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Scale Formation in Oil Reservoir During Water Injection at High-Salinity Formation Water

Amer Badr Bin Merdihah and Abu Azam Mohd Yassin
Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

Abstract: This study presents the results of Laboratory experiments carried out to investigate the formation of calcium and strontium sulfates in sandstone cores from mixing injected sea water and formation water contain high concentration of calcium and strontium ions at various temperatures (50 and 80°C) and differential pressures (100 and 200 psig). The morphology of scaling crystals as shown by Scanning Electron Microscopy (SEM) is presented. Results show a large extent of permeability damage caused by calcium and strontium sulfates deposit on the rock pore surface. The rock permeability decline indicates the influence of the concentration of calcium and strontium ions.

Key words: Scale deposition, solubility of scale, concentration of calcium and strontium ions, temperature, pressure

INTRODUCTION

Formation damage occurs during the life of many wells. Loss of well performance because of formation damage has been the subject of several review articles. Fines migration, inorganic scale, emulsion blockage, asphaltene and other organic deposition are a few mechanisms that can cause formation damage (Nasr-El-Din, 2003).

The most common oil field scales 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 (Table 1). 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, 2003).

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 ,

Table 1: Most common oil field scales

Name	Chemical formula	Primary variables
Calcium carbonate	CaCO_3	Partial pressure of CO_2 , temperature, total dissolved salts, pH
Calcium sulfate		
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Temperature, total dissolved salts, pressure
Hemihydrate	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	
Anhydrite	CaSO_4	
Barium sulfate	BaSO_4	Temperature, pressure
Strontium sulfate	SrSO_4	Temperature, pressure, total dissolved salts
Iron compounds		
Ferrous carbonate	FeCO_3	Corrosion, dissolved gases, pH
Ferrous sulfide	FeS	
Ferrous hydroxide	Fe(OH)_2	
Ferrous hydroxide	Fe(OH)_3	

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).

Scale deposition is one of the most serious oil field problems that inflict water injection systems primarily when two incompatible waters are involved. Scale deposition in water-flooding operations often results from the incompatibility of injected and formation waters. 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, 2004a).

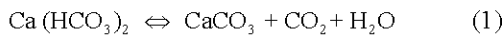
WATER FLOODING

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 for satisfactory 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.

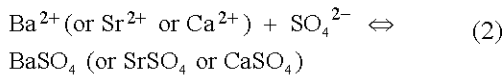
This objective, however, cannot be achieved unless this water has certain characteristics. The water, therefore, should be treated and conditioned before injection. This treatment should solve problems associated with the individual injection waters, including suspended matter, corrosivity of water scale deposition and microbiological fouling and corrosion.

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

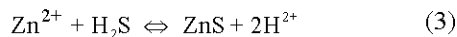
- Decrease in pressure and/or increase in temperature of a brine, goes to a reduction in the solubility of the salt (most commonly these lead to precipitation of carbonate scales, such as CaCO₃).



- 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 BaSO₄).



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



- 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

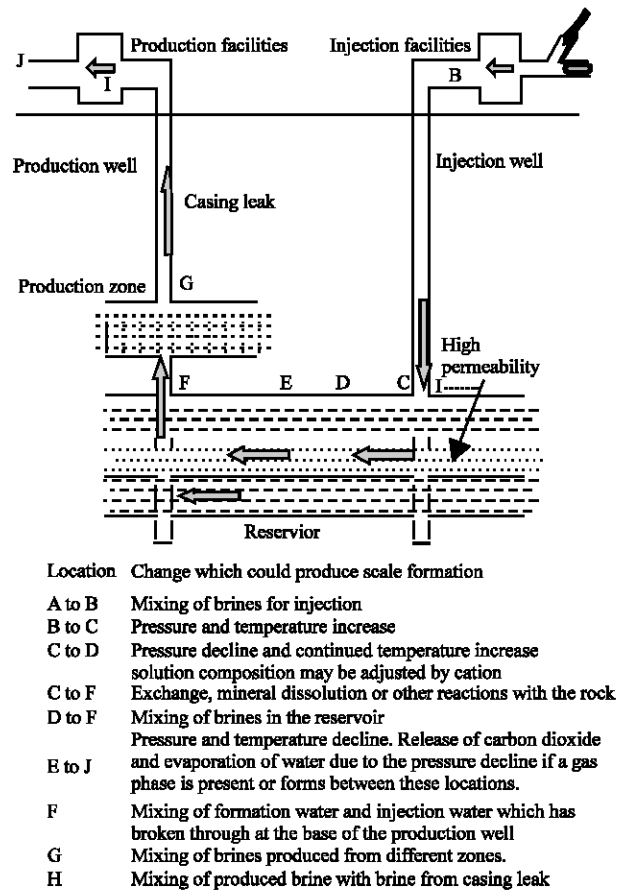


Fig. 1: Changes which could produce scale at different locations during water injection

a dry gas stream may mix with a low rate brine stream resulting in dehydration and most commonly the precipitation of NaCl).

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). Figure 1 gives some indication of which changes occur at which part of an oil field (Moghadasi *et al.*, 2004b).

THE SCALING PROBLEM IN OIL FIELDS

A scale problem will occur, if at a high water cut part of the water is present as free water. The rate of scale deposition will then be approximately proportional to the rate of free water production. Depending upon where the

formation water becomes supersaturated, scale may be deposited in the flow line only, in both flow line and tubing and in some cases even in the perforations and in the formation near the wellbore.

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.

The production problems caused by mineral scale in oil production operations have long 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.

Many case histories of oil well scaling by calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate have been reported by Mitchell *et al.* (1980), Lindlof and Stoffer (1983), Vetter *et al.* (1987) and 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 by Mitchell *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 oil field where calcium and strontium sulfate scales have been found in surface and subsurface production equipment (El-Hattab, 1982).

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. According to Odde *et al.* (1991), calcium sulfate scale formation is somewhat dependent on temperature, but is typically precipitated because of a decrease in pressure or an increase in the relative concentrations of calcium or sulfate. CaSO₄ solubility is fairly independent of pH and hence, can readily precipitate in an acid environment.

Strontium sulfate solubilities may play a role in many disciplines of science and engineering. For example, strontium sulfate forms scale in oil and/or geothermal fields which are frequently accompanied by other sulfates of alkaline earth metals. Jacques and Bourland (1983) described a solubility study of strontium sulfate in sodium chloride brine. His study showed that the solubility of strontium sulfate increased with increasing ionic strength and decreased with increasing temperature.

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.

MATERIALS AND METHODS

The general purpose of the laboratory test was to investigate permeability reduction by deposition of calcium and strontium sulfates in a porous medium and knowledge of solubility of calcium and strontium sulfates and how their solubility are affected by changes in salinity and temperature.

Core material: The rock cores used in the testes were sandstone from Malaysia with 3 inch length and of diameter 1 inch with average porosity of 34% and of absolute permeability varied from 12.32-13.87 md.

Brines: The ionic compositions of synthetic formation water and water injection (Angsi seawater) are given in Table 2. Note the formation water has calcium and strontium ions and the sea water contains sulfate ions. It is clear that the mixing of these waters can lead to calcium and strontium sulfates precipitation.

Scaling test rig: Experiments were carried out using a test rig, which is schematically shown in Fig. 2. The core test equipment consists of five parts: constant pressure pump, transfer cell, oven, pressure transducer and core holder. There follows a brief description of each part.

Constant pressure pump: Plunger pump with 1.5 hp motor and the maximum design pressure of the pump is 35 bars was used to injection the brines during flooding at different pressures.

Transfer cell: stainless steel transfer cells are used to store and transfer the injection brines to the core holder with a capacity of 1000 mL has a free-floating piston,

Table 2: Ions of synthetic formation and injection waters

Ionic	Normal salinity formation water (ppm)	High salinity formation water (ppm)	Angsi seawater (Malaysia) (ppm)
Sodium	52,000	52,000	10,804.500
potassium	1,800	1,800	375.050
Magnesium	4,260	4,260	1,295.250
Calcium	7,000	30,000	429.200
Strontium	500	1,100	6.577
Barium	10	10	-
Chloride	143,200	143,200	19,307.450
Sulfate	108	108	2,750.000
Bicarbonate	350	350	158.800

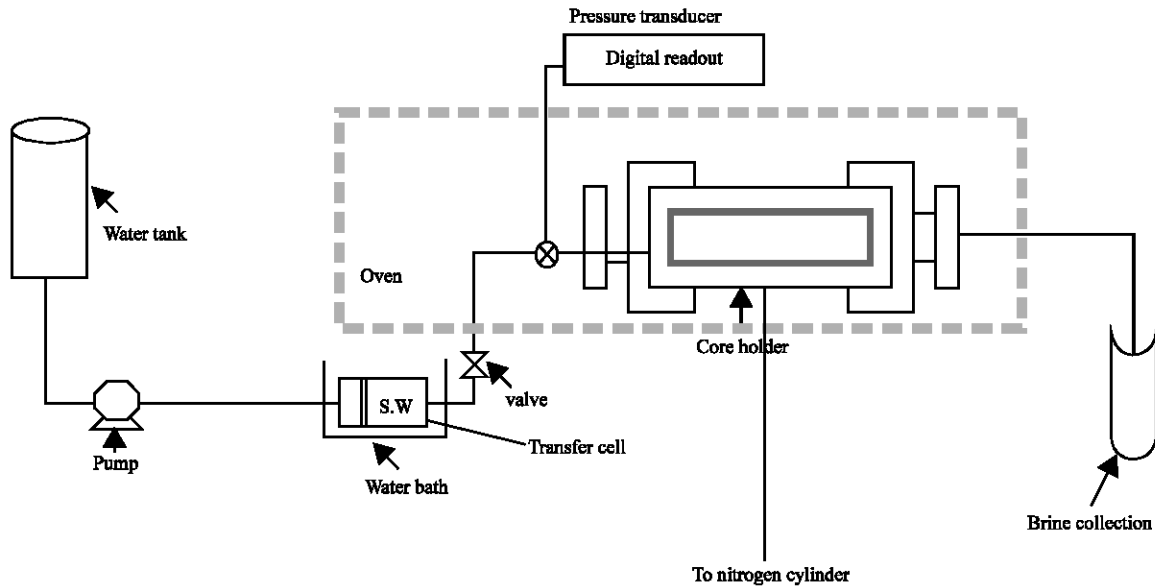


Fig. 2: Schematic of the core flooding apparatus

which separates the pump fluid (distilled water) from the injection brines. The pump fluid is pumped into a transfer cell to displace the brines into the core.

Oven: During all flooding runs, the core holder is placed inside a temperature controlled oven.

Pressure transducer: The differential pressure across the core during flooding runs was measured using pressure transducers (model E-913 033-B29) with a digital display.

Core holder: Stainless steel core holder designed for consolidated core samples 3 inch length and 1 inch diameter was used. A rubber sleeved core holder, subjected to an external confining pressure, into which a sandstone core is placed.

Test procedures

Beaker test: For each experiment of calcium and strontium sulfates, 100 mL of each filtered opposite waters were poured simultaneously into beaker. The synthetic brines were heated on hot plate and the solution was stirred by magnetic stirrer and after that the solution was filtered through 0.45 μm filter paper. After filtration, 5 mL of the filtrate were pipetted into a 50 mL volumetric flask and filled up to 50 mL. This instantaneous dilution of the CaSO₄ and SrSO₄ containing brines just after filtration was performed in order to prevent CaSO₄ and SrSO₄ precipitation during the period between filtering and analytical determination of the Ca and Sr concentrations. Calcium and strontium concentrations in the diluted filtrates were determined by atomic absorption

spectrometry. The calcium and strontium determinations were calibrated by measuring five standard solutions was prepared from CaCl₂ and SrCl₂ solutions.

Core test: Before each run, the core sample was heated and dried in preparation for installation in the core-holder. A vacuum was drawn on the core sample for several hours to remove all air from the core. The core was then saturated with formation water at room temperature and a base permeability determined. After the appearance of formation water at the outlet flooding was continued long enough to ensure 100% saturation. The core holder assembly placed inside the oven and transfer cell containing sea water placed inside the water bath and heated to the desired temperature of the run. The required confining pressure was adjusted to be double inlet pressure. The sea water was injected into the core and mixed with formation water inside porous media. During each run, the flow rate across the core was recorded continuously and the permeability of core was calculated with Darcy's linear-flow equation before and after scale deposition, in order to observe the effect of scale on well productivity. scale deposition have been observed, the core sample was removed at the end of flooding then dried and cut into sections for Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

Beaker test: Based on the analytical calcium and strontium concentrations in the diluted filtrates were determined by atomic absorption spectrometry. The

solubility of CaSO_4 and SrSO_4 at various temperatures (40-90°C) and 1 atm of this study were calculated (Fig. 3 and 4).

The experimental results confirm the general trend in solubility dependencies for CaSO_4 and SrSO_4 scales with temperatures is obvious and is similar to that observed in the earlier studies (Jacques and Bourland, 1983; Oddo *et al.*, 1991). The expected trend in this temperature range is decrease of CaSO_4 and SrSO_4 solubilities with increasing temperature (Fig. 3 and 4) illustrates this trend in these experiments. The SO_4^{2-} content in the sea water brine was reacting with calcium and strontium ions content in the formation water during heating. The more precipitation of CaSO_4 and SrSO_4 resulting from the presence of a high concentrations of calcium and strontium ions with comparison less precipitation at normal concentrations of calcium and strontium ions.

Core test: The test rig was designed to operate at temperatures of 50 and 80°C. The differential pressure used in these experiments range from 100 to 200 psig.

During each run, the flow rate across the core was recorded continuously and the permeability of core was calculated with Darcy's linear-flow equation. The flow rate decreased during the experiments only when a super-saturated solution was flowing through the cores. This confirms that the decrease is due to precipitation of the calcium and strontium sulfates inside the cores with the consequent reduction in their permeability and porosity. In the following, extend of permeability damage, permeability decline trend and the results for various temperatures, concentrations and differential pressure are discussed individually.

Extend of permeability damage: Extend of permeability loss caused by CaSO_4 and SrSO_4 scaling in the rock pores varied in different situations. Figure 9a shows the permeability change of a less damaged core at temperature (50°C) and differential pressure (100 psig); Fig. 10b shows that of a severely damaged core after CaSO_4 and SrSO_4 scaling at temperature (80°C) and differential pressure (200 psig). About 4-14% permeability loss is observed in Fig. 9a, but more than 15-23% initial permeability reduction could occur in a heavily scaled core, as Fig. 10b indicates. The reduction in permeability is possibly caused by crystals blocking the pore throats as shown in the SEM view of Fig. 11. The amount of precipitation varied within the sandstone cores, there being more scale near the formation water inlets and least scale was observed furthest from the inlet parts.

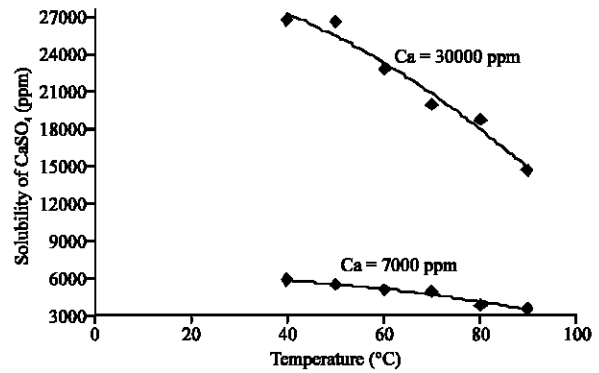


Fig. 3: CaSO_4 solubility is dependent on temperature

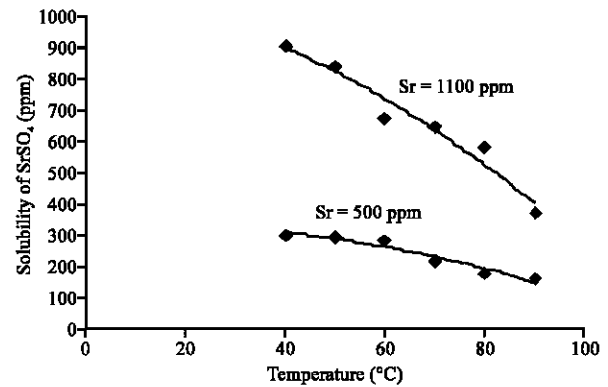


Fig. 4: SrSO_4 solubility is dependent on temperature

Permeability decline trend: Figures 5-8 show the permeability decline trend changes with brine-injection time. During the initial flow period, the permeability declined sharply soon after the two waters mixed in the pores. The permeability decline then slowed and gradually leveled out after the permeability decreased greatly. This phenomenon was observed in all the core tests in which the scaling damage was severe.

Effect of temperature: Temperature has a significant influence on solubility and crystal growth of calcium and strontium sulfates. To study its effect on the permeability reduction, a number of tests were carried out where concentration of injected brine was kept constant at differential pressure from 100 to 200 psig and temperatures of 50 and 80°C. Figure 5 and 6 show that by increasing the temperature, the rate of permeability decline becomes faster. Comparing the findings from the scale formation study at 50°C with those obtained from 80°C experiments reveals some aspects of the effects of temperatures. The permeability decline is more rapid at higher temperature, since the rate of precipitation increase with temperature.

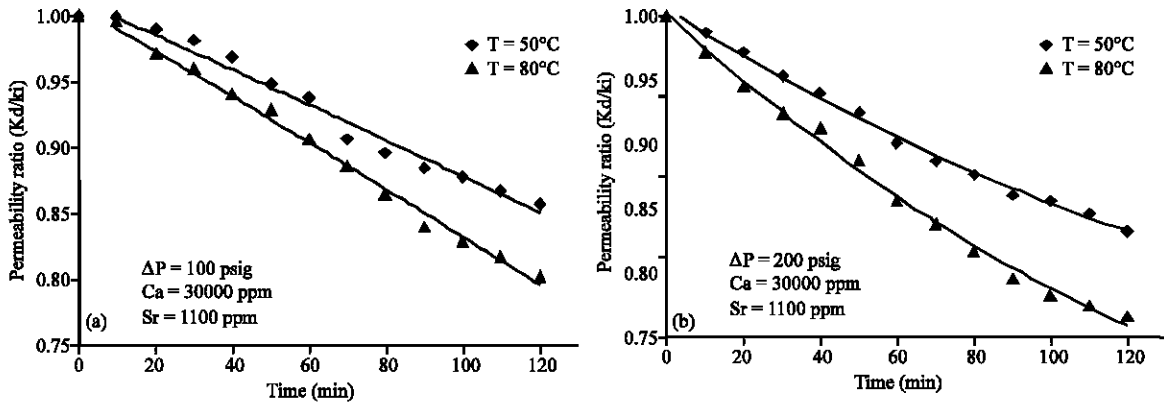


Fig. 5: Variation of permeability ratio as a function of time showing the effect of temperature at (a) 100 psig and (b) 200 psig and high salinity

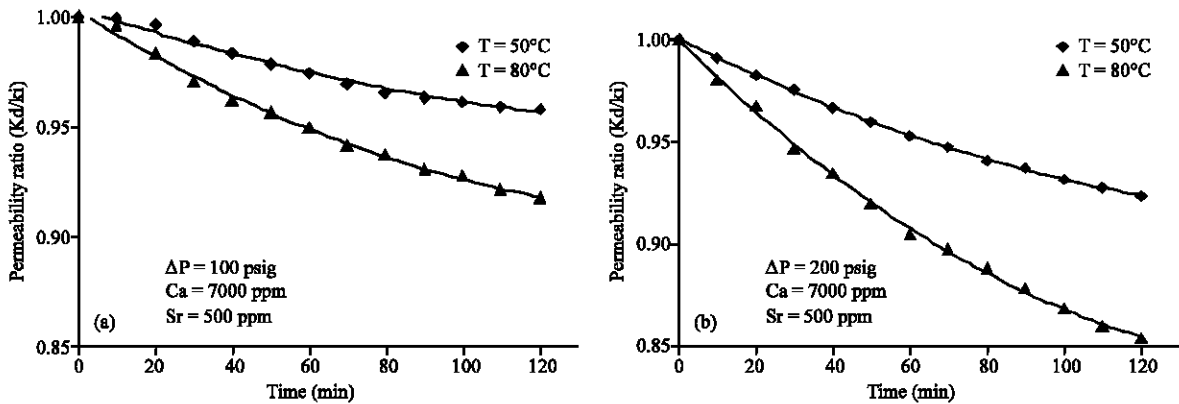


Fig. 6: Variation of permeability ratio as a function of time showing the effect of temperature at (a) 100 psig and (b) 200 psig and normal salinity

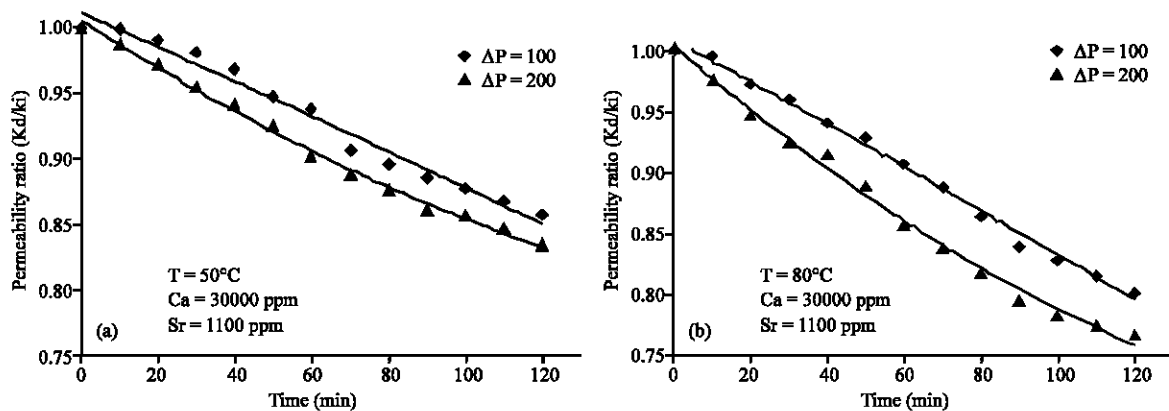


Fig. 7: Variation of permeability ratio as a function of time showing the effect of differential pressure at (a) 50°C and (b) 80°C and high salinity

At higher temperatures $CaSO_4$ and $SrSO_4$ scales is increased because the solubilities of $CaSO_4$ and $SrSO_4$ decrease with temperature.

Effect of differential pressure: To investigate the effect of differential pressure on flow rate and permeability reduction a number of tests were carried out. In these

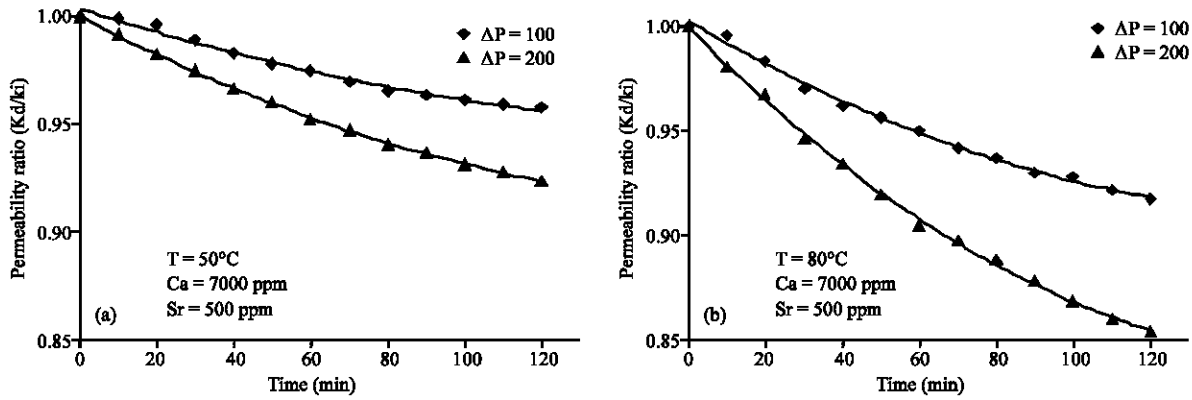


Fig. 8: Variation of permeability ratio as a function of time showing the effect of differential pressure at (a) 50°C and (b) 80°C and normal salinity

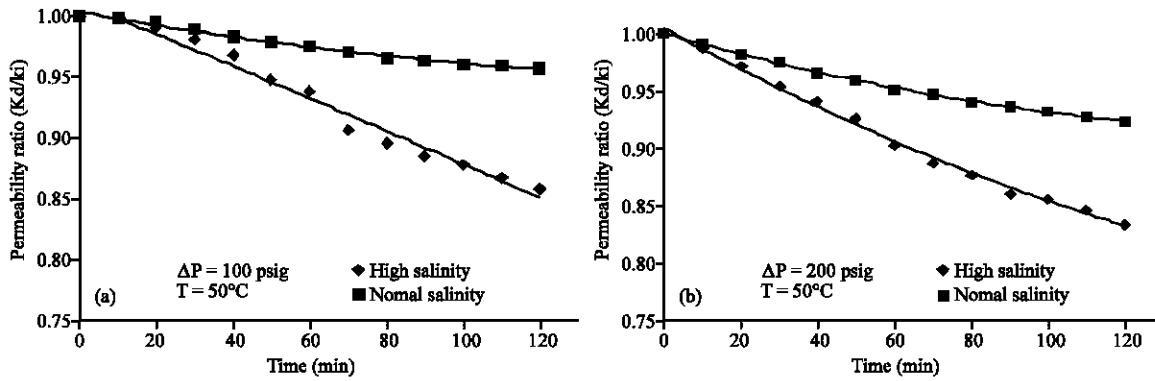


Fig. 9: Variation of permeability ratio as a function of time showing the effect of concentration at (a) 100 psig and (b) 200 psig and 50°C

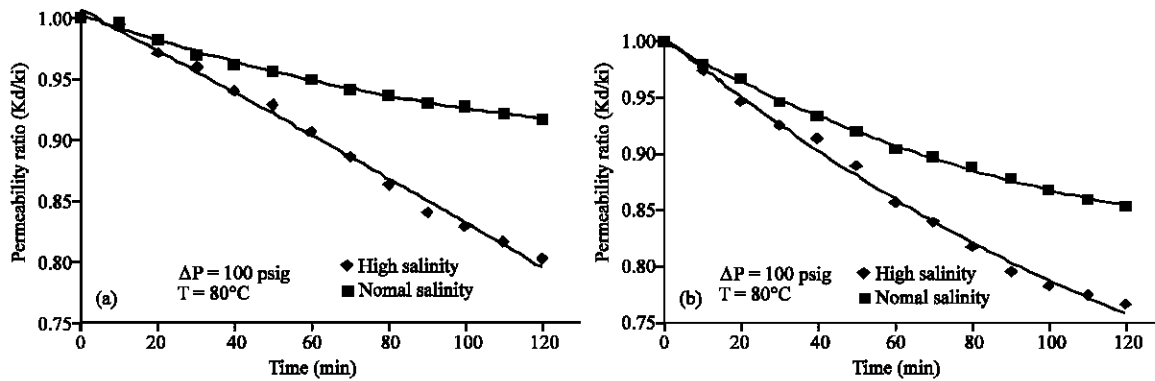


Fig. 10: Variation of permeability ratio as a function of time showing the effect of concentration at (a) 100 psig and (b) 200 psig and 80°C

experiments, the concentration of brine and temperature were kept constant and differential pressure varied from 100 to 200 psig. The permeability decline of porous medium is evident, even at such low differential pressures. The results show that at low differential pressure, scale

formation has already as significant effect on the permeability decline (Fig. 7 and 8). As, the differential pressure was increased, the rate of permeability decline becomes more rapid. Moreover, at higher differential pressure more sulfate ions will pass through the porous

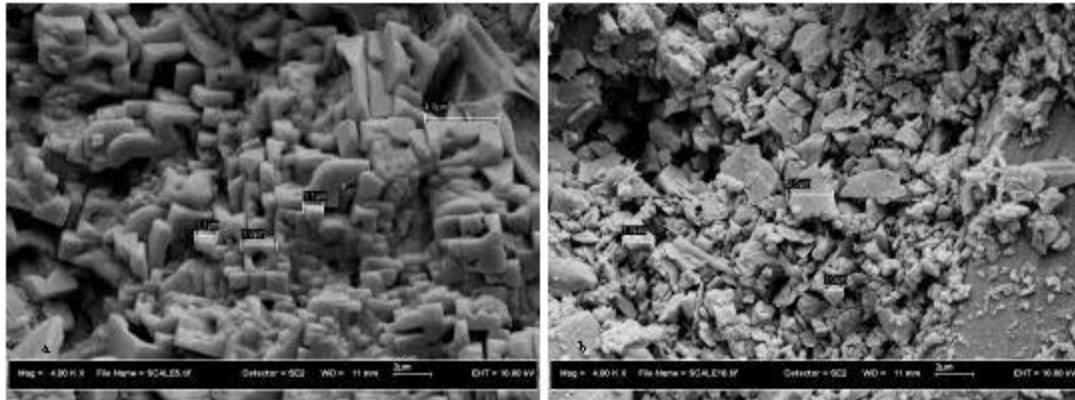


Fig. 11: SEM photograph of CaSO_4 and SrSO_4 scales in sandstone cores

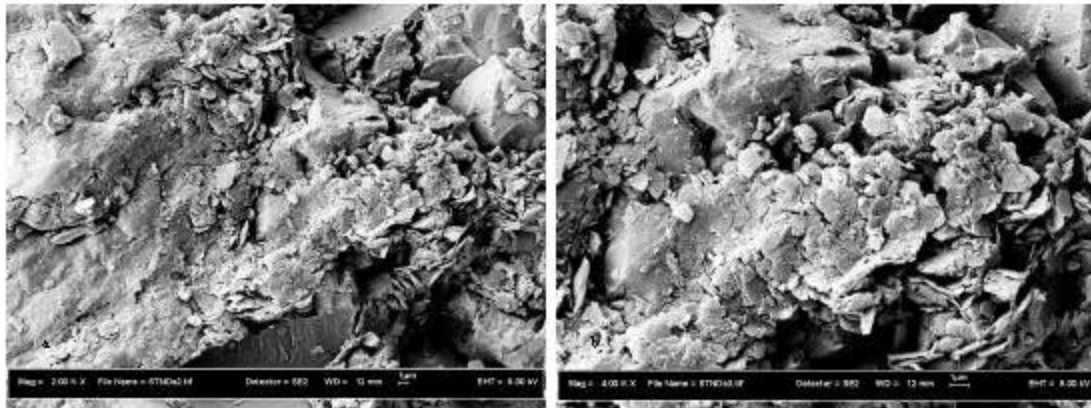


Fig. 12: SEM photograph of an unscaled sandstone core

medium in a given interval of time. The super-saturation at the porous medium will therefore increase the rate of precipitation. This increased precipitation rate will produce a larger permeability decline. Furthermore, the overall permeability of porous medium at high salinity decreased to between 14-23% of initial permeability and normal salinity between 4-15% of initial permeability depending on the differential pressure used.

Effect of concentration: A number of tests were carried out to study the effect of brine concentration on permeability reduction. These tests were carried out at differential pressure from 100 to 200 psig and temperatures of 50 and 80°C with two different brine concentrations (high and normal salinity, Table 2). Figure 9 and 10 show the variation in permeability decline with time for different concentrations of calcium and strontium ions. When the concentration of brine (i.e., super-saturation) is increasing plugging and hence permeability loss occurs more rapidly. The permeability decline due to high

concentration of calcium and strontium is greater than for normal concentration of calcium and strontium ions, for given experimental conditions.

Scanning electron microscopy analysis: The scaled core samples were examined by SEM to observe the particle size and morphology of the precipitates. The formation of CaSO_4 and SrSO_4 during flow of injection and formation waters in porous media have been proved by Scanning Electron Microscopy (SEM)-micrographs show CaSO_4 and SrSO_4 crystals formation in porous space. In all core tests, the abundance of scale reduced significantly from the front of the core to the rear indicating that scale formation in porous media was rapid with the observation that the flow rate decreased soon after two incompatible waters were mixed into a core. The average size of the crystals was about 2 μm . In general, Fig 11 indicates that the front sections of a core suffered considerable greater scaling damage. The reason the scaling decreased downstream of a core is clear: most of the scaling ions had

deposited within the front sections as soon as they were mixed and left few ions to precipitate from the flow stream in the rear sections. Figure 12 shows an SEM photograph of an unscaled core samples.

CONCLUSIONS

- The experimental results confirm the general trend in solubility dependencies for calcium and strontium sulfate scales, determined at various temperatures: A temperature rise from 40 to 90°C causes decrease in CaSO₄ and SrSO₄ solubilities.
- Permeability decline caused by calcium and strontium sulfate scale formation in the porous bed ranged from 4-23% of the initial permeability, depending on brine composition, initial permeability, temperature and differential pressure and brine injection period.
- The pattern of permeability decline in a porous medium due to scaling injection was characterized by a concave curve with a steep initial decline which gradually slowed down to a lower. The initial steepness of these curves generally decreased with increasing distance from the point of mixing of the incompatible brines. The concave shape of the permeability-time curves was common to the majority of the porous medium flow tests.
- Several factors influencing scale formation had been examined. Increasing temperature, concentration of brine (i.e., super-saturation) and differential pressure had a detrimental effect on the permeability reduction.
- The permeability decline due to high concentration of calcium and strontium ions is greater than for normal concentration of calcium and strontium ions, for given experimental conditions.
- The formation of CaSO₄ and SrSO₄ during flow of injection and formation waters in porous media have been proved by Scanning Electron Microscopy (SEM)-micrographs show CaSO₄ and SrSO₄ crystals formation in porous space

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