4. CONCLUSIONS

- The studied oil-field waters are either nearly neutral (pH = 6.8 to 7.3) or acidic (pH = 3.8 to 5.5). Their densities at 15°C vary from 1.08 to 1.22 g/mL, thus the specific gravities at 60/60°F are nearly of the same values. The electrical conductivities at 25°C range from 142 to 245 mS/cm, and corresponding resistivities from 0.071 to 0.041 ohm m. The dissolved solids determined at 105, 180, and 600°C are, respectively, 114000 to 456000, 108000 to 319000 and 106000 to 264000 mg/L. The salinity ranges from 104000 to 339000 mg/L, nearly equal to dissolved solids at 180°C. The acidity, alkalinity, and calcium, magnesium and total hardness, all as $CaCO_3$, vary from about 900 to 1870, 30 to 150 and 8000 to 66000, 3000 to 114000 and 12000 to 163000 mg/L, respectively.

- In these oil-field waters, concentrations of the alkali cations including lithium, sodium and potassium vary from about 30 to 160, 31600 to 98900 and 360 to 4730 mg/L respectively. Concentrations of the alkaline earth cations, i.e. magnesium, calcium, strontium and barium, range from nearly 830 to 27800, 3260 to 26600, 85 to 690 and 1 to 9 mg/L respectively. Cocentrations of iron and manganese cations are in the range of 0.1 to 0.3 and 1 to 17 mg/L in the neutral water samples, respectively; however both have higher values in the acidic ones. Thus, concentrations of the total cations vary from nearly 40000 to 121000 mg/L.

- In the studied water samples, the halide anions, namely fluoride, chloride, bromide and iodide, have concentrations of about 20 to 100, 63000 to 206000, 280 to 2520 and 1 to 17 mg/L respectively. Concentrations of the sulphate, nitrate, bicarbonate and borate anions vary from about 740 to 1580, 2 to 20, 30 to 300 and 90 to 1810 mg/L, respectively. Thus, concentrations of the total anions range from nearly 65000 to 211000 mg/L.

- The reaction values, in milliequivalent per litre (me/L), of the cations in these waters are in the range of about 4 to 23, 1370 to 4300, 9 to 120, 70 to 2290, 160 to 1330, 2 to 16 and 0.02 to 0.13 for lithium, sodium, potassium, magnesium, calcium, strontium and barium, respectively, so totalling 1780 to 5920. The reactions values (me/L) of the anions vary from nearly 1 to 5, 1780 to 5800, 4 to 32, 0.01 to 0.13, 15 to 33, 0.04 to 0.35, 0 to 5.0 and 4.5 to 90 for fluoride, chloride, bromide, iodide, sulphate, nitrate, bicarbonate and borate respectively, thus summing 1820 to 5950. The reaction values, in equivalent per million (epm), of both cations and anions have the same trend but with lower values.

- In the studied waters, probable compounds dissolved as calculated from hypothetical combinations of positive and negative ions indicate that strontium bicarbonate and sulphate vary from about 60 to 300 and 280 to 1450 mg/L respectively. Calcium bicarbonate is present in one sample (150 mg/L), while calcium sulphate and borate vary from about 210 to 1720 and 210 to 3650 mg/L, respectively. Calcium, magnesium, iron and manganese chlorides are present in all the samples, ranging from about 7100 to 49000, 3200 to

109000, 15 to 1250 (in three samples) and 3 to 420 mg/L respectively. Finally, potassium, sodium and lithium chlorides are found in all the samples, varying from approximately 690 to 9000, 80000 to 251000 and 180 to 950 mg/L respectively. This indicates that the chloride anions are present in excess to combine with the latter cations. The total probable compounds in these samples vary from about 103000 to 318000 mg/L.

- In the examined waters, the reaction values, in equivalent percentages (e %), for the groups of alkalis, alkaline earths, strong anions, and the properties of primary and secondary salinity are about 21.6 to 43.5, 6.5 to 28.4, 49.9 to 50.0, 43.2 to 86.9 and 12.8 to 56.8, respectively. Both the tertiary salinity and primary alkalinity are absent in all the samples, while the secondary alkalinity is present in four samples at very low values (0.01 to 0.28 e %).

- In these waters, 16 genetic coefficients of ions are calculated from their equivalents. They are formed from relations of chloride, sulphate, bromide, sodium, magnesium and calcium together; i.e. Cl/Na, Cl/Mg, Cl/Ca, Cl/(Ca + Mg), (Cl - Na)/Mg, (Na - Cl)/SO_4, Na/Cl, Na/Mg, Na/Ca, Na/(Ca + Mg), Na/$\sqrt{(Ca + Mg)/2}$, Ca/Mg, (Ca + Mg)/Mg, Cl/SO_4, (SO_4 x 100)/Cl and Cl/Br.

- Water classification systems of Palmer, Sulin, Bojarski modification, Chebotarev and Schoeller have been applied to classify the studied oil-field waters. Applying the Palmer system, the waters are classified in class 3 or 4. Using the Sulin system, all the water samples are of the chloride-calcium type and chloride group, but five samples are of the sodium subgroup and one sample is of the magnesium subgroup and another one of the calcium subgroup. Thus, four, one and two samples belong to $S_1S_2A_2$, S_1S_2 and $S_2S_1A_2$ classes respectively. With the Bojarski modification of the chloride-calcium type water in the Sulin system, one, four and two of the studied waters belong to class I, II and V respectively. Application of Chebotarev system, all the waters are of the chloride major group, class V and chloride genetic type water. According to the Schloeller system, all the studied waters are hyperchlorinated, two samples sulphated and five ones oligosulphated, and five and two samples hypo- and normal-carbonated respectively. They generally contain no infiltrating meteoric waters. Their predominant sequences of anions and cations are: all samples: Cl > SO_4 > CO_3; four samples: Na > Ca > Mg and three samples: Na > Mg > Ca; all samples: HCO_3 < Ca.

- During the geologic age, the studied oil-field waters are generally concentrated by factors of about 3 to 9 for both total ions and sodium, 3 to 11 for chloride, 5 to 12 for potassium, 4 to 39 for bromide, 3 to 14 for boron, 2 to 21 for magnesium, 5 to 49 for calcium, 2 to 86 for strontium, 42 to 290 for barium, and 150 to 780 for lithium. On the other hand, the sulphate is depleted by a factor of about 0.3 to 0.6.

- Statistical correlations between the density and physico-chemical properties of the studied waters indicate that they are very strong for the specific gravity, both TDS at 180 and 550°C, salinity, total cations, chloride and total anions. Correlations are strong for the

conductivity and resistivity. They are moderate for both Mg and total hardness, sodium, potassium, magnesium, strontium, barium, bromide, borate, NaCl, KCl and Mg Cl_2. Correlations are minor for Ca hardness, lithium, calcium, fluoride, LiCl and $CaCl_2$.

- Intercorrelations of the physico-chemical properties of the examined waters indicate that correlations of the conductivity are very strong with TDS at 550°C, salinity, total cations, chloride and total anions, moderate with both Mg and total hardness and sodium, and minor with Ca hardness.

- Correlations of the depth of the productive zone and physico-chemical properties of the studied waters indicate that they are moderate for Ca hardness, sodium, calcium, iodide and nitrate, and minor for lithium, strontium, total cations, chloride, bromide, sulphate and total anions.

- Concerning the organic constituents extracted from the studied waters, the fatty acids and oils vary from 0.9 to 2.0 and 8.0 to 12.0 mg/L, respectively. The fatty acids after methylation and analyzed by gas chromatography, vary from C_8-to C_{20}-fatty acids identified, representing 42 to 84 % of the fatty acid esters.

- The extracted oils, as separated by column chromatography, are formed of saturates, aromatics and resins, being about 21 to 27, 35 to 39 and 32 to 38 % of the oils, respectively. The *n*-paraffins in the saturates, as determined by gas chromatography, vary from about 7.3 to 20 %. The polyaromatics in the aromatics, as analyzed by high performance liquid chromatography, indicate that they range from about 60 to 125 µg/L of the water sample, and dibenzo(a,h)anthracene represents about 79 to 93 % of the polyaromatics identified.

- Infrared spectra, in the range of 4000 to 400 cm^{-1}, of the extracted oils reflect their chemical constituents of the saturates, aromatics and fatty acids as indicated by their characteristic infrared bands of functional groups, such as CH_3, CH_2 and CH in paraffins, CH and C=C in aromatics, and OH, C=O and C–O in fatty acids.

5. SUMMARY

The aim of the present work is to study oil-field waters, associated with crude oils produced from oil-fields in Sinai, Gulf of Suez and Western Desert of Egypt.

This work has been carried out on seven samples of oil-field waters, associated with crude oils produced from six individual wells of Belayim (Sinai), Ashrafi, Ramadan and Zeit Bay (Gulf of Suez), Meleiha and Razzak (Western Desert) oil-fields.

The oil-productive zones in the wells have lithology consisted of sand, sandstone, limestone, dolomite, shale and granite. This is composed of Basement, Nubia, Alamein Dolomite, Baharia, Kareem carbonate and South Gharib Formations. Their geological ages of these Formations are Pre-Cambrian, Carboniferous, Lower and Upper Cretaceous, as well as Lower and Middle Miocene, depths from about 4770 to 11400 ft, pressures from about 400 to 4300 psi, and temperatures from nearly 120 to 280 ^{o}F.

The analysis of the studied oil-field waters have been performed through the determination, mainly using standard methods of water analysis, of general physico-chemical properties, cations and anions, as well as their reaction values and genetic coefficients. Different water classification systems are applied. Concentration ratios of ion constituents during the geologic age are estimated. Correlations among analytical and geological data are statistically calculated using linear regression analysis. Oraganic constituents, including oils and fatty acids, are extracted from the waters. The oils are fractionated into their components of saturates, aromatics and resins. The fatty acids, *n*-paraffins, polyaromatics and functional groups are determined.

General physico-chemical properties of the waters include pH, density, specific gravity, conductivity, resistivity, total dissolved solids, salinity, acidity, alkalinity and hardness.

The ions determined in the waters are lithium, sodium, potassium, magnesium, calcium, strontium, barium, iron and manganese cations as well as fluoride, chloride, bromide, iodide, sulphate, nitrate, bicarbonate, carbonate, hydroxide and borate anions.

For both cations and anions, their reaction values (me/L, epm and e %), reaction groups and properties, probable compounds from their hypothetical combinations and genetic coefficients are calculated.

Different water classification systems applied to the waters include those of Palmer, Sulin, Bojarski modification, Chebotarev and Schoeller.

The analytical results obtained indicate the following conclusions:

- The studied oil-field waters are either nearly neutral (pH = 6.8 to 7.3) or acidic (pH = 3.8 to 5.5). Their densities at 15^{o}C vary from 1.08 to 1.22 g/mL, thus the specific gravities at 60/60^{o}F are nearly of the same values. The electrical conductivities at 25^{o}C range from 142 to 245 mS/cm, and corresponding resistivities from 0.071 to 0.041 ohm m. The

dissolved solids determined at 105, 180, and 600°C are, respectively, 114000 to 456000, 108000 to 319000 and 106000 to 264000 mg/L. The salinity ranges from 104000 to 339000 mg/L, nearly equal to dissolved solids at 180°C. The acidity, alkalinity, and calcium, magnesium and total hardness, all as $CaCO_3$, vary from about 900 to 1870, 30 to 150 and 8000 to 66000, 3000 to 114000 and 12000 to 163000 mg/L, respectively.

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