland, 1983, described a solubility study of strontium sulfate in sodium chloride brine [34]. Their study showed that the solubility of strontium sulfate increased with increasing ionic strength and decreased with increasing temperature [34].

3) Effect of Pressure

The sulfates of calcium, barium and strontium are more soluble at higher pressures. Consequently, formation water will often precipitate a sulfate scale when pressure is reduced during production. The scale may deposit round the wellbore, at the perforations, or in the downhole pump (if used). Barium sulfate is common at perforations or downstream of chokes, where the pressure is reduced considerably. A drop in pressure can cause calcium sulfate deposition. The reason is quite different from that for calcium carbonate. The presence or absence of CO_2 in solution has little to do with calcium sulfate solubility. The solubility of scale formation in a two-phase system increases with increased pressure for two reasons.

- 1) Increased pressure increases the partial pressure of CO_2 and increases the solubility of CaCO_3 in water.
- 2) Increased pressure also increases the solubility due to thermodynamic considerations.

4) Effect of Ionic Strength

The solubility of calcium sulfate is strongly affected by the presence and concentration of other ions in the system. 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, as shown in Figure 2. For example, Figure 2 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 remarkably. This is known as the common ion effect. The solubility reaches a maximum in highly concentrated brines.

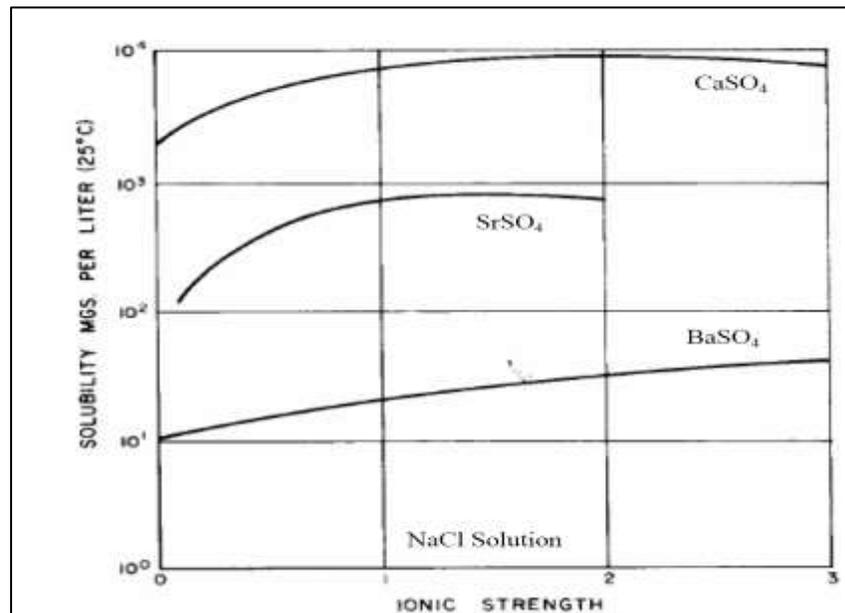


Fig. 2: Relative solubilities of three sulfates in brine [32].

5) Effect of PH

The amount of CO₂ present in the water affects the pH of the water and the solubility of calcium carbonate. However it really does not matter what causes the acidity or alkalinity of the water. The lower the pH, the less likely is CaCO₃ precipitation. Conversely, the higher pH, the more likely that precipitation will occur.

6) Effect of Carbon Dioxide Partial Pressure

As opposed to most sulfate scales, the prediction of carbonate scales requires not only the consideration of pressure, temperatures, and water composition, but also the knowledge on the chemical reactions within the brine and CO₂ in the gas phase. Most oilfield reservoirs contain carbonate mineral cements and carbon dioxide, therefore the formation water is normally saturated with calcium carbonate under reservoir conditions where the temperature can be as high as 200°C and the pressure up to 30 MPa. Solubility of calcium carbonate is greatly influenced by the carbon dioxide content of the water. CaCO₃ solubility increases with increased CO₂ partial pressure. The effect becomes less pronounced as the temperature increases. The reverse is also true. It is one of the major causes of CaCO₃ scale deposition. At any point in the system where a pressure drop is taken, the partial pressure of CO₂ in the gas phase decreases, CO₂ comes out of solution, and the pH of the water rises. The amount of CO₂ that will dissolve in water is proportional to the partial pressure of CO₂ in the gas over the water.

IV. CURRENT AND FUTURE RESEARCH

The two common, most insoluble types of inorganic scale formed during the extraction of the oil, are calcium carbonate (CaCO₃) and barium sulphate (BaSO₄). Both types of mineral scale are widely known from the different applications in daily life. However, when it comes to the oil field processes both mineral types like others (i.e., CaSO₄, FeCO₃) are undesirable since they result in blockage of pipes and in many other flow assurance problems. A number of past and ongoing projects of this research group focus on the CaCO₃ and BaSO₄ formation processes that occur in the bulk phase and on the surfaces. Furthermore, the scaling activity is investigated in terms of both thermodynamics and kinetics. High importance is given in with the performance of different chemical retarders (inhibitors) on the forming scale. The applied inhibitors are characterized by different chemical properties and they belong in different levels concerning their "green" character. In addition, the application of combined products with a double action on the scale and corrosion phenomena consist an interesting and further ambitious approach in the oil field. The first attempt from using combined inhibitors has shown that scale and corrosion phenomena can be both inhibited simultaneously. Besides, the processes that take place in the topside facilities, recently the scale formation processes occurring at the bottom hole were also given attention. The induction of the nanotechnology in the research and development of the anti-scaling techniques in the oilfield, offers the ability to understand and accurately simulate the bottom hole scaling activity. Current, related research projects include: Nanotechnology for Enhanced Squeeze Retention and Coating of the Wellbore Grain Surface to Prevent Scale Deposition/Adhesion, respectively. In addition to their high industry relevance and impact, 'scale formation' studies are academically attractive since they are closely related to the dominant topics of (i) nucleation and (ii) crystallization of inorganic material. This is why the assessment of the actual mechanisms of the scale formation processes is such a prominent and active focus of this research group. A deeper investigation of the scale and formation damage phenomena can inform the anti-scaling techniques and further it will contribute to an improved scale management in the oilfield.

A. Facilities

Many of well-established techniques are used for scaling studies. The main techniques enable investigation into the physicochemical processes that occur on the surfaces and provide information related to the bulk phase of the system and/or the surface kinetics. Relevant techniques include: Tube blocking tests, Insitu flow rig, Quartz Crystal Microbalance, Rotating Cylinder Electrode, Electrochemical methods and modern, dynamic techniques such as Synchrotron X-ray Diffraction. The formed deposits are analyzed with high accuracy techniques such as the FTIR (Fourier Transform Infrared Spectroscopy) and the deposits are observed with SEM (Scanning Electron Microscope) or AFM (Atomic Force Microscopy).

V. SCALE PREVENTION METHODS

One of the most serious problems encountered in using hot geothermal liquids for producing electric power results from scaling of the equipment used to confine and contain the liquid. Because geothermal liquids have usually been confined in subterranean reservoirs for extraordinarily long periods of time at elevated temperatures, large amounts of minerals are leached from the reservoirs into the brine. Typically, salts and oxides of heavy metals, such as lead, zinc, iron, silver, cadmium and molybdenum, are found in geothermal brine. Other more common minerals, such as calcium and sodium, are also dissolved in the brine, as are naturally occurring gases, including carbon dioxide, hydrogen sulfide and methane. An especially troublesome component of the hot brine may be silica, which is found in large concentrations in the form of silicic acid oligomers [35]. Various proposals have been made to decrease the scale formation in equipment used in producing and handling geothermal brine [36].

Scale prevention can be achieved by performing squeeze treatments in which chemical scale inhibitors are injected in the producers near wellbore [37]. Scale inhibitors are a chemical treatment used to control, delay or reduce scale from forming in a producing well. In all the cases considered below, however, the term “prevention” really refers to a reduction in scaling rates rather than a complete elimination of scale forming pathways. Adding chemical antiscalant is an economical and simple effective route for the prevention of scaling. Scale inhibitors (SI) have, for many years, been the preferred downhole treatment for the prevention or control of scale formation and its subsequent deposition, by application in a ‘squeeze’ treatment [38]. They can reduce the rate of scale formation to almost zero. A good scale inhibitor must:

- Be sufficiently stable under the conditions imposed.
- Not interfere with the action of other oilfield chemicals, nor be affected itself by them. It must be compatible with the chemical injection system under operating conditions.
- Be able to inhibit the scale in question, irrespective of the mechanisms operating.

Most of the modern scale inhibitors used in the oilfield functions by one or both of the following mechanisms [8]:

- When scale first begins to form, very tiny crystals precipitate from the water. At this point, the scale inhibitor absorbs on to the crystal surface thus preventing further growth.
- In some cases, scale inhibitors prevent the scale crystals from adhering to solid surfaces such as piping or vessels.

A. Conventional scale inhibitors

Conventional scale inhibitors are hydrophilic, that is, they dissolve in water. In the case of downhole squeezing, it is desirable that the scale inhibitor is adsorbed on the rock to avoid washing out the chemical before acting as desired. The most common inhibitor chemicals are inorganic phosphates, organophosphorous compounds, and organic polymers. PPCA (Poly phosphono-carboxylic acid) and DETPMP (diethylene triamine penta (methylene phosphonic acid)) are the two common commercial scale inhibitors used in the oil and gas industry by inhibit ion mechanism, PPCA is said to inhibit by nucleation while DETPMP operates by inhibiting crystal growth [39].

B. Green scale inhibitors

The oil industry is facing severe restrictions concerning the discharge of oil field chemicals into the environment. More and more severe environmental constraints have prompted users to assume a rational management of industrial waters and brines and to take more restrictive steps concerning its disposal. Green chemistry or pollution prevention at molecular level is the chemistry designed to minimize or eliminate the use or re-generation of hazardous materials associated with manufacture and application of chemicals. It combines critical elements of environmental improvement, economic performance and social responsibility [40]. The number of chemicals allowed to be used as inhibitors has thus been limited mainly to three criteria-tier level of biodegradability, bioaccumulation and toxicity. According to the PARCOM (Paris Commission), an ideal green inhibitor should be non-toxic, readily biodegradable and shows no bioaccumulation. Though the use of green scale inhibitors to inhibit scale in oil and gas wells is relatively an unexplored area [41], there have been several works on this promising alternative [42]. The biodegradation data of commonly used scale inhibitors are given in Table 2.

Table – 2

Commonly used scale inhibitors and their bio degradation data

Inhibitor type	Acronym	Inherent biodegradability result
Phosphonates	PBTC	17% in 28 days
	ATMP	23% in 28 days
	HEDP	33% in 28 days

Polyacrylic acid	PAA	10% in 35 days
Phosphino polyacrylates	PPCA	0% in 35 days
Polymaleic acid	PMA	18% in 35 days
Maleic acid terpolymer	MAT	35% in 35 days
Sulfonic acid copolymers	SPOCA	7% in 28 days (OECD306)
Poly aspartate	PASP	83-87 % in 28days
Carboxy methyl Inulin	CMI 4	> 20% (OECD306)
Poly carboxylic acid	PCA	68.6% in 28days (OECD306)
Maleic acid polymer	MAP	54.9% in 35 days

C. Scale Removal

Calcium sulfate (CaSO₄) and strontium sulfate (SrSO₄) scale deposits that are formed in sandstone formations are difficult to remove chemically and impossible to remove mechanically whereas scale deposits form from incompatible water mixing occurring in tubing are accessible to both chemical and mechanical removal [43].

1) Mechanical methods

Mechanical removal has been used in the past for removing scales. Use of mechanical method (drilling or reaming) is quite easy to understand and has been used to remove different kinds of scale depositions. However, it is not without several limitations and therefore should only be considered as the last option. It is very expensive, a drilling rig has to be moved in and, particularly in deep well, with a lot of complications associated with the drilling process. Also, the method is not very effective for re-stimulating a well because it does not remove the scale deposits from the formation i.e. from outside the wellbore, thus ignoring all the formation damage. An impermeable skin may also remain inside the wellbore caused by the drilling cuttings squeezed in to the perforation holes or production slots in the tubing or liner; and this can cause the productivity to drop to zero. Therefore chemical procedures of removing scale are preferred over mechanical methods [44].

2) Chemical treatment method

Chemical scale removal is often the lowest cost approach, especially when scale is not easily accessible or exists where conventional mechanical removal methods are ineffective or expensive to deploy. The role and the impact of the different reactants used for the chemical treatments (hydrochloric acid (HCl), hydrofluoric acid (HF), chelatants and mixed compounds) will be discussed.

Acid stimulation (acidizing), Acidizing is the most widely used stimulation practice in the oil industry. The rate of flow of oil or gas out of production wells or the rate of flow of oil displacing fluids into injection wells may be increased by dissolving all acid soluble components with in underground rock formations, or removing material at the wellbore face. Different carbonates scales like calcium carbonate (CaCO₃) and iron carbonate (FeCO₃) as well as iron sulfide, and iron oxide (Fe₂O₃) are soluble in acid. Carbonate scale can be dissolved in both organic acid (e.g. citric, formic or sulfamic acid) and in inorganic acids (e.g. hydrochloric acid). Hydrochloric acid (HCl) is the cheapest and easiest acid to use, but the disadvantage is that the acid is very corrosive. This means that a corrosion inhibitor must often be added to the acid solution when being used [45]. Most of the reaction products of HCl and carbonates are water soluble and are easily removed shown in equation (17.)

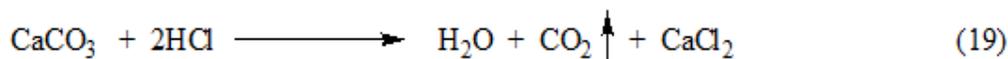
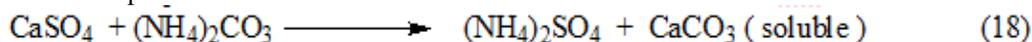


Although hydrochloric acid is considered to be the best oilfield acid for most applications, the system can be very costly, particularly in high temperature environments that require additives to control reaction rates. Hydrochloric acid reacts so quickly with carbonates and thus may require chemical retardants to extend the reaction time and allow the acid to dissolve the carbonate formation completely as un-dissolved impurities in the limestone can plug the formation if they are allowed to settle after a matrix treatment.

Table – 3
Relative solubility of calcium carbonate in various acids

Acid	Dissociation constant, K_a at 77° F	Relative solubility of carbonate (lb/1000 gal. of acid)
HCl	10	3500
Formic	1.77×10^{-4}	700
Acetic	1.75×10^{-5}	400

Table 3 shows a comparison of the solubility of calcium carbonate in different acids [46]. HCl is not a good solvent for CaSO₄. The maximum solubility of calcium sulfate in HCl is only 1.8wt % at 25 °C and atmospheric pressure. Gypsum can be converted to acid soluble compounds by using converters such as (NH₄)₂CO₃, Na₂CO₃, NaOH and KOH. The following reactions illustrate the mechanism of converter performance. The calcium carbonate is then dissolved with HCl.



D. Chemical stimulation with Chelating Agents:

An alternative to acid treatment is the use of chelating agents such as Ethylenediaminetetraacetic acid (EDTA) or Nitrilotriacetic acid (NTA). Chelating agents have the ability to chelate, or bind, metals such as calcium ion in the scale deposits [47]. Through the process of chelation, a calcium ion would be solvated by the chelating agent, allowing the calcite to be transported either to the surface by the well or further into the formation by injecting into the well. The chelating agents are mainly used in oil and gas wells with the advantage of having very low corrosion rates, much lower than that of HCl solutions, in the same conditions. As a consequence, the use of chelating agents needs small amounts of inhibitor to protect the casings.



Among the chelating agents, the most commonly used are compounds of the EDTA family (Ethylenediaminetetraacetic acid (EDTA), Hydroxyethylenediaminetriacetic acid (HEDTA), Hydroxyethyliminodiacetic acid (HEIDA), Nitrilotriacetic acid (NTA)). The disadvantages of using chelating agents are their high cost compared to acids and for some of them, their impact on the environment. There are some commercially available chemicals such as EDTA and diethylenetriaminepentaacetic acid (DTPA), which can remove gypsum scale without conversion. Calcium sulfates are soluble in many chelate solvers and is therefore the easiest sulfate scale to handle. In contrast, barium sulfate is more difficult to handle, being very hard [48]. It has also been found that a mixture of 2% citric acid and 2% EDTA is extremely effective in dissolving iron oxide deposits and deposits containing copper oxides [49]. According to the authors, sulfate containing deposits will even be dissolved when this mixture of chelating agents is employed.

VI. CONCLUSION

Many oil fields are under threat of scale formations in production facilities. When scale deposits are held on to the production equipment surface, it reduces its diameter and subsequently grows continuously until it blocks the tubing as well as the surface equipment. This leads to production stoppage, and results in losses to the production company. Therefore, scale formation should be given a priority treatment because of its threat to flow assurance. A good management strategy must be put in place to prevent it from building up or having further occurrence. Just as it has been acknowledged over the years that scale prevention is better than waiting until it forms and then taking remedial action. Many different technologies that could potentially be deployed by the oilfield operators to reduce the risk of scale formation, control scale formation and to remove it if formed within downhole and topside oil/gas facilities are critically reviewed. With the significant advancement and improvements in chemistry and fluid finish for effective scale inhibitions, oilfield scale can be removed from inside the tubular without risk to the steel tubing. Scaling is precipitation of sparingly soluble salts at surfaces. This can occur when a supersaturated regime is established. Formation of scale can occur and cause problems both down in the well, along the pipelines and in the processing units on the platform or onshore. If scale is left untreated, the worst case can be blocked wells, blocked pipelines and blocked processing equipment. Since, this is highly unwanted, prevention of scale is important. In order to prevent scale in an environmentally friendly way as possible, a good understanding of the chemical background for scale formation is necessary. There are fundamental differences between different scales that can lead to more scaling if the wrong choices are made. To avoid all extra costs related to scaling is unrealistic. But the costs can be minimized by thoroughly risk analyses and a focus on scale prevention.

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