

Investigation Of The Influence Of Scaling On Corrosion Behavior Of Tubing In Oil Wells

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Abstract: Calcium/iron carbonate and barium/strontium sulfate are major scales in downhole condition of oil wells. Formation of scale in wellbore and inside tubulars not only reduces the production rate but also influences the corrosion of metallic materials. It is widely accepted that formation of some scales such as iron carbonate and iron sulfide help protection of metals from corrosion attacks. While, some other scales do not offer protective properties due to their different physicochemical properties such as porosity and density. This paper discusses the common type of scales in oil wells and their possible influence on corrosion behavior of metallic infrastructure. The paper particularly focuses on iron/calcium carbonate and barium/strontium sulfate.

Index Terms: Corrosion, Oil well, Tubing, Scale, CaCO_3 , FeCO_3 .

1 INTRODUCTION

Hydrocarbon is the main source of world's energy [1]. It needs to be transported via pipeline networks from production zones to treatment facilities and finally end users [2]. Pipeline failure due to corrosion phenomena is a major challenge in oil and gas industry [3]–[10]. Numerous studies have been done to unveil the secrets behind aqueous corrosion of pipelines [11]–[15]. Downhole condition with high temperature and pressure combined with high concentration of dissolved ions is a favorable place for precipitation of mineral scales such as calcium carbonate, barium sulfate, and strontium sulfate. Scales can form within the wellbore and/or along the production tubing inside the oil well's column [16]. Generally, mineral scale in oilfield condition refers to a hard, adherent inorganic compound. Scales precipitate out of the brine (water phase produced along hydrocarbon) if the activity product ions of that particular scale exceeds the solubility limits at the operational condition [17], [18]. Calcium carbonate (CaCO_3), calcium sulfate (CaSO_4), barium sulfate (BaSO_4), and strontium sulfate (SrSO_4) are the main forms of scales reported in oilfields. BaSO_4 and SrSO_4 are more seen in high pressure and high temperature of downhole environments [19]. The water injection (water flooding) is one of the common practices in oil industry as a form of enhanced oil recovery (EOR), especially in offshore production where the seawater is available. Water flooding is employed to maintain the pressure of oil reservoir and thus prevent declining of production rate when the oil reservoir is aging. Injection of seawater into reservoir accelerates the formation of BaSO_4 and SrSO_4 by introducing a considerable amount of sulfate ions (SO_4^{2-}) which normally present in seawater. Presence of Ba^{2+} and Sr^{2+} into water formation comingling with the SO_4^{2-} coming from water flooding, favors precipitation of BaSO_4 and/or SrSO_4 . In such conditions, oil operators use scale inhibitors to prevent scale formation into the system [20], [21].

Precipitation of scales not only decreases the production rate of the oil and gas (by reducing the effective internal diameter of the pipe), but also there is a possibility to influence the corrosion behavior of the tubing steel by changing the physicochemical properties of the surface layers. Pure iron carbonate layers can offer protectiveness against corrosion if its precipitation rate is higher than corrosion rate [22]. Therefore, precipitation of such scale is welcome in a corrosion standpoint as far as flow assurance is not an issue (massive scale formation and blockage problem). However, in oilfields, other ions exist in the brine and they can interfere precipitation of pure iron carbonate. For example, calcium ions can replace iron ions into the crystal structural of iron carbonate and form a metal solid solution carbonate as $\text{Fe}_x\text{Ca}_y\text{CO}_3$ where $x+y=1$. Co-existence of calcium and iron carbonate within a solid solution is due to the fact that they have a similar crystal structure (hexagonal unit lattice). The contribution of "x" and "y" within the mixed solid solution depends on the concentration of individual ions, temperature, pressure, solution pH, etc. Protective properties of such mixed carbonates can be completely different from pure iron carbonate [23]–[25]. A porous scale layer can not be protective since it is not able to separate the corrosive species present in the water phase from the surface of the pipeline. There are some documented research about the effect of CaCO_3 scale on the corrosion of carbon steel [26]–[33]. However, the influence of BaSO_4 and SrSO_4 precipitation on corrosion behavior of carbon steel in downhole condition and the formation of FeCO_3 layer is not investigated or at least documented.

2 MECHANISM OF SCALE FORMATION IN OILFIELDS

The general chemical reaction mechanism of mineral scales is described in Equation (1):



where Me represents cation species such as Ca^{2+} , Ba^{2+} and An represents anion scale forming constituents such as CO_3^{2-} and SO_4^{2-} . The precipitation happens when the water solution (brine) becomes oversaturated with respect to that particular scale. Saturation level is an essential parameter to evaluate the scale formation either thermodynamically or kinetically. Saturation level is defined as the ratio of the ion activity product over the solubility product limit at the system condition, Equation (2):

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$$S_{MeAn} = \frac{[Me][An]}{K_{sp,MeAn}} \tag{2}$$

which K_{sp} is a thermodynamic value known as the solubility product limit at the system's condition [16], [34], [35]. For instance, the solubility product of iron carbonate ($K_{sp,FeCO_3}$) can be determined by Equation (3):

$$\log K_{sp,FeCO_3} = -59.3498 - 0.041377 * T - \frac{2.11963}{T} + 24.5724 \log(T) + 2.518 * I^{0.5} - 0.6578 * I \tag{3}$$

Where T is the absolute temperature in Kelvin and I is the ionic strength of the solution [36]. When $S=1$, the solution is saturated (equilibrium condition). Solution is at supersaturated condition if $S>1$. In this scenario, there is a possibility of scale formation. When $S<1$, it means that the solution is under saturated and is no chance of scale formation. Supersaturation is the main driving force for kinetic of scale formation. The scenario of scale formation is followed by nucleation, crystal growth, and finally precipitation. There are two types of nucleation, homogeneous nucleation and heterogeneous nucleation shown in Figure 1 [37]. Heterogeneous nucleation is the typical nucleation process in downhole environment due to presence of sands in the produced hydrocarbon, sediments on the surface, and inherit roughness of the pipe's surface.

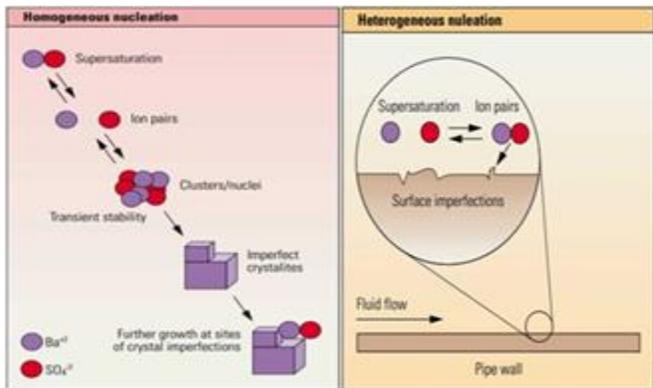


Figure 1. Left: Scale growth mechanism in the bulk of liquid phase (homogeneous). Right: Scale growth mechanism on the preexisting surface defects (heterogeneous) [37].

There are two common practices to remove the formed scales in oilfields, mechanical and chemical treatments. Milling and drilling are two normally used physical methods to remove scales in pipelines. Chemical methods such as using a chelator and acid washing are applied when mechanical treatments are not achievable. However, some chemical methods are expensive and there are some scales which are not soluble in the acid solutions. The application of scale inhibitor is the most popular way to prevent the formation of scales from the beginning. Phosphonate and polyacrylate are the core part of most scale inhibitors in oilfields [38], [39]

3 DOWNHOLE CONDITION OF OIL WELLS

The extreme condition in oil and gas wells is a favorable environment for scale formation. Typical conditions in downhole are listed in Table 1 [40], [41]. These conditions can change greatly not only from field-to-field and well-to-well but

even from downhole to wellhead of a single well [42]. In the oil and gas field, water injection (water flooding), as a form of enhanced oil recovery (EOR), is very common. Figure 2 shows a schematic view of water injection process and downhole. Water injection introduces a great amount of sulfate ions into the reservoir. A typical compositions of formation water at North Sea oilfield operated by BP and the injected seawater are listed in Table 2 [43]. Comingling of SO_4^{2-} in the injected water and the Ba^{2+} and Sr^{2+} present in the formation water results in precipitation of $BaSO_4$ and $SrSO_4$. Although some scale, for instance $CaCO_3$ and $FeCO_3$, forms without water flooding programs, the mixing of injected water and formation water makes the scaling problems more complicated.

Table 1. Typical condition in downhole of oil wells

Temperature	30-175 °C
Total pressure	20-450 bar
Components in gas phase	CO_2 , H_2S , N_2 , hydrocarbon gases (methane, etc.)
Components in liquid phase	Cations: Ca^{2+} , Ba^{2+} , Sr^{2+} , Na^+ , etc. Anions: HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^- , etc.

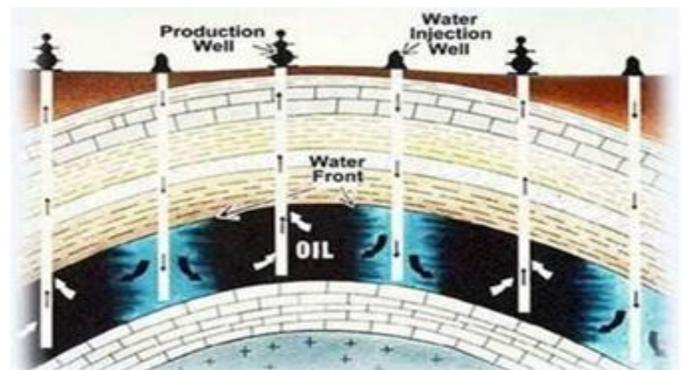


Figure 2. A simplified schematic view of water flooding as a popular EOR method [44].

Table 2. Water chemistries of the produced (formation) water and the injected seawater in North Sea oilfield operated by BP (a major oil company).

Ions	Produced water in field A (ppm)	Produced water in field B (ppm)	Injected seawater (ppm)
Na^+	52555	65340	10890
K^+	3507	5640	460
Mg^{2+}	2249	2325	1368
Ca^{2+}	34675	30185	428
Sr^{2+}	1157	1085	8
Ba^{2+}	91	485	0
Cl^-	153025	167400	19700
SO_4^{2-}	44	0	2960
CO_3^{2-}	0	0	0
HCO_3^-	134	76	124

4 INFLUENCE OF SCALE FORMATION ON CORROSION OF TUBING MATERIALS

The scale formation affects the corrosion behavior of the tubing materials by changing the morphology and physiochemical properties of the surface layers. If a dense and non-porous scale form, it can cover a portion of the steel surface and acts as a diffusion barrier between the corrosive species, such as hydrogen ions, and the metal surface. In CO_2 corrosion environments, FeCO_3 is the common type of the corrosion product scale. The FeCO_3 layer is believed to be protective if its precipitation rate exceeded that of corrosion rate, while a dense scale was formed on the surface [22]. When the precipitation rate is lower than the corrosion rate, a porous and non-protective scale will form. Even a thin layer of a dense iron carbonate scale can significantly reduce corrosion rate. Figure 3 shows how a thin layer of FeCO_3 , only 4-6 μm , offers a good protectiveness and reduces corrosion rate [45]. In the downhole condition of oil wells, due to the presence of Ca^{2+} and HCO_3^- , formation of CaCO_3 is expected. The formation of CaCO_3 can affect the corrosion behavior of tubing and interfere protectiveness of pure FeCO_3 layers. X. Jiang, *et al.*, claimed that presence of Ca^{2+} in the system accelerated the pitting corrosion rate [46]. Indeed, they reported the formation of a mixed calcium and iron carbonate at higher temperatures. Ding, *et al.*, performed experiments at 75 °C and partial pressure of CO_2 up to 10 bar with different concentrations of Ca^{2+} . They claimed the presence of calcium ions increased the general corrosion rate and changed the morphology of corrosion product layers in compare to the tests without calcium [28]. Other than CaCO_3 scale, BaSO_4 and SrSO_4 are expected in downhole environments especially in water flooding systems. The K_{sp} for BaSO_4 and SrSO_4 in pure water at 25 °C are 1.15×10^{-10} and 3.8×10^{-7} [21]. This means that they are sparingly soluble in water. Therefore, presence of only of 10 ppm Ba^{2+} or 50 ppm Sr^{2+} with 100 ppm SO_4^{2-} results in formation of BaSO_4 and SrSO_4 at room temperature. Unlike CaCO_3 , there is almost no data in the literature about the influence of BaSO_4 and SrSO_4 scale on the corrosion of tubing steel in downhole condition.

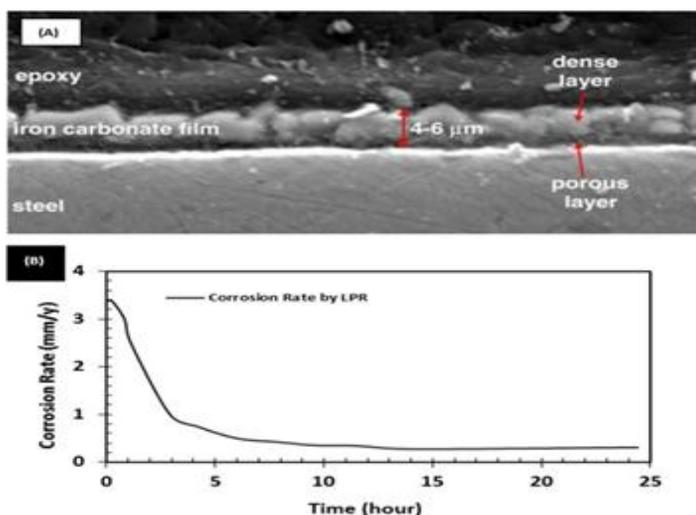


Figure 3. (A) Cross sectional SEM image of a steel specimen shows formation of a dense and protective iron carbonate layer. Image (B) shows the experimentally measured corrosion rate by LPR technique; reduction of corrosion rate due to formation of protective surface layer.

5 CONCLUSION

Scale formation in the extreme condition of oil wells is very possible. Barium and strontium sulfate are common type of scale reported in the water flooding systems. Barium and strontium sulfate are not soluble in acid solution thus, they are usually removed by mechanical treatments. Calcium and iron carbonate have similar crystal structure, therefore, they can co-exist as a solid solution. A carbonates solid solution ($\text{Fe}_x\text{Ca}_y\text{CO}_3$, $x+y=1$) is not as protective as pure iron carbonate. Pure iron carbonate can be protective if its precipitation rate exceed that of corrosion rate. Literature data shows that presence of Ca^{2+} can accelerate both pitting and general corrosion rate. However, more experiments that are systematic needed in this area. Almost there is no data about the protective properties of barium and strontium sulfate and their interaction with iron carbonate in oilfield condition.

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