

Scaling and Corrosion in Oil Production-How Do They Relate to Each other?

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Abstract— Formation of mineral scales and metallic corrosion are main concerns in flow assurance of oil production wells. Carbonates, sulfates, oxides and hydroxides are compounds observed in oilfield condition. Formation of such solid compounds, due to characteristics of the brine and/or corrosion processes, reduce the effective internal diameter of the production tubing in the well's column. Presence of acid gases such as CO₂ and H₂S in aqueous environment of oil wells triggers chemical and electrochemical reactions involved in metallic corrosion. At the first glance, scaling and corrosion are separate issues, but in fact, they can influence each other. Corrosion products such as iron carbonate, any forms of iron sulfides and/or iron oxides are directly affected by the magnitude of corrosion rate. On the other hand, formation of scales on the surface of tubulars either decrease or increase the corrosion rate depends on the physiochemical characteristics of the surface layers. This paper briefly reviews such interaction between main mineral scales and corrosion processes in oil well condition based on the available literature data.

Index Terms— Oilfield scale, Corrosion, Oil well, Tubing, FeCO₃, CaCO₃.

I. INTRODUCTION

World's energy mainly depends on hydrocarbon production [1]. Hydrocarbon is transported via pipeline networks from production zones to processing facilities and then to end users at downstream [2]. Pipeline failure due to corrosion is a major concern in oilfields [3]–[12]. Many studies have been conducted to understand the corrosion of pipelines in aqueous environments [13]–[15].

Downhole condition with high temperature and pressure combined with high concentration of dissolved ions favors 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]. Calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), barium sulfate (BaSO₄), and strontium sulfate (SrSO₄) are the main forms of scales reported in oilfields. BaSO₄ and SrSO₄ are more seen in high pressure and high temperature of downhole environments [18].

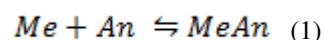
The water injection (water flooding) is one of the common practices in oil industry as a form of enhanced oil recovery (EOR), especially in offshore production where the seawater is available. Water flooding is employed to maintain the

pressure of oil reservoir and thus prevent declining of production rate when the oil reservoir is aging. Injection of seawater into reservoir accelerate the formation of BaSO₄ and SrSO₄ by introducing a considerable amount of sulfate ions (SO₄²⁻) which normally present in seawater. Presence of Ba²⁺ and Sr²⁺ into water formation comingling with the SO₄²⁻ coming from water flooding, favors precipitation of BaSO₄ and/or SrSO₄. In such conditions, oil operators use scale inhibitors to prevent scale formation into the system [19], [20].

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 physiochemical properties of the surface layers. Pure iron carbonate layers can offer protectiveness against corrosion if its precipitation rate is higher than corrosion rate [13]. 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 Fe_xCa_yCO₃ where x+y=1. Co-existence of calcium and iron carbonate within a soil 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 [21]–[23]. 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 CaCO₃ scale on the corrosion of carbon steel [24]–[31]. However, the influence of BaSO₄ and SrSO₄ precipitation on corrosion behavior of carbon steel in downhole condition and the formation of FeCO₃ layer is not investigated or at least documented.

II. GENERAL MECHANISM OF SCALE FORMATION

Mineral scales generally forms when constituents are paired as described in Equation (1):



where Me represents cation species such as Ca²⁺, Ba²⁺ and An represents anion scale forming constituents such as CO₃²⁻ and SO₄²⁻. The precipitation happens when the water solution (brine) becomes oversaturated with respect to that particular scale. Saturation level is an essential parameter to

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evaluate the scale formation either thermodynamically or kinetically. Saturation level is defined as the ration of the ion activity product over the solubility product limit at the system condition, Equation (2):

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

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

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

Where T is the absolute temperature in Kelvin and I is the ionic strength of the solution [32].

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 [33]. 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.

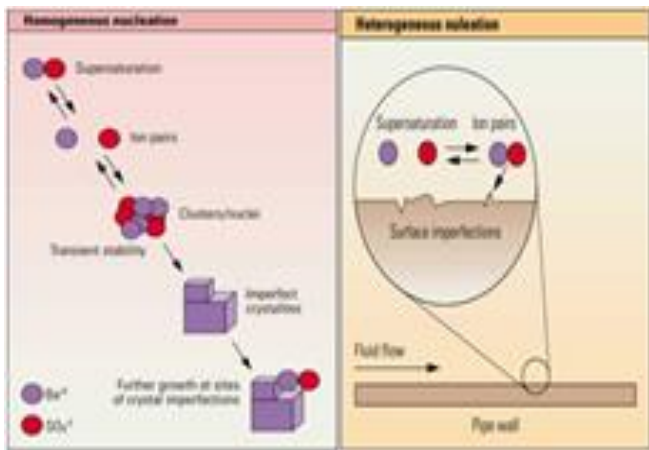


Figure 1. Left: Scale growth mechanism in the bulk of liquid phase (homogeneous). Right: Scale growth mechanism on the preexisting surface defects (heterogeneous) [33].

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 [34], [35]

III. 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 [36], [37]. 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 [38]. 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 [39]. 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 well

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

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

Temperature	30-175 °C
Total pressure	20-450 bar
Components in gas phase	CO ₂ , H ₂ S, 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.

IV. THE IMPACT OF SCALING 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 CO₂ corrosion environments, FeCO₃ is the common type of the corrosion product scale. The FeCO₃ layer is believed to be protective if its precipitation rate exceeded that of corrosion

rate, while a dense scale was formed on the surface [13]. 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 FeCO₃, only 4-6 μm, offers a good protectiveness and reduces corrosion rate [41].

In the downhole condition of oil wells, due to the presence of Ca²⁺ and HCO₃⁻, formation of CaCO₃ is expected. The formation of CaCO₃ can affect the corrosion behavior of tubing and interfere protectiveness of pure FeCO₃ layers. X. Jiang, *et al.*, claimed that presence of Ca²⁺ in to the system accelerated the pitting corrosion rate [42]. 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 CO₂ up to 10 bar with different concentrations of Ca²⁺. 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 [26].

Other than CaCO₃ scale, BaSO₄ and SrSO₄ are expected in downhole environments especially in water flooding systems. The K_{sp} for BaSO₄ and SrSO₄ in pure water at 25 °C are 1.15×10⁻¹⁰ and 3.8×10⁻⁷ [20]. This means that they are sparingly soluble in water. Therefore, presence of only of 10 ppm Ba²⁺ or 50 ppm Sr²⁺ with 100 ppm SO₄²⁻ results in formation of BaSO₄ and SrSO₄ at room temperature. Unlike CaCO₃, there is almost no data in the literature about the influence of BaSO₄ and SrSO₄ scale on the corrosion of tubing steel in downhole condition.

V. CONCLUSIONS

High pressure and temperature of oil wells along with high concentration of dissolved ions favors precipitation of corrosion products and scales. 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 (Fe_xCa_yCO₃, 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 high concentration of Ca²⁺ can accelerate both pitting and general corrosion rate. However, more systematic experiments are needed in this area. Almost there is no data about the protective properties of other scales such as barium and strontium sulfate and their interaction with iron carbonate in oilfield condition.

REFERENCES

- [1] H. Mansoori, D. Mowla, and A. Mohammadi, "Natural Gas Hydrate Deposits-An Unconventional Energy Resource," *J. Explor. Prod. Oil Gas*, vol. 1, no. 84, pp. 33–38, 2012.
- [2] H. Mansoori, V. Mobeidifard, A. M. kouhpeyma, and A. H. Mohammadi, "Study Finds Simulation Flaws in Multiphase Environment," *Oil Gas J.*, vol. 112, no. 11, pp. 102–105, 2014.
- [3] M. Orazem, *Underground Pipeline Corrosion*. Elsevier, 2014.
- [4] H. Mansoori, R. Mirzaee, and A. H. Mohammadi, "Pitting Corrosion Failures of Natural Gas Transmission Pipelines," presented at the International Petroleum Technology Conference, Beijing, China, 2013.
- [5] W. Zhiying *et al.*, "Stress Corrosion Crack Initiation Behavior for the X70 Pipeline Steel Beneath a Disbonded Coating," *Acta Metall. Sin.*, vol. 48, no. 10, pp. 1267–1272, Oct. 2012.
- [6] H. Mansouri, S. A. Alavi, R. Javaherdashti, H. Esmaeili, H. Mansouri, and A. Kariman, "pH effect microbial corrosion of Corten steel and Carbon steel in oily waste water with *Pseudomonas Aeruginosa*," *IOSR J. Eng.*, vol. 04, no. 01, pp. 28–32, 2014.
- [7] Z. A. Majid, R. Mohsin, Z. Yaacob, and Z. Hassan, "Failure analysis of natural gas pipes," *Eng. Fail. Anal.*, vol. 17, no. 4, pp. 818–837, Jun. 2010.
- [8] H. Mansoori, R. Mirzaee, A. H. Mohammadi, and F. Esmaeelzadeh, "Acid Washes, Oxygenate Scavengers Work Against Gas Gathering Failures," *OIL GAS J.*, vol. 111, no. 7, pp. 106–111, 2013.
- [9] F. M. Sani, A. Afshar, and M. Mohammadi, "Evaluation of the Simultaneous Effects of Sulfate Reducing Bacteria, Soil Type and Moisture Content on Corrosion Behavior of Buried Carbon Steel API 5L X65," *Int. J. Electrochem. Sci.*, vol. 11, no. 5, pp. 3887–3907, 2016.
- [10] H. Mansoori, R. Mirzaee, F. Esmaeelzadeh, and D. Mowla, "Altering CP Criteria Part of Unified Anti-SCC Approach," *Oil Gas J.*, vol. 111, no. 12, pp. 88–93, 2013.
- [11] H. Mansoori, "Determination of Optimum C-value in Erosional Velocity Formula for Parsian Gas Field," M.Sc. Thesis, Shiraz University, Shiraz, Iran, 2012.
- [12] Mansoori, "Formation of Natural Gas Hydrate in Gas Pipelines and its Impact on Initiation of Corrosion Processes," presented at the The First International Conference of Oil, Gas, Petrochemical and Power Plant, 2012.
- [13] S. Nešić, "Key Issues Related to Modelling of Internal Corrosion of Oil and Gas Pipelines – A Review," *Corros. Sci.*, vol. 49, no. 12, pp. 4308–4338, Dec. 2007.
- [14] C. de Waard, U. Lotz, and D. E. Milliams, "Predictive Model for CO₂ Corrosion Engineering in Wet Natural Gas Pipelines," *CORROSION*, vol. 47, no. 12, pp. 976–985, Dec. 1991.
- [15] H. Esmaeili and H. Mansouri, "Failure Analysis of Air Cooler Tubes in a Gas Refinery," *Int. J. Sci. Eng. Investig.*, vol. 6, no. 62, pp. 191–195, 2017.
- [16] J. E. Oddo, M. B. Tomson, and others, "Why Scale Forms in the Oil Field and Methods to Predict It," *SPE Prod. Facil.*, vol. 9, no. 01, pp. 47–54, 1994.
- [17] J. C. Cowan and D. J. Weintritt, *Water-formed Scale Deposits*. Gulf Publishing Company, Book Division, 1976.
- [18] S. He, A. T. Kan, and M. B. Tomson, "Mathematical Inhibitor Model for Barium Sulfate Scale Control," *Langmuir*, vol. 12, no. 7, pp. 1901–1905, Jan. 1996.
- [19] P. G. Bedrikovetsky, R. P. J. Lopes, P. M. Gladstone, F. F. Rosario, M. C. Bezerra, and E. A. Lima, "Barium Sulphate Oilfield Scaling: Mathematical and Laboratory Modelling," presented at the SPE International Symposium on Oilfield Scale, 2004.
- [20] A. G. Collins and J. W. Davis, "Solubility of barium and strontium sulfates in strong electrolyte solutions," *Environ. Sci. Technol.*, vol. 5, no. 10, pp. 1039–1043, Oct. 1971.
- [21] S. M. Hoseinih and T. Shahrabi, "Influence of ionic species on scaling and corrosion performance of AISI 316L rotating disk electrodes in artificial seawater," *Desalination*, vol. 409, pp. 32–46, May 2017.
- [22] J. Zhijun, D. Cuiwei, and L. Zhiyong, "Effect of Calcium Ions on CO₂ Corrosion of 3Cr Low-Alloy Steel," *Acta Metall. Sin. Engl. Lett.*, vol. 24, no. 5, pp. 373–380, 2011.
- [23] S. L. Wu, Z. D. Cui, F. He, Z. Q. Bai, S. L. Zhu, and X. J. Yang, "Characterization of the surface film formed from carbon dioxide corrosion on N80 steel," *Mater. Lett.*, vol. 58, no. 6, pp. 1076–1081, 2004.
- [24] L. Sanders, X. Hu, E. Mavredaki, V. Eroini, R. Barker, and A. Neville, "Assessment of Combined Scale/Corrosion Inhibitors – A Acombined Jar Test/Bubble Cell," *J. Pet. Sci. Eng.*, vol. 118, pp. 126–139, 2014.
- [25] Z. F. Yin, W. Z. Zhao, Y. R. Feng, and S. D. Zhu, "Characterisation of CO₂ corrosion scale in simulated solution with Cl⁻ ion under turbulent flow conditions," *Corros. Eng. Sci. Technol.*, vol. 44, no. 6, pp. 453–461, Dec. 2009.
- [26] C. Ding, K. Gao, and C. Chen, "Effect of Ca²⁺ on CO₂ corrosion properties of X65 pipeline steel," *Int. J. Miner. Metall. Mater.*, vol. 16, no. 6, pp. 661–666, Dec. 2009.
- [27] L. M. Tavares, E. M. da Costa, J. J. de O. Andrade, R. Hubler, and B. Huet, "Effect of Calcium Carbonate on Low Carbon Steel Corrosion Behavior in Saline CO₂ High Pressure Environments," *Appl. Surf. Sci.*, vol. 359, pp. 143–152, Dec. 2015.
- [28] N. Sridhar, D. S. Dunn, A. M. Anderko, M. M. Lencka, and H. U. Schutt, "Effects of water and gas compositions on the internal corrosion of gas pipelines-modeling and experimental studies," *Corrosion*, vol. 57, no. 3, pp. 221–235, 2001.

Scaling and Corrosion in Oil Production-How Do They Relate to Each other?

- [29] E. Eriksrud and T. Sontvedt, "Effect of Flow on CO₂ Corrosion Rates in Real and Synthetic Formation Waters," Proc. Corros. Symp. CO₂ Corros. Oil Gas Ind. NACE, vol. 1, pp. 20–38, 1984.
- [30] G. ZHAO, X. LU, J. XIANG, and Y. HAN, "Formation Characteristic of CO₂ Corrosion Product Layer of P110 Steel Investigated by SEM and Electrochemical Techniques," J. Iron Steel Res. Int., vol. 16, no. 4, pp. 89–94, Jul. 2009.
- [31] G. A. Zhang and Y. F. Cheng, "Localized corrosion of carbon steel in a CO₂-saturated oilfield formation water," Electrochimica Acta, vol. 56, no. 3, pp. 1676–1685, 2011.
- [32] W. Sun, S. Nešić, and R. C. Woollam, "The Effect of Temperature and Ionic Strength on Iron Carbonate (Feco₃) Solubility Limit," Corros. Sci., vol. 51, no. 6, pp. 1273–1276, 2009.
- [33] M. Crabtree, D. Eslinger, P. Fletcher, A. Johnson, and G. King, "Fight scale - removal and prevention," Oilfield Rev., pp. 30–45, 1999.
- [34] J. R. Kerr et al., "Sulfide Scale Control: A High Efficacy Breakthrough Using an Innovative Class of Polymeric Inhibitors," 2014.
- [35] C. E. Inches, K. El Doueiri, and K. S. Sorbie, "Green Inhibitors: Mechanisms in the Control of Barium Sulfate Scale," presented at the CORROSION 2006, 2006.
- [36] G. V. Chilingar, R. Mourhatch, and G. D. Al-Qahtani, The Fundamentals of Corrosion and Scaling for Petroleum & Environmental Engineers. Elsevier, 2013.
- [37] M. Abdou et al., "Finding Value in Formation Water," Oilfield Rev., vol. 23, no. 1, pp. 24–35, 2011.
- [38] H. Mansoori, D. Mowla, F. Esmaelzadeh, and A. H. Mohammadi, "Case Study: Production Benefits from Increasing C-Values," OIL GAS J., vol. 111, no. 6, pp. 64–69, 2013.
- [39] M. M. Jordan, K. Sjuraether, G. Seland, H. Gilje, and others, "The Use of Scale Inhibitor Squeeze Placement Software to Extend Squeeze Life and Reduce Operating Costs in Mature High Temperature Oilfields," Corros. 2000, 2000.
- [40] Admin, "PILOT OF WATER INJECTION," Petroblogger.com, 16-Jan-2011. .
- [41] W. Sun and S. Nešić, "A Mechanistic Model of Uniform Hydrogen Sulfide/Carbon Dioxide Corrosion of Mild Steel," CORROSION, vol. 65, no. 5, pp. 291–307, May 2009.
- [42] X. Jiang, Y. G. Zheng, D. R. Qu, and W. Ke, "Effect of calcium ions on pitting corrosion and inhibition performance in CO₂ corrosion of N80 steel," Corros. Sci., vol. 48, no. 10, pp. 3091–3108, Oct. 2006.