

An Experimental Investigation of Different Formation Waters and Injection Water Incompatibility to Obtain the Optimum Water Mixing Ratio in Injection Processes

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ABSTRACT

Scale formation and well plugging due to the incompatibility of injected waters is a critical field problem in oil recovery. A water injection process was successfully performed when the identification of the source of water, water quality considerations, and laboratory compatibility tests were considered. When different waters are mixed, it is necessary to evaluate their compatibility prior to the injection into oil wells. Jar test is conventionally performed in the laboratory to estimate formation damage by scale formation in the wellbore and facility. The individual waters may be quite stable under all system conditions and present no scale problems. However, once they are mixed, the reaction between ions dissolved in the individual waters may form insoluble products that cause permeability damage in the vicinity of the wellbore. The obtained results from the jar test for different mixtures of waters can be used to know the type of scale in the reservoir. This work was undertaken to experimentally identify the composition of mineral scales that occur in a raw water and different volume mixings. The formation of CaSO_4 , SrSO_4 , and CaCO_3 during the sampling of production waters, including different reservoir layers and mixing of their different volumes with K sample have been proved by scanning electron microscopy micrographs and X-ray diffraction. The results of jar tests for the mixing of different waters indicated that the main constituents of the scale were strontium sulfate and calcium carbonate. The results showed that mixing ratio of 75 to 25% of K water to different produced waters were the most suitable ones.

Keywords: Incompatibility, Formation Damage, Produced Water, Inorganic Scale, Water Injection, Jar Test

INTRODUCTION

Water injection is a widely used method during improved oil recovery stage as it is more cost-sufficient and simple compared to other available enhanced oil recovery (EOR) methods; it also helps to dispose of unwanted produced water from oil

and gas wells in an environmentally responsible fashion. Water quality and compatibility plays an important role in determining the effectiveness of the water injection [1].

Injection water may be derived from different sources such as underground aquifers, produced water from production wells, or surface waters

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as seawater and river water. The produced water can be the result of a mixture of the waters originally present in the petroleum reservoir and different layers, which can be classified as connate water (or formation water), saturation water in the reservoir fluid, aquifer water, and injected water [2, 3]. Typical injection water may contain one or more of these source constituents, blended together in a variety of possible ratios (blend mixtures) over the life of the water [4, 5].

Waters that can be mixed without the formation of precipitation are termed compatible. Henkel reported testing brine and wastewater compatibility by allowing a mixture of the two liquids to stand for from 8 to 24 hours at the approximate aquifer temperature [6]. The mixture is considered compatible if it remains free of precipitates. Others, Lansing and Hewett, Macloed have suggested that this criterion may not be entirely satisfactory in all cases, since reaction may require considerable time for completion and because gaseous reaction products may also cause a reduction in permeability.

The precipitate or scale can be analyzed to determine its composition. When conducting tests for compatibility, water from the proposed injection interval is used rather than the synthesized formation water, because a small difference in water chemistry creates unexpected reactions [7-10]. In addition, synthesizing specific formation water in the laboratory is nearly impossible. Waters are compatible, if they can be mixed without scale formation. The precipitated insoluble compounds are undesirable, because they can deposit in the pores to reduce permeability. Moreover, it causes scale formation in water pumps, flow lines, and on the face of the formation in the wells. Some of more common ions, which are frequently available in oilfield waters and cause precipitation in incompatible water, are barium, strontium, calcium, sulphate, and carbonate [11].

The seawater as injection water is rich in sulphate and carbonate, while the formation water usually contains significant amounts of precipitating cations

such as barium, strontium, and calcium. Therefore, mixing them may cause scale formation in an oil reservoir. Thermodynamic changes as pressure and temperature can be other reasons for scale formation [13]. Solid scale formation mainly results from changes in the 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 [14-16].

There is limitation in the produced water sampling with reliable accuracy due to especial conditions for reservoirs such as high pressure and temperature. Despite this, the analysis of the produced waters can provide valuable information about the formation water fractions and its' chemical compositions. The simplest way of monitoring the chemical variation of the produced water is the inspection of individual analysis in different times. Mixing different water types may, however, cause precipitations in the reservoir or in production wells and equipment. The injected water may also react with the formation causing dissolution [17-20].

For the investigation of the compatibility of the produced waters from different reservoir layers with the Karoon River, their individual and mixed waters chemical composition have been determined. The qualitative and quantitative analyses of different waters and their mixing show that they contain cations of calcium, magnesium, strontium, potassium, and hydrocarbonate and anions of sulfate, carbonate, and chloride. The quantitative composition of salts has been determined by X-ray diffraction (XRD), and scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX).

The results include the assessment of the chemical composition of the produced water and the filtered precipitate by atomic absorption spectroscopy (AAS), XRD, SEM, and analytical methods for identifying waters compatibility at a mixing ratio of the produced waters and Karoon River. The produced water samples were collected from different layers

(reservoirs) in one of the oil fields in southwest of Iran. Also, the injection water is collected from Karoon River. Then, the compatibility of them at different mixing ratios was evaluated from the view of scale formation in each of them.

EXPERIMENTAL PROCEDURES

Material and Apparatus

Experimental methods, namely the AAS, XRD, and SEM, were used to identify the minerals and the composition of the waters. For the AAS method, the samples were analyzed by aspirating through the nebulizer using the atomic absorption spectrophotometer. The numbers of water samples were four samples as the name of F, U, L, and K (Karoon River).

Water Composition and Properties

The pH of the produced water indicates whether a water source is alkaline, neutral, or acidic. Electrical conductivity (EC) is a simple indicator of the level of dissolved mineral in the produced water. EC and pH are water quality characteristics that are helpful to recognize changes and to assess suitability. The concentration and particle size distribution of the dispersed hydrocarbons and suspended solids are important characteristics, which bear upon the water injection process. In addition, water contains a wide range of dissolved and suspended materials that may affect the compatibility of waters. These substances include:

- Major cations (Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Ba^{+2} , Sr^{+2} , and Fe^{+2});
- Major anions (Cl^- , Br^- , SO_4^{-2} , HCO_3^{-1} , CO_3^{-2} , NO_3^{-1} , OH^- , and PO_4^{-3});
- Dissolved gases (CO_2 , H_2S , and O_2);
- Total and oil-free suspended solids.

Mixing of Waters

First, 1000 ml of each non-filtered water is kept constant in the ambient condition. Next, the solution is filtered through a 0.45 μm filter

paper. The produced waters from different layers are mixed with the K water sample according to various mixing ratios as shown in Table 1. The mixed waters were stored for 24 hrs in room conditions and were then filtered through 0.45 micron filter membranes. The filtered waters and filtered precipitate are again analyzed to determine their composition and structures.

Table 1: Mixing ratios of waters.

Sample Pseudo-name	Waters	Mixing Ratios
A	F:K	1:4
B	F:K	1:1
C	F:K	7:3
G	U:L	1:1
D	G:K	1:4
E	G:K	2:3
H	G:K	3:2

Determination Procedures

First, 5 ml of the filtrated water is added to a 50 ml volumetric flask and is diluted with distilled water to make up 50 ml of the solution. This instantaneous dilution is performed in order to prevent scaling precipitation between the filtering and analytical determination of metal ion concentration. The calcium, barium, and strontium determinations are calibrated by measuring five standard solutions. Standard solutions are prepared from CaCl_2 , BaCl_2 , SrCl_2 etc. solutions. Calcium, barium, and strontium concentrations in the diluted filtrates are determined by AAS. After multiplying with the dilution factor, the exact concentrations of calcium, barium, strontium etc. are computed. XRD and SEM were used to identify the composition and structure of the minerals on a filter paper.

RESULTS AND DISCUSSION

Initial Water Composition and Properties

A few selected analyses of the produced water of different reservoir layers and Karoon River are shown in Table 2.

Table 2: Waters compositions of the produced water of different reservoir layers and Karoon River.

Sample Name		U	L	F	K	Standard Method No.
CO ₂ *	mg/l	158	220	352	18	St. Method 2550B
Electrical Conductivity	µmhos/cm at 20°C	227036	288300	418035	1960	St. Method 2510B
TDS	mg/l	147566	146328	210754	1224	St. Method 2540C
Calcium	mg/l	7500	9100	11500	136	St. Method 2340C
Magnesium	mg/l	853	937	1375	43	St. Method 2340C
Alkalinity	mg/l as CaCO ₃	550	138	520	128	St. Method 2320B
Carbonate	mg/l as CO ₃ ⁻²	Trace	Trace	Trace	Trace	St. Method 2320B
Bicarbonate	mg/l as HCO ₃ ⁻¹	671	168	634	156	St. Method 2320B
Chloride	mg/l as Cl ⁻¹	84194	93000	131165	417	St. Method 4500- Cl ⁻¹ E
Sulfate	mg/l as SO ₄ ⁻²	342	157	360	397	St. Method 4500- SO ₄ ⁻² D
Sodium	mg/l	43297	51314	66621	288	ASTM D3561
Potassium	mg/l	332	246	2579	3	ASTM D3561
Strontium	mg/l	1495	1350	1390	5	ASTM D3352
Barium	mg/l	45.4	20.6	14.2	0.6	ASTM D3651

The total dissolved solids (TDS) of the produced waters of reservoirs have typically a 147566–210754 mg/l. Lower TDS is found for Karoon River mainly collected from River in the south of Iran. The strontium contents of the reservoirs are also very similar together. The most important distinctions from K sample are the concentrations of calcium, barium, and strontium, which are very low, but the concentration of carbonate and sulphate are about equal to the produced waters. The results show a lower salinity of K sample compared to the produced water. The obtained results showed that the produced water contains levels of salinity, calcium, and strontium, which are relatively higher than K sample water, while the latter contains higher levels of carbonate and sulphate. Barium concentration is usually low in K water sample but high in the produced waters. Therefore, mixing the formation water, containing high concentrations of cation, with the injection water, containing high anion concentrations, favors the formation of the salt precipitates of scales, which are usually deposited in the oil well. Thus abrupt

decreases in the levels of cations in the produced water, with the concomitant presence of high sulphate and carbonate concentrations may be associated with scaling formation. Although gas solubility in water is generally low, some gases, notably carbon dioxide and H₂S, have finite solubility in aqueous solutions. This solubility is decreased as temperature rises. The problems of the solubilization of gases into the injection water may be created by poorly located pump suction lines, which result in the cavitation or direct suction of the entrained gas along with the injected fluid.

Stiff Diagram

Figure 1 is a “stiff diagram” depicting the ion concentration of the produced waters samples and the Karoon water sample.

The comparison of the obtained stiff diagram of the produced waters and Karoon sample water shows that the composition of the Karoon sample is different from the produced waters but the latter has an almost similar composition.

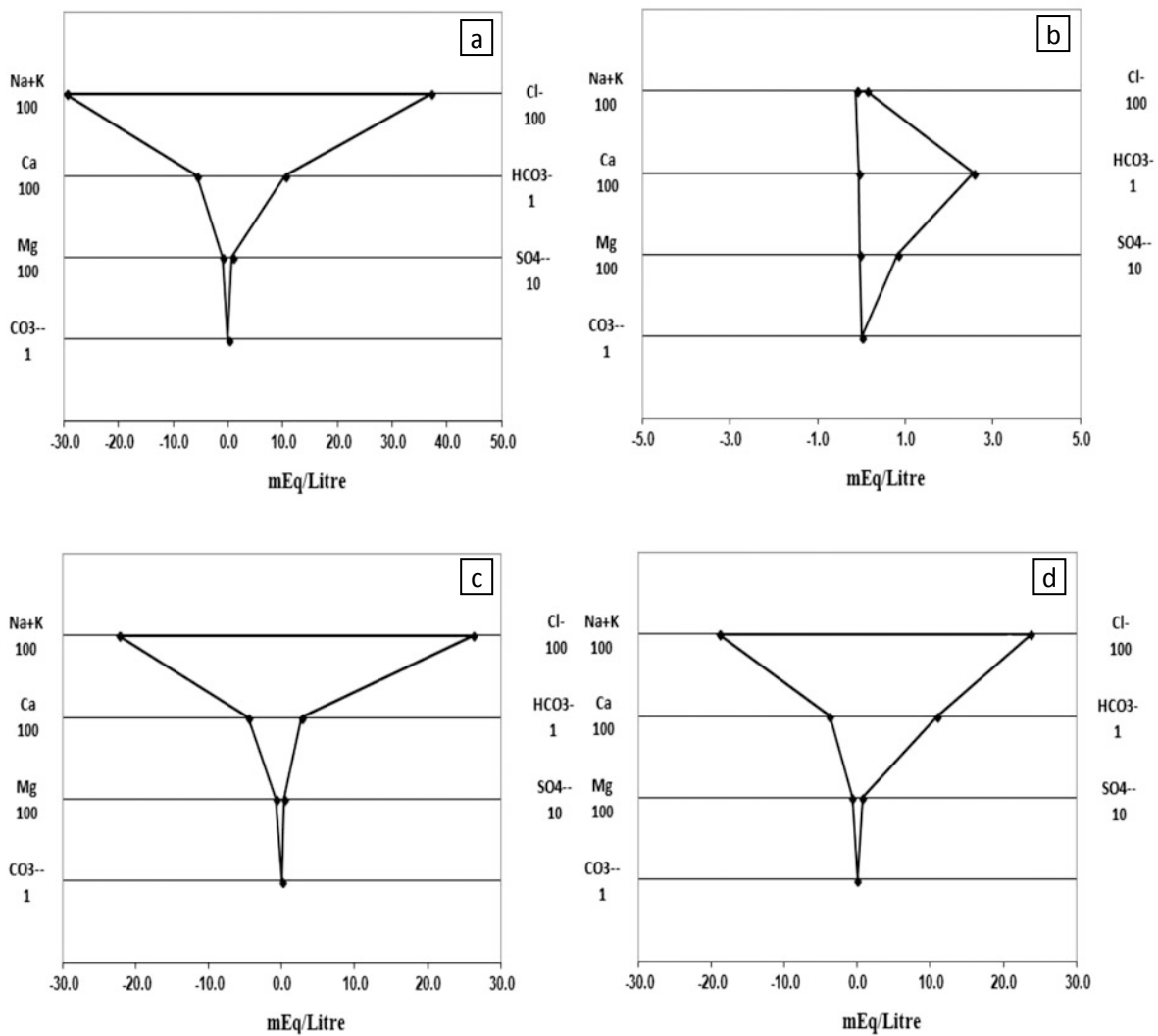


Figure 1: Stiff diagram of different waters: a) F stiff Diagram, b) Karoon Stiff Diagram, c) L Stiff Diagram d) U Stiff Diagram

Analysis of Scales on Filters

Scales and precipitates can be formed in the produced waters from a number of root causes. Changes in the temperature and pressure of the produced waters, as it comes to surface, may initiate pH changes, which may begin the formation of scales. The scale filtered samples were examined by SEM and XRD to observe the particle size and morphology of the precipitates. The formations of CaSO_4 , SrSO_4 , and BaSO_4 during the transition of waters to the surface were detected by SEM micrographs. The morphology of BaSO_4 , CaSO_4 , and SrSO_4 formed in the filtered paper was compared by XRD. The XRD analysis of the membranes

showed barium sulfate scale for U sample and L water samples, while F sample is not detected because of an amorphous structure, since XRD detects crystalline structures. The results are given in Table 3.

To cover the inability of XRD to detect amorphous structures or the low amount of scales, EDX is performed on scales seen by SEM images to determine the types of scales present on the filters. SEM and EDX results are given below. Figures 2 and 3 show the SEM and EDX images of typical scaling crystals in the filtrate precipitated from the produced waters.

Water Composition and Properties

Since the water production started in 2012, the produced water has been mixed with K sample

water for reinjection. The selected analyses of the mixed water are represented in Table 4.

Table 3: XRD analysis of scales (suspended solids) existing within the initial water samples.

Samples	Method	Results
F	XRD	Identified compounds: Amorphous samples
L		BaSO ₄ Barite
U		BaSO ₄ Barite

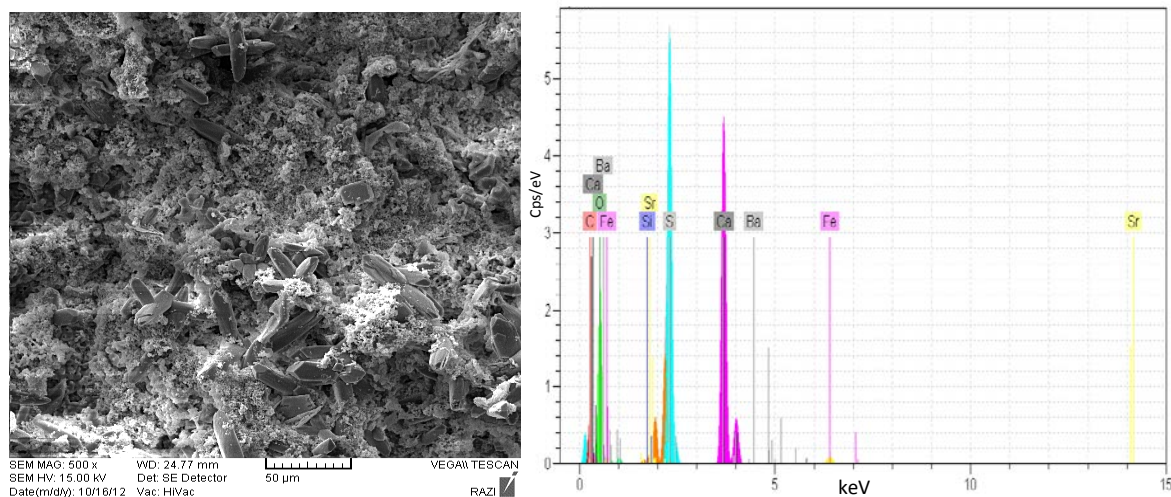


Figure 2: (a) SEM of F produced water filtrate and (b) Spectrum of the elemental analysis of precipitated F produced water.

Table 4: Composition of mixed waters (A, B, C, D, E, and H).

Sample Name		A	B	C	D	E	H
Mixing Ratio		F:K (1:4)	F:K (1:1)	F:K (7:3)	G:K (1:4)	G:K (2:3)	G:K (3:2)
CO ₂	mg/l	<1	<1	<1	<1	<1	<1
Turbidity	NTU	1.19	0.62	1.48	1.25	1.32	2.98
Electrical Cond.	µmhos/cm/20°C	70310	169159	46922	94615	141280	234677
TDS	mg/l	43708	107313	30801	60288	89793	149761
Calcium	mg/l	2430	5815	1765	3400	5034	8090
Magnesium	mg/l	302	693	210	389	561	997
Alkalinity	mg/l as CaCO ₃	130	160	130	190	210	180
Carbonate	mg/l as CO ₃ ⁻²	Trace	Trace	Trace	Trace	Trace	Trace
Bicarbonate	mg/l as HCO ₃ ⁻¹	158	195	158	231	256	219
Chloride	mg/l as Cl ⁻¹	26678	66028	18731	37012	55282	92218
Sulfate	mg/l as SO ₄ ⁻²	345	286	316	270	240	242
Phosphate	mg/l as PO ₄ ⁻³	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Sodium	mg/l	13597	33579	9717	19150	28576	46867
Potassium	mg/l	519	1295	60	118	175	1811
Strontium	mg/l	233	575	278	520	807	802
Barium	mg/l	0.3	0.9	0.3	0.7	1.2	1.4

To provide sufficient amounts of injection waters, the produced water is therefore gathered from different reservoir layer zones. As the produced water is mixed at different volumes with Karoon water to obtain a compatibility ratio, the ideal solution for mixing the incompatible produced water is to first process the anticipated scale forming produced waters separately, and then to selectively remove the potential scale from the targeted water before blending. However, such an ideal solution almost does not exist in any oil-gas production facility. Among the problems of mixing incompatible produced waters is the further increase of the TSS content. Unlike the injection of seawater, where water incompatibility in the forms of alkaline/sulfate scale is obvious, the water incompatibility of the produced water with Karoon River is more elusive. Changing the pH will consequently alter the thermodynamic equilibrium of the water mixing process in terms of physical and chemical properties. This could create water incompatibility problems, at least theoretically, even if, for instance, the produced water is mixed with Karoon River.

Change in Ca, Sr, and Ba contents with time can be observed in some of mixings. The common types of scale found in mixing different values are classified into two types, namely carbonate scale and sulfate scale. The main influencing factors are partial pressure of CO_2 , pH, and the salinity of water in the process of carbonate fouling.

Carbonate is separated out, when the relative conditions change and only a little HCO_3^- is dissociated to CO_3^{2-} ; when the pH is higher than 7.5, Ca^{+2} and CO_3^{2-} react to form CaCO_3 , whereas, when the pH is less than 7.5, the main reaction is between Ba^{+2} , Ca^{+2} , Sr^{+2} , and SO_4^{2-} in the mixing of water to form deposits.

The solubility of BaSO_4 in water is very low, about 2.8×10^{-10} mg/l at normal room temperature (25 °C). However, the solubility of CaSO_4 is relatively high in similar conditions (about 1061 mg/l), and it will

decline rapidly when the temperature rises. The solubility of SrSO_4 is about 104 mg/l (25 °C). For carbonate fouling, the reversible reaction shifts right, and the carbonate scale is readily formed, when CO_2 content in water is lower than the content, which the dissolving balance needs. For sulfate fouling, the solubility increases but scaling tendency decreases gradually, when the salinity rises. When the water pH value is very high, the carbonate scaling tendency increases; however, the sulfate solubility is not influenced. To a certain extent, the formation of carbonate and sulfate fouling is inhibited in water with high total salinity. The carbonate solubility is increased, when the salt content (not including Ca^{+2} or CO_3^{2-}) rises. Here, the decrease in the salinity of the mixing water is the important reason for the form of the precipitate.

Analysis of Scales on Filters

The scales on all the six filters are exposed to XRD analysis, but due to the low amount of scales as well as the amorphous structure of scales, XRD could not detect any crystalline structure and turned out to be amorphous. Therefore, elemental analysis (EDX) is conducted along with SEM to cover XRD inability to detect the composition of scales on the filters.

The produced water mixtures were filtered by a 0.45 micron filter for the purpose of weighting the scales and then these scales were analyzed in order to determine their types and compositions. The weight of scales resulted from the mixtures of the produced and K waters at different ratios of waters was analyzed; the highest weight was obtained at a F sample to K water sample ratio of 70 to 30. The potential of scale deposition decreases, as the K water ratio increases. Figure 4 shows the SEM images and the spectrum of the elemental analysis for a scale sample resulted from, for instance, 70% F water and 30% K water at ambient temperature.

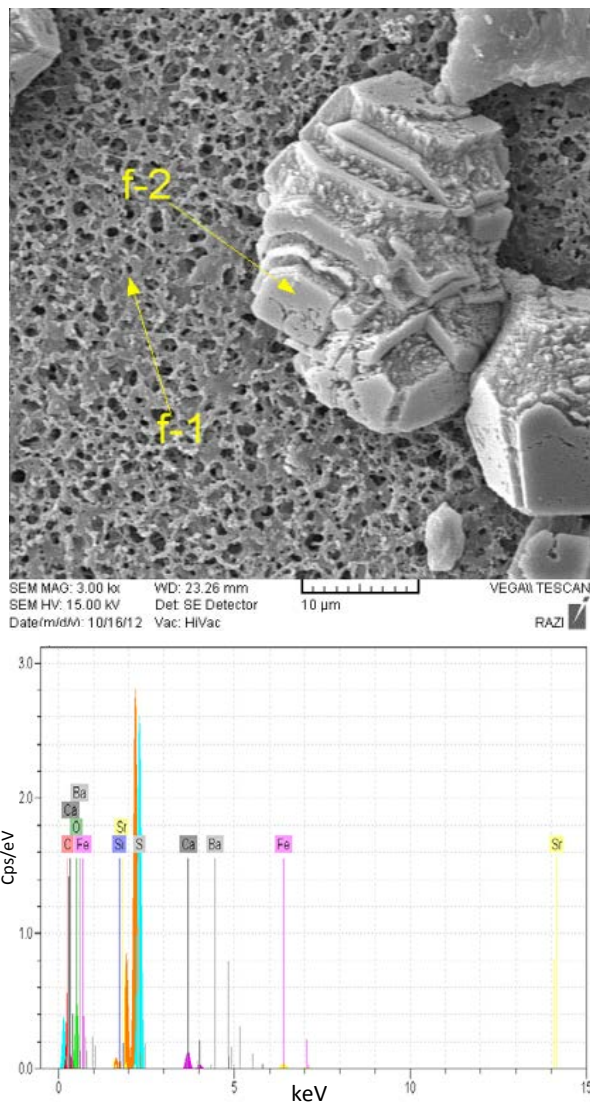


Figure 4: (a) SEM image of the precipitate filter paper and (b) Spectrum of elemental analysis of a typical mixing ratio.

Furthermore, the scaling index (SI) study method was employed to examine the possibility of the deposition of the mentioned salts in the mixing conditions at their ratios. The conditional constants required to solve the SI equations for the salts of interest were gathered from literature data. These equations are function of temperature, pressure, and ionic strength. When the calculated SI equals 0, the solution is at equilibrium with the solid scale; as SI is lower than 0, the solution is a under saturated or non-scaling condition, while a positive SI value states the scaling condition for the solution with respect to the scale in question. In this study, a procedure was used for SI calculations and the

results show that the SI values for calcium carbonate, barium sulphate, and strontium sulphate are above zero, which means that these salts can precipitate in the mixing. However, SI values for calcium sulphate confirm that this salt will not deposit for any mixture of the injected and formation waters under reservoir conditions. This figure also demonstrates that, as the fraction of the injected water decreases, the calcium carbonate deposition and strontium sulphate increase and the maximum deposition occurs at a mixing ratio of the injected water of 30%. It can be concluded that calcium carbonate, calcium sulphate, and strontium sulphate have a tendency for deposition based on the theoretical analysis, while, in experimental studies, only strontium sulphate deposition was observed in all mixing ratios.

CONCLUSIONS

Various parameters such as ionic composition of the water, chemical incompatibilities such as scales and precipitates, suspended solids content, and entrained gas were described as the potential quality issues in the injection water process. The obtained results indicated that the main constituents of the scale deposited at a typical water mixing ratio were strontium sulphate, calcium carbonate, and barium sulphate. The results obtained for different produced waters and Karoon water sample showed that the composition of Karoon sample was completely different from the produced waters; however, the produced waters had an almost similar composition, although they were obtained from different reservoir layers. The concentration of cation ions in K water sample was very low, but the concentration of carbonate and sulphate was almost similar to the produced waters. The results show a lower salinity of K sample compared to the produced water. The obtained results illustrated that the levels of salinity and cation ions for the produced water was relatively higher than the K sample water. Therefore, the mixture of the formation water containing high concentrations

of cations with K water favors the formation of salt precipitates of scales. However, several groups of constituents were present in most types of the produced water. The major constituents in the produced water were salt content (expressed as salinity, total dissolved solids, or electrical conductivity) and various natural inorganic and organic compounds (e.g., chemicals that cause hardness and scaling such as calcium, magnesium, sulfates, and barium). The SEM and XRD analysis confirmed the presence of scales based on sulphate and carbonate at different mixing ratios. The optimum mixing ratio can be used for a further study and even in field application to experience less severe scale precipitation problems as well as taking preventative measures by knowing the type of scales. Then, the above-mentioned steps altogether are recommended to verify the type of the scales formed due to water mixings to ensure reliable results.

Overall, injection waters introducing the typical scale-inducing anions like sulphate and carbonate can cause carbonate and sulphate type scales, especially in sea water, where sulfate concentrations are high. However, in the river sample studied herein, although the anions exist and induce the mentioned scales, the extent of scale deposition would be much lower due to lower salinity and anion concentrations. Regarding the above-mentioned procedure, one can assure the type of scale and maintain the optimum mixing ratio for the water mixing, where needed. The weight of scales from mixtures of the produced and K waters at different ratios of waters was obtained at an F sample to K water sample ratio of 70 to 30. The XRD analysis of the membranes showed barium sulfate scale for U sample and L water samples, while F sample was not detected because of an amorphous structure, since XRD detects crystalline structures.

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