World Journal of Engineering and Technology, 2024, 12, 426-437
https://www.scirp.org/journal/wjet
ISSN Online: 2331-4249
ISSN Print: 2331-4222

Corrosion and Scaling Threat in Upstream Oil Operation

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How to cite this paper: Ullattumpoyil, N., Al-Ghamdi, T.M. and Al-Hajri, N.R. (2024) Corrosion and Scaling Threat in Upstream Oil Operation. *World Journal of Engineering and Technology*, **12**, 426-437.
https://doi.org/10.4236/wjet.2024.122027

Received: April 28, 2024
Accepted: May 25, 2024
Published: May 28, 2024

Abstract

Corrosiveness or scaling is an inherent threat to oil operations. The primary cause for this threat is the presence of water having complex geochemical matrix. Unanticipated water production, particularly if it contains unwanted impurities, can significantly impact hydrocarbon production. The current paper discusses the degree of threat posed to oil operation facilities based on the water characteristics. Methodology involved the collection and analysis of water samples from major sources in oil industry such as groundwater, wellheads and seawater. The parameters tested include geochemical, microbiological and pollutants. The lab data was used to develop scaling and corrosion prediction indices such as Langelier Saturation Index (LSI), Ryznar Stability Index (RSI) and Puckorius Scaling Index (PSI). The study indicated varying water chemistry for different sources. Mixing of those waters may lead to ionic saturation and scaling in different facilities. Presence of the SRB and GAB in some water sources also posed threat to water system by forming fouling and corrosion. Seawater used for offshore oilfields water injection to maintain reservoir pressure and improve oil recovery showed scaling tendency, whereas under different reservoir pressure, it can cause corrosion. Some of the samples also had corrosion residuals such as iron, which indicated active corrosion. Current study showed higher alkalinity with high sulfate for one groundwater sample with presence of active corrosion residuals such as dissolved iron and manganese. The study showed positive value for LSI which indicated supersaturation of the water samples with respect to calcium carbonate ($CaCO_3$) and scale forming. Similarly, for RSI and PSI, the value was below six which confirmed the scaling potential for all the samples. Even though the index value was pointing towards scaling potential, the geochemistry, microbiology and presence of other impurities indicated corrosion threat to the oil and gas industrial facilities. The study concluded the importance of different scale inhibition mechanism and corrosion control in Oil and Gas industry.

Keywords

Formation Water, Petroleum Reservoirs, Groundwater, Saturation Indices, Corrosiveness

1. Introduction

Within the oil and gas industry, water is produced as a by-product. The water could be either from direct formation or from different sources such as groundwater and seawater, which are used during production activities for different purposes such as improved oil recovery and gas oil separation process. The processes and systems involved in producing and distributing oil and gas are highly complex, capital-intensive, and require state-of-the-art technology. The presence of water can result in many production challenges, including the formation of mineral scales, increased corrosion of metallic equipment, gas well loading, emulsions, and bacterial activity. While water, to the oil and gas industry, is viewed as a by-product of production, it can yield vital information on the reservoir characteristics, corrosiveness within a well, the tendency for the deposition of mineral scales, and influences many other factors pertaining to oil and gas production. Without water, many of the production challenges experienced within the oil and gas industry would be substantially minimized. An accurate water analysis can indicate the tendency for many of these production problems. A water analysis is one of the basic analytical tests performed within the oil and gas industry; however, its accuracy and interpretation are often left to chance.

Scale and corrosion can be a major cause of equipment failure and related problems in oil and gas industry. Corrosion and scaling processes are complex and interactive. It is most often an issue with wells that produce a great deal of water. Corrosion is the destruction of a metal by chemical or electrochemical action of the surrounding environment. Water corrosivity depends on many factors including pH, oxygen content, the presence of metabolizing bacteria, and its suspended solids, which tends to promote microbially assisted corrosion. Localized corrosion processes, such as that related to bacterial sulphate reduction, can cause severe damage to steel. Scales are inorganic deposits formed due to the precipitation of solids resulting from brines that are present in the oilfield reservoir and production system. Due to geochemical processes between injection water, connate water and rock, the complex composition of reservoir fluids makes it difficult to control the inorganic scale formation. The scale formation depends on several factors that include, but not limited to, temperature, pressures, solution saturation and hydrodynamic behavior of the flow. The tendency of water to deposit insoluble and protective scales is a function of its corrosivity. One of the cost-effective methods of mitigating the corrosion and scale in the oil and gas industry is the use of Corrosion and scale Inhibitors Protection (CIP) technology. In most of the cases, scale dissolver is required to remove the scale, even after utilizing scale inhibitors as a primary control method.

The Kingdom of Saudi Arabia possesses around 17 percent of the world's proven petroleum reserves. Most are located in the Eastern Province. The corrosion and scaling process is very complex and has many causes. One of the major causes is the complex nature of the water system observed in production activities. Hence, the objective of the paper is to discuss the degree of threat posed by corrosion and scaling to oil operation facilities based on water characteristics.

2. Literature Review

Produced water characteristics and its impact to corrosion and scaling are discussed in many studies [1]. Corrosion of metal surfaces is greatly influenced by their chemical composition electronic properties, microstructure, and passive film properties [2]. Since corrosion is linked to almost all pipe failures, it has become a global problem for all stakeholders, in particular engineers and asset managers of buried metal pipes [3]. Experience and investigation of pipe failures suggest that corrosion of metalsis the most predominant cause of pipe failures [4] [5]. In the last two decades, different studies have pointed out to the oil industry the advantages that aluminium alloys may present for tubular manufacturing compared to steel [6] [7]. As is well appreciated, the consequence of pipe failures can be socially, economically, and environmentally catastrophic, resulting in massive disruption of daily life, considerable economic loss, widespread flooding, subsequent environmental pollution and even casualties and so forth [8]. Many studies have shown that high TDS content in produced water is the major cause of scale formation and pipe clogging [9]-[13]. The scale deposit can take place in surface water injection facility, injection wells, formation, production well, topside production facilities, pipelines, and at disposal wells [14]. The production capacity can reach zero within a few hours and could cause a huge treatment cost [15]. In the case of water injection wells, the scale could deposit in the formation of pores that can reduce the injectivity with time [16]. The variation in rock permeability depends on injection rate and temperature [17] [18]. Scale inhibitors (SIs) are a class of specialty chemicals that is used to slow or prevent scale formation in water systems. There are different types of scales and they are usually prevented by using scale inhibitors [19]. There are different scenarios where scale inhibitors are not totally effective in scale prevention such as when scale formation is not predicted accurately in advance and when placement of inhibitor is non-optimal owing to reservoir heterogeneity [20].

3. Materials and Method

The current study focused on samples collected from seven water sources belonging to shallow well, crude oil well, and seawater; the water types available in upstream oil operation in one of the Saudi Arabian Oil field. The water samples were collected and transported to laboratory using standard procedures. The samples were labelled as Well-A, Well-B, Well-C, Well-D, Well-E, Well-F and Seawater. Well-A to F is groundwater resources used in Gas Oil separation process except Well-D, which is the oil well. Seawater is injected into oil reservoirs for enhanced production. The objective of the sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. Before sample collection began, field personnel took steps to ensure that the samples collected are representative of the system being investigated.

Samples received by the lab are checked for the integrity and logged into the Laboratory Information Management System (LIMS). The samples are then distributed into respective lab sections and performed the geochemical and trace metal analysis. Necessary quality control samples were also run to ensure the accuracy and precision of the data. Lab is equipped with different quality assurance programs including running Certified Reference Materials (CRMs), Lab Control Samples (LCS), Unknown QA and Spike. The data obtained are then reviewed by senior lab chemist and authorized in the system. The lab data further used to develop following indices.

3.1. Langelier Saturation Index

Langelier Saturation Index (LSI) is an equilibrium model derived from the theoretical concept of saturation and provides an indicator of the degree of saturation of water with respect to calcium carbonate and can be calculate from

$$\text{LSI} = \text{pHa} - \text{pHs} \tag{1}$$

where:

pHa: the measured water pH.

pHs: the pH at which water with a given calcium content and alkalinity is in equilibrium with calcium carbonate.

The equation expresses the relationship of pH, calcium, total alkalinity, dissolved solids, and temperature as they are related to the solubility of calcium carbonate in waters with pH of 6.5 to 9.5. This is known as the pH*s*:

$$\text{pHs} = (9.3 + A + B) - (C + D) \tag{2}$$

where:

$$A = \left[\text{Log}_{10}(\text{TDS}) - 1\right]/10 \tag{3}$$

$$B = -13.12 * \text{Log}_{10}\left({}^{\circ}\text{C} + 273\right) + 34.55 \tag{4}$$

$$C = \text{Log}_{10}\left(\text{Ca}^{2+}\ \text{as}\ \text{CaCO}_3\right) - 0.4 \tag{5}$$

$$D = \text{Log}_{10}\left[\text{Alkalinity as CaCO}_3\right] \tag{6}$$

3.2. Ryznar Stability Index (RSI)

The Ryznar index is an empirical method for predicting scaling tendencies of water based on study of operating results with water at various saturation indices. The Stability Index developed by John Ryzner in 1944 used the Langelier Index (LSI) as a component in a new formula to improve the accuracy in predicting the scaling or corrosion tendencies of water.

The Ryznar index (RSI) takes the form:

$$\text{RSI} = 2\text{pHs} - \text{pH} = \text{pHs} - \text{LSI} \tag{7}$$

The criteria used to give an indication of the stability indices are summarized in Table 1.

3.3. Puckorius Scaling Index (PSI)

The Puckorius scaling index is calculated in a manner similar to the Ryznar stability index. The Puckorius scaling index provides another tool for evaluating the calcium carbonate scale potential for water and is included in the Water Cycle indices of calcium carbonate scale potential. LSI, RSI, and PSI are designed to be predictive tools for calcium carbonate scale only. They are not suitable for estimating calcium phosphate, calcium sulfate, silica or magnesium silicate scale. The PSI can be calculated as follows:

$$\text{PSI} = 2\text{pHs} - \text{pHeq} \tag{8}$$

where

$$\text{pHeq} = 1.465\log\left(\text{M alk}\right) + 4.54 \tag{9}$$

4. Results and Discussion

Geochemical analysis was performed for water samples collected from the selected

Table 1. Summary of water stability indices.

Index Value	Water Condition
LSI > 0	Water is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming and $CaCO_3$ precipitation may occur.
LSI = 0	Water is considered to be neutral. Neither scale-forming nor scale removing. Saturated, $CaCO_3$ is in equilibrium. Borderline scale potential.
LSI < 0	Water is under saturated with respect to calcium carbonate. Under saturated water has tendency to remove existing calcium carbonate protective coatings in pipelines and equipment. No potential to scale, the water will dissolve $CaCO_3$.
RSI, PSI ≤ 6	Supersaturated, tend to precipitate $CaCO_3$. The scale tendency increases as the index decrease.
6 < RSI, PSI < 7	Saturated, $CaCO_3$ is in equilibrium. The calcium carbonate formation probably does not lead to a protective corrosion inhibitor film.
RSI, PSI ≥ 7	Under saturated, tend to dissolved $CaCO_3$. Mild steel corrosion becomes an increasing problem.

six wells named Well A, Well B, Well C, Well D, Well E, Well F and one seawater. The collected water samples were analyzed for different geochemical parameters by following the standard procedures. Similarly, different index values were also calculated based on the equations mentioned in the methodology section. The results are tabulated in Table 2.

4.1. Physical Characteristics

One of the most important properties of water is its pH. The pH is a measure of the acidity or alkalinity of water. It is extremely important in a water analysis for several reasons. The solubility of calcium carbonate ($CaCO_3$) and iron compounds is highly dependent on the pH of the water. Generally, oil-field waters have a pH ranging from 5.0 - 8.0. If water's pH is below 7.0, it is said to be acidic, and corrosion rates can increase. If water's pH is above 7.0, it is said to be alkaline in nature, and calcium carbonate and iron compounds are less soluble.

With increasing amounts of acid gases (hydrogen sulfide and carbon dioxide) the pH of the water will decrease. Understanding their effect on pH will help us to understand and predict their impact on the corrosivity of the water. The constituents affecting the pH are very unstable upon a pressure release (*i.e.*, H_2S, CO_2, HCO_3), therefore, the pH of water will rapidly change when removed from a pressurized system. Dissolved carbon dioxide acid gas or dissolved hydrogen sulfide gas present in the water, when combined with the low pH and high chloride content, would indicate the water is potentially corrosive in nature. It is

Table 2. Geochemical analysis results for the respective wells.

Well/Tests	Well A	Well B	Well C	Well D	Well E	Well F	Sea Water
pH	7.62	6.98	6.75	6.93	6.95	7.15	6.97
Conductivity mS/cm	6540	32,700	34,900	14,900	124,000	3050	72,400
Sp. Gravity	1.0034	1.0163	1.0182	1.0073	1.0715	1.0015	1.0404
Ca mg/L	351	1370	5260	692	12,000	111	558
Mg mg/L	128	440	108	111	1520	30	1880
Na mg/L	890	5600	2400	2400	24,000	490	18,000
K mg/L	35	221	121	132	1270	14	579
Dissolved Fe, mg/L	0.54	0.61	1.55	10.8	_		
Sr, mg/L	9	35	12	13	550	1.2	12
Cl mg/L	1790	12,300	13,200	4700	58,900	715	31,300
Sulfate mg/L	771	935	950	994	516	246	4460
T. Alkalinity mg/L	170	153	182	194	390	216	95
LSI	**1.15**	**0.98**	**1.41**	**0.77**	**1.98**	**0.11**	**0.13**
RSI	**5.32**	**5.01**	**3.93**	**5.38**	**3.00**	**6.93**	**6.70**
PSI	**5.00**	**4.12**	**2.70**	**4.29**	**1.57**	**5.99**	**6.11**

imperative that the pH be measured immediately upon sampling. For the present study all the water sources indicated pH values (Laboratory value) between 6.0 and 8.0.

Electrical Conductivity gives a preliminary indication of how much of ions are dissolved in the system. Total dissolved solids (TDS) gives an idea about the scaling tendency of water. Normally EC, Sp. Gravity and TDS all are indication of level of ions in water. In the present study, the concentration of dissolved solids varies between the sources. Well-F had the least dissolved solids for the shallow groundwater, whereas deep crude formation water showed highest dissolved solids. Seawater reported to have comparatively higher salinity.

4.2. Major Cations

1) Calcium (Ca)

The calcium ion is a major constituent of oilfield brines and can range in concentration up to 30,000 mg/L, although it is generally much lower. This ion is of major importance due to its ability to combine with bicarbonate, carbonate or sulfate ions and precipitate mineral scales, adherent and/or suspended. In our present study calcium ion concentration ranged from 111 mg/L to 12,000 mg/L, which is proportion to electrical conductivity values. Seawater showed comparatively less calcium level with respect to deep formation.

2) Magnesium (Mg)

The magnesium ion concentration is generally much lower than the calcium ion concentration. The primary importance of the magnesium ion is also its ability to form scales with the carbonate ions; however, these magnesium scales are 50 times more soluble in water than the $CaCO_3$. Most other magnesium salts, such as $MgSO_4$ are quite soluble in water and cause few problems in the oil-field environment.

3) Sodium (Na)

Most sodium salts are soluble in water; therefore, sodium is a major constituent of oil-field and drinking waters. Generally, sodium does not result in any specific problems. The exception would be the precipitation of sodium chloride (NaCl) from extremely salty brines.

4) Dissolved Iron (Fe)

Natural iron content in most oil-field waters varies. Many times, its presence signifies active corrosion. Iron counts are often utilized in “sweet” systems to monitor and semi-quantify corrosion rates. In “sour” systems, the iron will be present as a form of iron sulfide and is often responsible for plugging issues down hole or within surface equipment. Iron sulfide is almost always an indicator of corrosion, bacterial activity, or incompatible mixtures of water. Similarly, high Iron and Manganese levels can be indicative of active corrosion occurring down hole or in surface equipment. From the current study the Well-D have higher alkalinity with high sulfate concentration, which can cause higher corrosion which is confirmed by indicating high dissolved iron and manganese in this sample. The same sample was analyzed for SRB’s indicating higher population.

5) Strontium (Sr)

Strontium is important because of its ability to combine with sulfate ion and precipitate insoluble strontium sulfate. The formation of strontium sulfate will result in serious plugging problems. Although more soluble than the barium sulfate, it is very likely to co-precipitate with the barium sulfate. The sample collected from the deep formation, Well-E has recorded highest concentration of strontium, which is 550 mg/L. All the shallow wells and seawater samples indicated low level of strontium.

4.3. Major Anions

1) Chloride (Cl)

The chloride is almost always the major anion produced in oil-field brines. It is also a major constituent of fresh waters. Although salt deposition in high saline brines can be a problem, usually the concern with chlorides is that with increasing chlorides comes increasing conductivity and thus, increased corrosion. Furthermore, chlorides are utilized to assist in determining the identity of a producing formation. The chloride levels can assist in monitoring wells for casing or packer leaks as well as flood-water break-through in water flood applications.

2) Carbonates and Bicarbonates (CO_3 and HCO_3)

These ions are important because they are the natural buffer for the water. These ions will influence the pH of water, and the pH of the water will define which ion, or if both ions, are present in a water sample. Bicarbonates are present in waters with pH's ranging from 4.5 - 8.2. Above 8.2, carbonates can also be present. These ions can combine with cations to form insoluble mineral scales. Most carbonate scales are soluble in hydrochloric acid. Comparatively bicarbonates were low in almost all samples, which indicates less tendency for carbonate scaling.

3) Sulfate (SO_4)

The sulfate ion is important because of its ability to react with calcium, barium and/or strontium to form acid insoluble scales. This also serves as a nutrient for sulfate reducing bacteria (SRB's). In the current paper, deep formation has recorded least sulfate level, whereas the seawater showed highest concentration. Similarly, shallow formations also showed moderate level of sulfate. The data indicate that mixing up of water from different sources may lead to calcium sulfate scale deposition. A graphical representation using Tickler diagram was posted to realize the changes in the geochemical ionic concentration with respect source (**Figure 1**).

4.4. Water Stability Indices

Although a number of indices have been developed, none has demonstrated the ability to accurately quantify and predict the corrosively or scaling of water. They can only give a probable indication. Experience has shown that if conditions encourage the formation of a protective calcium carbonate film, then

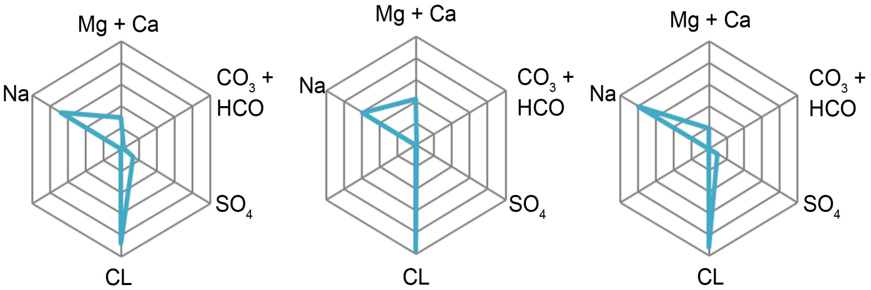

Figure 1. Tickler diagrams for oil well water-D, groundwater-E and seawater.

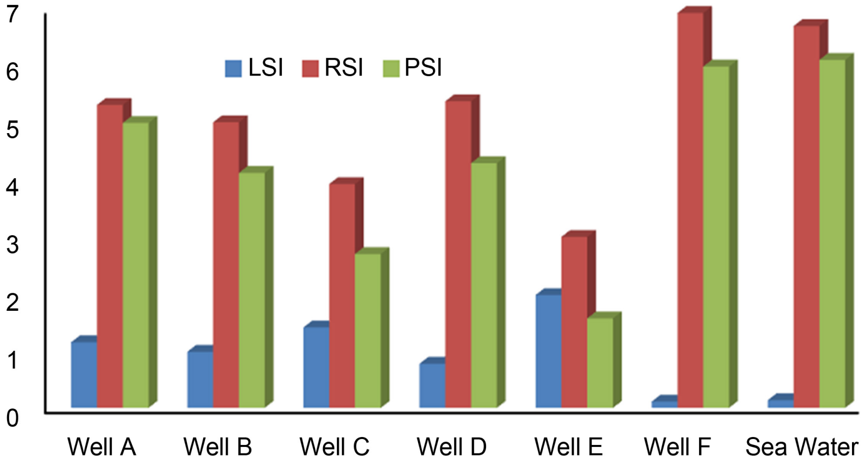

Figure 2. Graphical plot for different scaling indices.

corrosion will generally be minimized. The most common methods used for calculating the stability of water are Langelier saturation index (LSI) and Ryznar stability index (RSI). LSI and RSI are designed to be predictive tools for calcium carbonate scale and they are not suitable for estimating calcium phosphate, calcium sulfate, silica or magnesium silicate scales. In the current paper Langelier Saturation Index varied from 0.13 for seawater to 1.98 for deep formation. The value indicated scaling potential for all the type of samples. Ryznar Stability Index also showed same trend with respect to LSI. Highest RSI was reported for seawater sample, whereas the deep formation has showed the least value showing the tendency for scaling. From the above table, the value of RSI for Well-F and seawater sample has less saturation potential. So, in favorable condition, the system may lead to corrosion. Similar trends were also recorded for Puckorius Scaling Index. Variation of different indices is shown in **Figure 2**.

At present we know that the extent of mineral scaling from water is not wholly dependent upon the water itself, or it's dissolved ion content. The mechanism of mineral scales formation is dependent upon the degree of supersaturation of the water with respect to a particular mineral, the rate of temperature change and changes in the pressure as well as the pH of the water. Thus, where water is used, one can expect a variety of potential deposition problems. Mineral scales are defined as a mineral deposition that results from an oversaturation of a given compound within a solution under a certain set of conditions. Scales can result in plugging problems within the producing formation, within the down hole equipment, and/or within the surface piping/equipment. Additionally, under-deposit corrosion can occur beneath scale depositions, resulting in high corrosion rates and pre-mature failure of production equipment. For the current study all the water samples showed positive value for LSI which indicates that the water is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming and $CaCO_3$ precipitation may occur. Similarly, for RSI and PSI, the value is below six which confirms the scaling potential for all the samples.

5. Conclusion

The current paper discussed the degree of threat posed to oil operation facilities based on the water characteristics. A water analysis can be an extremely informative piece of analytical information. The water analysis can assist in identifying the production zone, contamination to the production zone, the tendency for corrosion and/or scale deposition, plays an integral role in production chemical selection, and can aid in the design and development of secondary and tertiary recovery systems for the oil and gas industry. The cycle of the study includes research review and investigation, field sampling, laboratory experiment and mathematical analysis of the generated data. Samples collected from different sources were tested for geochemical and microbial parameters. The lab data was used to develop scaling and corrosion prediction indices such as Langelier Saturation Index (LSI), Ryznar Stability Index (RSI) and Puckorius Scaling Index (PSI). The study indicated varying water chemistry for different sources based on tickler diagram. Mixing of those waters may lead to ionic saturation and scaling in different facilities. Presence of the SRB and GAB in some water sources also posed threat to water system by forming fouling and corrosion. Seawater used for offshore oilfields water injection to maintain reservoir pressure and improve oil recovery showed scaling tendency, whereas under different reservoir pressure, it can cause corrosion. Some of the samples also had corrosion residuals such as iron, which indicated active corrosion. Presence of sulfate reducing bacteria indicated corrosion threat to the upstream oil and gas facilities. Current study showed higher alkalinity with high sulfate concentration for one of the groundwater which lead to corrosion, which is confirmed by having presence of corrosion residuals dissolved iron and manganese in the sample. The study showed positive value for LSI which indicated supersaturation of the water samples with respect to calcium carbonate ($CaCO_3$) and scale forming. Similarly, for RSI and PSI, the value is below six which confirms the scaling potential for all the samples. Even though the index value was pointing towards scaling potential, the geochemistry, microbiology and presence of other impurities indicated corrosion threat to the oil and gas industrial facilities. The study concluded the importance of different scale inhibition mechanism and corrosion control in Oil and Gas industry.

Acknowledgements

The authors wish to express his gratitude to Saudi Aramco management for allowing us to complete and publish the scientific work.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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