

Chemical and Radioactive Content of Oilfield Produced Water in Libya

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Abstract: During the production of crude oil and natural gas, water naturally occurs in the reservoir and could be extracted along with oil, this water is also produced when brackish water is injected into the reservoir to enhance oil recovery. The volume of water from oil wells are very high and can be one order of magnitude higher than the oil produced. The produced water can be re-injected into abandon wells or discharged to surface soil pond. In order to evaluate the quality of the produced water, samples were collected and analyzed for various parameters from MB-A oilfield eastern south of Libya in January 2012. Physical and chemical parameters of produced water such as pH, salinity, electrical conductivity, TDS, the content of sulfate, nitrate, nitrite, barium, phosphate, oil content, carbonate, bicarbonate, hardness and turbidity were analyzed for produced water samples. Radioactive survey was done using GRM-260 to measure the activity of uranium, thorium and potassium. Oilfield impacted soil is the most common environmental problem associated with oil-production. The produced water associated with oil-production contaminates the soil and the subsequent erosion of topsoil. Also, impacted soil serves to contaminate surface waters and shallow aquifers. The results show wide variations in the different parameters measured, the main constituents (pollutants) that impact the soil are salts, hydrocarbon compounds and natural radioactivity.

Key words: Produced water • Oilfield water • Radioactivity • Libya

INTRODUCTION

Libyan oil production began in 1961 by producing approximately 18 thousand barrel/day. In early seventies, the oil production became the major industry in Libya, where the average production was about 1.5 million barrels/day [1]. In subsurface formations, naturally occurring rocks are generally permeated with fluids such as water, oil, or gas (or some combination of these fluids) [2]. This water is referred to as produced water, formation water or oilfield brine. Oil field water is also produced when brackish water is injected into the reservoir for enhanced oil recovery [3]. The volume of water from oil wells are very high and can be one order of magnitude higher than the oil produced. The properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years and the type of hydrocarbon product being produced [2]. Produced water properties and volume can even vary throughout the lifetime of the reservoir [4]. Naturally Occurring Radioactive Materials (NORM) such as uranium, radium and radon are dissolved in very low

concentrations during normal reactions between water and rock or soil [5, 6]. The radioactivity of the natural radionuclides of the uranium (^{235}U and ^{238}U) and thorium (^{232}Th) series is due essentially to alpha and beta decay modes plus gamma de-excitation of nuclei [3]. The source for most oil and gas NORM is dissolved radium that is transported to the surface in the produced water waste stream [7]. Environmental effects of produced water salts and radioactivity have occurred in all regions where oil and gas have been and are produced. The most significant of these effects are degradation of ground and surface water quality, death of plants and destruction of soil textures, contamination of production equipment and soils by radium-bearing produced waters, scale and sludge and adverse effects on ecosystem [8]. This study is intended to provide an approach for full characterization of contaminated soil by produced water of MB-A oilfield, where a bank of disposing pit has been chosen as a case study area and analysis of the produced water and the impacted soil samples have been carried out by mean of several recommended analysis and then identify and assay the main constituents that cause pollution of soil.

MATERIALS AND METHODS

Many parameters have been determined for both soil and produced water samples in order to characterize the polluted site. A total of 26 samples were collected from MB-A field eastern south of Libya during the period of (5-25 January 2012). Sixteen of these samples (S_1 - S_{16}) were soil samples collected from a depth of 40 cm around the evaporation ponds. In addition to four control samples (C_1 - C_4) far enough from the ponds and six water samples (W_1 - W_6) from the oil center (Fig 1).

All Soil samples were sieved and dried to be made as a soil extractor in ratio 1:1. Water samples were acidified by concentrated nitric acid to preserve for heavy metals measurements. Physical and chemical properties including the pH, electrical conductivity, alkalinity, total dissolved solids, salinity, carbonate, bicarbonate and hardness were determined as soon as the samples arrived to the field laboratory according to the standard methods [9]. Turbidity, sulfate, sulfide, nitrate, nitrite, phosphate, silica and oil content were measured according to the water analysis handbook [10] using (*Hach® Dr/2400*) spectrophotometer. Sodium, potassium, lithium, calcium and barium concentrations in water samples were determined by Flame photometer (*BWB TECHNOLOGIES UK LTD*).

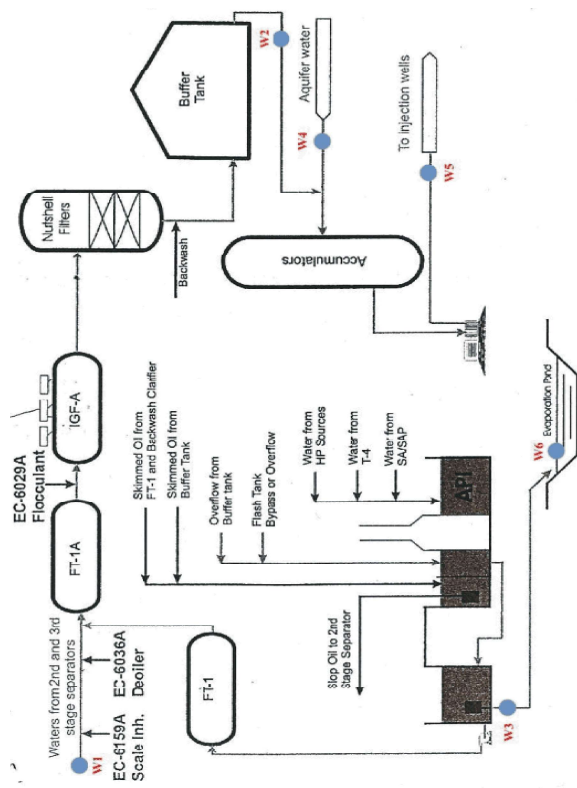


Fig.1: Water sampling points from MB-A oil center

Heavy metals such as copper, ferrous, manganese, zinc, cobalt, cadmium and chromium were determined by the atomic absorption (*Perkin Elmer 2380*). Radioactivity survey was conducted using GRM-260 during the sampling of produced water and soil from the ponds.

RESULTS AND DISCUSSION

Table 1 shows pH values for produced water which are ranged from 6.8 to 8.26. Soil samples have a similar range (Table 2) from 7.0 in S_{13} to 8.0 in S_4 . The normal pH range for soil is 6-9. Therefore it could be considered that pH of soil are within the normal range. The control samples have a little bit higher pH range (Table 3) from 7.9 in C_3 to 8.45 in C_1 .

Total dissolved solids (TDS) values in water samples was in range of 5690 mg/L in W_4 to the highest value in the evaporation pond sample (W_6) 31250 mg/L. Both W_1 , W_2 samples have convergent values of TDS despite the water passed through the produced water treatment plant (PWT). Soil samples have a various values of TDS in Table 2, ranged from 960 mg/L in S_7 to 5063 mg/L in S_{13} . Produced water samples have high salinity where the concentrations ranged from 10325 mg/L in W_5 to 38000 mg/L in W_6 . In comparison, brackish water sample W_4 has a salinity concentration of 2475 mg/L. The salinity concentration of produced water decreases when the aquifer water mixes with the water of the treatment plant before its injection in oil wells.

Alkalinity in produced water is mainly bicarbonate salts in Table 4. The highest value was 6039 mg/L in W_1 and the lowest value was 2562 mg/L in W_6 . Carbonate was only present in the evaporation pond sample W_6 . Hardness due to Calcium and magnesium ions was measured and its values ranged from 187.4 in W_4 to 572.5 mg/L in sample W_6 . The value of salinity increases in the evaporation pond due to the evaporation concentration of salts. This fact can be seen from the high salinity of sample W_6 . Soil salinity was measured for all sixteen samples, the lowest value of 1040 mg/L in sample S_6 , while the highest salinity value was 4661 mg/L in sample S_{13} . Control samples have lower salinity values ranging from 309 mg/L for C_2 to 862 mg/L for C_3 (Table 3).

High levels of hard-water ion such as Ca^{+2} and Mg^{+2} can cause scaly deposits in plumbing, appliances and boilers. These two ions also combine chemically with soap molecules, resulting in decreased cleansing action. Oil content was high in sample W_3 (427.92 mg/L) as given in Table 5. The API separator receives oil from all the drains of the production process. Produced water is

Table1: physical properties of water samples

	pH	TDS	Salinity	EC	Alkalinity
W1	6.85	26500	28059	53.20	6039
W2	6.86	28230	28141	56.60	6100
W3	7.50	15360	20654	30.70	5490
W4	7.52	5690	2475	5.33	3050
W5	7.01	9915	10325	19.08	2440
W6	8.26	31250	38000	62.18	3702

Table 2: Physical properties of soil samples (ppm).

	pH	TDS	Salinity	EC (μ s)	Alkalinity
S1	7.1	3880	1358	2590	915
S2	7.1	4540	3806	9440	732
S3	7.6	1700	1162	2960	915
S4	8.02	1320	1624	2270	393
S5	7.38	2400	2338	4620	1037
S6	7.43	1370	1040	2180	845
S7	7.86	960	2301	2520	915
S8	7.88	1570	2221	2980	793
S9	7.9	3226	4140	6536	671
S10	7.43	2540	3141	5073	1220
S11	7.39	1373	2572	2756	732
S12	7.29	1320	1899	2640	732
S13	7.00	5063	4661	10256	1098
S14	7.37	1833	2338	3680	1220
S15	7.25	1246	2119	2513	1281
S16	7.23	1470	1680	9380	1037

Table3: physical properties of control soil samples (ppm).

	pH	TDS	Salinity	EC (μ s)	Alkalinity
C1	8.45	165	657.5	397	1220
C2	8.24	775	309.78	1586	610
C3	7.9	225	862	449	976
C4	7.93	284	803.06	570	1098

Table 4: Hardness, Carbonate salts in produced water (ppm)

	CO ₃ =	HCO ₃ -	T. Hardness	Ca hardness	Mg hardness
W1	TR	6039	386	130.2	63.9
W2	TR	6100	424	126.4	111.2
W3	TR	5490	230	70.68	142.6
W4	TR	3050	187.5	30.6	109.3
W5	TR	2440	232.5	61.6	79.2
W6	1140	2562	572.5	197.8	85.0

Table 5: Turbidity and oil content in produced water

	Oil content	Turbidity
W1	13.88	92.0
W2	0.86	103.0
W3	427.92	232.0
W4	3.47	4.0
W5	1.73	22.0
W6	5.20	22.0



Fig. 2: Oil aggregation in the evaporation pond.



Fig. 3: Frozen heavy oil drops formed under 39°C



Fig. 4: Skimmed oil to the sides of the ponds.

diverted directly to the evaporation pond. High turbidity value was in the same sample W₃ (232 FAU) Table 5.

The oil concentration is decreased as soon as the water is disposed of to the evaporation pond as shown in Figure 2. When the temperature of water becomes under 39°C, the oil is frozen as shown in Figure 3 due to the pour point of oil (39.5-42°C) to form,

Table 6: Cations and anions concentrations in produced water (ppm)

	Na ⁺	K ⁺	Ca ⁺²	Li ⁺	Ba ⁺²	SO ⁼⁴	S=	NO ⁻²	NO ⁻³	PO ₃	Cl ⁻
W1	10074	86.13	862	8.33	299.3	533.33	10	0.10	27.33	5.86	16529.7
W2	10275	87.6	881	8.5	363.3	536.66	10	0.06	29.00	6.53	16631.75
W3	8508	77.36	679	6.66	278	626.66	226	0.16	25.50	10.20	11544.6
W4	752	44.46	98.16	0.9	10	900.00	43.3	0.07	25.33	5.10	1366.75
W5	4837	58.23	285	3.2	135.3	500.00	10	0.06	32.66	7.76	5800.7
W6	15690	177	1541	14.33	504	1000.00	30	0.10	21.5	7.43	21335.5

Table 7: Heavy metals concentration in produced water (ppm)

	Cu	Fe	Mn	Zn	Co	Cd	Cr	Pb	Ni
W1	5.28	1.06	0.92	1.10	-	-	0.32	0.55	2.14
W2	9.33	1.23	1.15	1.16	3.05	-	0.26	0.35	-
W3	1.64	0.21	0.69	0.77	2.73	0.7	0.06	0.26	-
W4	4.8	0.35	0.23	2.65	0.73	0.35	0.24	0.08	-
W5	5.13	0.78	1.23	-	1.47	0.55	0.19	0.35	1.42
W6	1.04	0.92	1.15	0.75	3.64	0.25	0.15	0.35	-

a heavy oil drops (Grease). The oil drops are skimmed and precipitate on the sides of the ponds as shown in Figure 4.

Cations concentrations of Na, Ca, Li, K and Ba as well as anions of SO₄⁼, NO₂, NO₃, PO₃, SiO₂, Cl⁻ and S are given in Table 6. Sodium ions concentrations are very high. The highest value was 15690 mg/L in sample W₆, the lowest value was 752 mg/L in sample W₄. These ions combined with chloride salts. The highest value of chlorides was 21335.5 mg/L in sample W₆ and the lowest value was 1366.75 mg/L in sample W₄. High concentration of Sulfides found in sample W₃ (226 mg/L), that might be due to the activity of some kinds of bacteria such as SRB (Sulfur reducing bacter). SRB consume sulfates to produce sulfides during its metabolism. Sulfate ions combined with barium to form BaSO₄ (Barite), which is the main carrier of radioactive radium (either Ra²²⁶ or Ra²²⁸). Radium and its progeny emit gamma rays when present in scale.

In comparison with W₄ (aquifer water) all produced water samples have high concentrations of Lithium ranged from 3.2 mg/L in sample W₅ to 14.33 mg/L in sample W₆ in, respectively. Heavy metals of Cu, Fe, Mn, Zn, Co, Cd and Cr concentrations are summarized in Table7.

In contrast of all heavy metals, Cu has high concentration in all samples. Sample W₆ has the highest value (31.04 mg/L), where the lowest value was 1.64 mg/L in W₃. Traces of cadmium were found in both samples W₁ and W₂. Radioactivity survey was done during the collection of water and soil samples, the infield results of

the water and soils samples indicate higher activity than the normal water and the control soil samples respectively.

CONCLUSIONS

- This study revealed the elevated concentration of cations, anions, petroleum hydrocarbons components and natural occurring radioactivity (NORM) that caused by oil-field produced water disposal on soil properties.
- Produced water treatment is benefit in case of de-oiling and decreasing the suspended solids. It has not high efficiency in case of water desalination.
- The accumulation of pollutants constituents in the soil during long term of disposal are lead to damage the environment at that area.

Recommendation:

- Further studies should be conducted to know more about produced water volumes and its components in many other places in Libya.
- Produced water (containing high levels of oil, salts and radioactive) is better to be re- injected than disposal to evaporation pond.
- The levels of natural radioactivity namely, these radionuclides ²³⁸U, ²³⁵U, ²³²Th and ⁴⁰K, as well as the radium-radionuclides (²²³Ra, ²²⁴Ra, ²²⁶Ra and ²²⁸Ra) and ²¹⁰Pb in water and soil samples should be analyzed by using α-ray spectrometry with high purity germanium (HPGe) detector, for precise measurements.

- Radioactivity regulation of oil and gas industry in Libya should be issued as soon as possible.

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