

## RECOVERY OF OIL FROM PRODUCED WATER

Tagelsir Awad Ahmed Digno

Faculty of Engineering, Sudan University of Science and Technology

E-mail tagelsir729@gmail.com

Received: 15/10/2018

Accepted: 29/11/2018

### ABSTRACT

The study was conducted in Malute Basin Block 3 and 7 located in the Republic of South Sudan in Palouge Field. Produced water is a mixture of organic and inorganic materials. Produced waters characteristics depend on the nature of the producing/storage formation from which they are withdrawn, the operational conditions, and chemicals used in process facilities. The composition of produced water from different sources can vary by order of magnitude. However, produced water composition is qualitatively similar to oil produced the major compounds of produced water include: Dissolved Oil, Dissolved formation minerals, Production chemical compounds, Production solids (including formation solids, corrosion and scale products). The data were collected using different methods: chemical and physical analysis, Analysis of produced water to study the effect and volume of dissolved oil in produced water. The study aimed to assess recovery of dissolved oil in produced water using produced water treatment package. Analysis run for 31 Samples of produced water which were taken within 31 days. Oil in water was measured using HACH DR/4000 Spectrophotometer. Results showed that the total dissolved oil in water is in the range 96.68 to 847.43 mg/L inlet in Palouge field and from 21.51 to 83.33 mg/L outlet. Then random samples were analyzed from Adar Field, Moleeta Field, and Gumry Field, to assess quantity of Total petroleum hydrocarbon (TPHC). Besides, many chemical treatments, whose initial and/or running cost are high and produce hazardous sludge. The most important study recommendations are to decrease the effect of discharging produced water to underground and surface water and reduce cost of handling of produced water by using a relatively new technology to separate oil and gas from produced water at the bottom of the well.

**Keywords:** Oil and Grease, Palouge Oilfield, Total Petroleum Hydrocarbon, Adar Field.

المستخلص - أجريت هذه الدراسة في حوض ملوط النفطي مربع 3 و 7 ويقع في جمهورية جنوب السودان حقل فلوج . المياه المصاحبه عباره عن خليط من المواد العضويه وغير العضويه .خصا ئص المياه المصاحبه تعتمد على طبيعة وبنية الكامن التي استخرجت منها, والكيمواويات المستخدمه في عمليات الانتاج . ان تركيب المياه المصاحبه من مصادر مختلفه تختلف حسب منزلة الترتيب . كيف ذلك , ان تركيب المياه المصاحبه نوعيا يشابه الزيت المنتج . اهم مكونات المياه المصاحبه تتضمن الزيت المذاب في الماء , المركبات المعدنيه المذابه , -مواد الكيمياءه المستخدمه في الانتاج واخيرا المواد الصلبه تتضمن المكونات الصلبه و نتاج التاكل والترسبات المعدنيه. . جمعت البيانات بواسطة طرق متعدده منها التحاليل الكيمياءه والفيزيائيه,تحاليل المياه المصاحبه لدراسة تأثيروكميات الزيت المذاب في الماء . هدفت هذه الدراسه الي استخلاص الزيت الذائب في المياه المنتجه عن طريق استخدام وحدة معالجه المياه,تم اجراء التحاليل لعدد 31 عينه لفترة 31 يوما باستخدام جهاز المقياس الطيفي هاك 4000.

خلصت الدراسه للنتائج الاتيه:الكميه الكليه للزيت المذاب في الماء المياه الداخله الي وحدة المعالجه تتراوح بين.96.90مج/ ل في حقل فلوج وترتفع الي 847.43 مج/ ل والمياه المعالجه تتراوح بين.21.51مج /ل في حقل فلوج وترتفع الي 83.33 مج/ ل. وايضا اخذت عينات من الحقول مثل حقل عداريل,موليتا,قمري وتم اجراء التحاليل الهيدروكربونيه للمقارنه, حاليا التقنيات المستخدمه لايمكنها ازالة المواد المذابه بالاضافه الي معظم المواد الكيمياءه( باهظة التكاليف) المستخدمه في معالجه النفط وتنتج مخلفات خطره.من اهم توصيات هذه الدراسه لتقليل

تأثير المياه المصاحبه التي يتم التخلص منها بتصريفها الى باطن الارض او السطح وايضا تقليل تكاليف معالجة ومعاملة المياه المصاحبه وذلك باستخدام تقنية فصل النفط والغاز من المياه المصاحبه في داخل ابار الانتاج.

## INTRODUCTION

The oil in water may be present as a separate oil layer floating on the surface of the water<sup>[1]</sup> phase or as distinct droplets of oil dispersed throughout the water phase. Due to the difference in density between the phases, the dispersed oil droplets will tend to rise to the surface and combine with other oil droplets in the surface layer<sup>[2,3]</sup>. As previously mentioned, when the flow regime is laminar, Stoke's Law can be applied to describe the rate of rise of the oil droplets. Oil removal is usually done in stages from primary bulk removal to final polishing. The number of stages required is a function of the type of oil in the stream, the size distribution of the oil droplets, the concentration of the oil and the level of removal required for the application<sup>[4]</sup>.

Of course, the larger and lighter-density particles will be easy to remove. Separation of oil droplets in this category can be accomplished simply by allowing enough retention time for the droplets to rise to the oil layer at the surface<sup>[5,6]</sup>. This is termed gravitational settling. This is the most simple and least costly solution to oil removal. Gravitational settling can be accomplished by using large settling tanks or skimmer tanks<sup>[7,8,9]</sup>. These types of tanks are common to land-based operational facilities due to the fact that space and weight constraints are not very stringent and the installed cost is relatively low.

## MATERIALS AND METHODS

32 water samples to be collected were representative of the water of interest or the analysis would have led to false conclusions<sup>[18,19,20]</sup>. An extremely accurate chemical analysis of water sample followed by assessment of the problems indicated by the analysis is worthless if the sample do not represent the water in the system. In analytical chemistry technology needed to characterize the individual water in a particular system and provide the fundamental chemical equilibrium and kinetics data that form the basis for the computer models. The analytical instruments now used include. HACH DR/4000 Spectrophotometer In certain special analyses<sup>[21,22]</sup>, more advanced techniques are used such as mass

Total petroleum hydrocarbon (TPH) content was sorted as aliphatic up to C16, combining the saturated aliphatic paraffins and naphthenes (cycloparaffins), and as aromatic hydrocarbons, unsaturated rings from C6 to greater than C21. Content of benzene/toluene/ethylbenzene/xylene (BTEX), content of the 16 EPA standard marker polycyclic aromatic hydrocarbons, and distribution of 4-6 ring polycyclic aromatic hydrocarbons (PAH) were determined<sup>[10,11,12]</sup>

Suspended oil must be removed prior to injection into a subsurface formation due to possible damage to the injection formation and to recover saleable oil. Most water treating equipment used for oil removal takes advantage of the density difference between the oil and water phases. It is advisable to collect samples of the suspended oil and the water phases<sup>[13,14]</sup> if possible, to perform an analysis of the physical properties of each phase. The analysis will provide detailed information that is required to properly specify a treatment scheme. For instance, the analysis will report on such items as the density of the oil and water<sup>[15]</sup>, the concentration of oil in the water stream and other vital information needed for a proper design. Having this information helps operating personnel better understand the problem that needs to be solved<sup>[16,17]</sup>.

spectroscopy, high performance liquid chromatography (HPLC), and various "hyphenated techniques" such as inductively coupled plasma-mass spectroscopy (ICP-MS), gas chromatography-mass spectroscopy, and HPLC-mass spectroscopy. In circumstances in which speciation of the inorganic constituents is particularly of interest, ion chromatography can be used along with ICP or ICP-MS detection. Laser light-scattering instruments are usually used for looking at suspended particles and entrained oil droplets and their size distribution.

Clean 500 ml. Plastic bottles with tightly fitting plastic caps were used for routine water samples. The bottles were carefully labeled so that samples could be easily identified. When the

sample was analyzed for oil content, a glass bottle was used. Oil or other organic materials will adhere to the walls of a plastic container or be absorbed by it.

A sample valve was available and a piece of plastic tubing was connected to the end of it. Valves were then opened and water was allowed to run for at least one minute to see if the color of the water is changing. The researcher made sure that there was no debris in the valve or in the bottom of the line. They were all flushed out because they prevent good sampling.

### RESULTS AND DISCUSSIONS

Oil in water is essentially petroleum compounds in water (Total Petroleum Hydrocarbon Criteria Working Group Series 1998). Petroleum compounds can be divided into two main groups: hydrocarbons and heteroatom compounds. Types of emulsions are Oil-in-water (o/w) emulsions, typically low oil levels Complex (w/o/w) emulsions Water –in – oil (w/o) Free oil Oil-coated particles These types may co-exist.

Hydrocarbons are usually measured as Total Petroleum Hydrocarbons (TPHs). These are molecules that only contain carbon and hydrogen.

Oil in produced water is a general term. As shown in Table (1) it can mean different things to different people. Since the results are method dependent, without specifying the method used to determine the oil concentration, values reported for oil in produced water can be misleading.

Dispersed oil – usually means oil in produced water in the form of small droplets, which may range from sub-microns to hundreds of microns. Dispersed oil will contain both aliphatic and aromatic hydrocarbons.

The method covers the determination of the oil concentration, in (ppm), for the water samples from (FPFs), Electrostatic treaters and evaporation ponds so as to determine the separation efficiency of the electrostatic treaters, to show the response of demulsifier and reverse demulsifier and to prevent the environmental contamination.

#### Procedure

APHA 5520 D. Oil and Grease. The standard for determination of oil in water was essentially followed. DR/4000 Spectrophotometer. Reagents Varsol.HCL1:1.

Dissolved oil – usually means oil in produced water in a soluble form. Aliphatic hydrocarbons in general have very low solubility in water. It is the aromatic hydrocarbons, together with things like organic acid that form the bulk of dissolved oil.

#### Water treating systems

Water produced in conjunction with oil and gas must be conditioned for it to be disposed of or used in water flooding operations. The produced water will normally contain produced oil, solids, and/or corrosion products that were not removed by the equipment separating the oil and water. There are several pieces of equipment available that can be used separately or in series with one another to condition the water. Three such pieces of equipment are a skimmer, a coalesce and a precipitator. All three are used to reduce the oil and/or solids content of the water. Equipment is also available which can be used to remove corrosive gases from the water. The types of solids or materials to be removed and their quantity, in respect to the location of the treating facilities, will normally determine the type of equipment to be used to condition the water

**Table (1) Produced water Treatment Analysis Oil Content**

Sample No.	Inlet Tank A (ppm)	Outlet Tank A(ppm)	Temperature °C
1	130.09	66.01	72.10
2	207.25	83.33	72.60
3	128.22	72.30	73.60
4	156.34	46.21	73.20
5	111.78	34.06	72.10
6	108.65	49.06	73.40
7	847.43	48.07	75.00
8	119.51	30.87	73.40

9	96.68	29.20	73.60
10	143.63	24.10	73.30
11	168.75	24.31	73.40
12	132.01	29.32	70.60
13	140.18	30.36	72.80
14	287.01	41.72	72.10
15	177.99	31.61	71.90
16	135.34	38.22	70.80
17	308.03	42.01	71.70
18	115.47	31.97	71.40
19	172.64	28.70	72.40
20	111.36	24.53	72.30
21	126.88	30.72	72.60
22	173.40	30.57	71.30
23	115.72	24.68	70.58
24	134.59	27.82	71.30
25	421.09	23.73	72.10
26	462.32	59.11	73.60
27	402.22	28.11	73.80
28	96.90	20.01	74.30
29	192.01	35.20	73.60
30	401.38	35.71	75.30
31	438.31	21.51	74.40

Reverse demulsifiers Table (2) are used to remove oil and suspended solids from oilfield produced water. Usage of Water Clarifier is critical for the Operation to achieve clean water with the minimum oil carryover to the produced water meets allowed standard specifications. Tables (3),(4),(5)and(6) the results Shows that TPH, Oil & grease in Produced Water Palouge Field. Mooleta Field ,Adar Field and Gummy Field its differ from place to other . Determination of effective product and dose optimization by testing the products on-site and field trials result. Residual amounts of oil in the produced water not only represent lost profit for producers but also can contribute to plugging of formations receiving the injectate. Various treatment chemicals are available to break emulsions or make dissolved oil more amenable to oil removal treatment. The Emulsions those two immiscible liquids, such as oil and water, an emulsifying agent, and a

source of agitation can form an emulsion. Most of the time, emulsions are water-in-oil. Dispersions and reverse emulsions are just the opposite: oil is the internal phase and water is the external phase. More specifically, in dispersion, the tiny droplets of oil will eventually break free and rise to the top of the water given enough time. A true reverse emulsion, however, will not separate regardless of the time involved. Reverse emulsions are typically formed in the reservoir by natural processes. Additionally, they tend to form more readily with fresh water. This may be related to the specific gravities of these two liquids. Fresh water has a specific gravity close to 1.0, which is more similar to the lower specific gravity of oil than heavier brines with higher specific gravities. Since they are technically still an emulsion by definition, these conditions are caused by the same factors identified in the emulsions unit.

They are:

- a) Two immiscible liquids    b) Emulsifying agent    c) Agitation

**Table (2) Compositions of reverse demulsifier**

Chemical Type	Composition	Ratio	Precautions
Reverse Demulsifier	Cationic organic polymer Aerylic acid –acrylamide copolymer Water	30-40 0.5-2 58-69	Prevent the product from entering into drains and surface water

**Table (3) Show TPH, Oil & grease in Produced Water, Palouge Field**

Name	Method	Unit	inlet	outlet
TPH	APHA 5520F	mg/l	114.35	60.3
Oil & grease	APHA 5520D	mg/l	203.25	70

**Table (4) Produced Water, TPH, Oil & grease Moleeta Field**

Name	Method	Unit	inlet	outlet
TPH	APHA 5520F	mg/l	8.60	2.6
Oil & grease	APHA 5520D	mg/l	16.20	8.70

**Table (5) Produced Water, TPH, Oil & grease Adar Field**

Name	Method	Unit	inlet	outlet
TPH	APHA 5520F	mg/l	356	27.90
Oil & grease	APHA 5520D	mg/l	737.90	27.90

**Table (6) Produced Water ,TPH, Oil & grease Gummry Field**

Name	Method	Unit	inlet	outlet
TPH	APHA 5520F	mg/l	53.95	10.6
Oil & grease	APHA 5520D	mg/l	68.85	53.95

The cause of treating oily water are:-

Some or all of the following:

- Loss of oil revenue (Discharge may be prohibited)
- Limits vary e.g. <40 ppm or lower
- Re-injection difficulties (Plugging formation)

- Environmental concerns

Example:

100'000 Barrels/day containing 100 ppm oil:

100'000 Barrel = 15900 m<sup>3</sup>

100 ppm of 15900 m<sup>3</sup> = 10 barrel / day

Figure (1) Show Accumulation of Crude in Produced Water Pit and Figure (2) Show Manual Collection of Crude from Produced water Pit. a) Palouge crude contains high water content. b) Separators in the FPF are not fitted to Palouge crude type, (80% of water should be removed by separators before reaching the produced tank!)

c) Skimming process in Produced tank is controlled manually! So some times the oil remains in the produced tank for days till the test readings for the out let come high!  
d) Cartridge filters are removed from produced water treatment package system, because it's not designed to work with water oily high content.



Figure (1) Accumulation of Crude in Produced Water Pit



Figure (2) Manual Collection of Crude from Produced water Pit

## CONCLUSIONS

Water produced in conjunction with oil and gas must be conditioned to be disposed of or used in water flooding operations. The produced water will normally contain oil, solids, and/or corrosion products that were not removed by the equipment for separating the oil and water. There are several pieces of equipment available that can be used separately or in series with one another to condition the water. Three of such pieces of equipment are a skimmer, a coalesce and a precipitator

-The total quantity of oil in water is 203 mg/L in Palouge field where In Adar Field inlet the system of produced water treatment is 753 mg/L. Total petroleum hydrocarbon (TPHC) 114 mg/L in Palouge Field and 356 mg/L in Adar Field. Besides many chemical treatments, whose initial and/or

running cost are high and produce hazardous sludge.

- Reverse demulsifiers are used to remove oil and suspended solids from oilfield produced water. Usage of Water Clarifier is critical for the Operation to achieve clean water with the minimum oil carryover to the produced water that meets allowed standard specifications. Determination of effective product and dose optimization is achieved by testing the products on-site and field trials outcome

- Residual amounts of oil in the produced water not only represent lost profit for producers but also can contribute to plugging of formations receiving the injectate. Various treatment chemicals are available to break emulsions or make dissolved oil more amenable to oil removal treatment.

## REFERENCES

- [1] Anaensen G, Volker A (2006) Produced water characterization using ultrasonic oil-in-water monitoring– recent development and trial results. In: A paper presented at NEL’s 8th oil-in-water monitoring workshop, 21 September 2006, Aberdeen, UK
- [2] ASTM D 3921 – 85 (1985) Standard test method for oil and grease and petroleum hydrocarbons in water
- [3] ASTM D 4281 – 95 (1995) Standard test methods for oil and grease (fluorocarbon extractable substances) by gravimetric determination
- [4] ASTM D 7066-04 (2004) Standard test method for dimer/trimer of chlorotrifluoroethylene (S-316) recoverable oil and grease and nonpolar by Infared determination.
- [5] -Orem, W.; Varonka, M.; Crosby, L.; Haase, K.; Loftin, K.; Hladik, M.; Akob, D.M.; Tatu, C.; Mumford, A.; Jaeschke, J.; Bates, A.; Schell, t.; Cozzarelli, I, 2017. Organic geochemistry and toxicology of a stream impacted by unconventional oil and gas wastewater disposal operations; Applied Geochemistry, 80, 155-167.
- [6] Barwick V (2005) Best practice guidance for preparing calibration curves. In: A paper presented at TUV NEL’s 7th oil in water monitoring workshop, 23–24 November 2005, Aberdeen, UK
- [7] Brost DF (2008) Sample preparation methodology for oil in water analysis by UV fluorescence, a presentation made at TUV NEL’s 10th Oil in Water Monitoring Club meeting, Aberdeen, UK, 19 September 2008
- [8] Wei, X.; Wang, S.; Zheng, W.; Wang, X.; Liu, X.; Jiang, S.; Pi, J.; Zheng, Y.; He, G.; Qu, W 2013. Drinking water disinfection byproduct iodoacetic acid induces tumorigenic transformation of NIH3T3 cells; Environmental Science & Technology, 47, 5913-5920.
- [9] Aires, C., Gonz lez-Irusta, J. & Watret, R., 2014. Updating Fisheries Sensitivity Maps in British Waters, Scottish Marine and Freshwater Science Report. Vol 5 No 10: Marine Scotland ISSN: 2043-7722.
- [10] Emadi, A., Sohrabi, M., Jamiolahmady, M., Ireland, S. and Robertson, G (2011). Mechanistic study of improved heavy oil recovery by CO<sub>2</sub>-foam injection. Society of Petroleum Engineers - SPE Enhanced Oil Recovery Conference, EORC v. 1, p. 6785.
- [11] J. Tian, M. Ernst, F. Cui, M. Jekel, Effect of particle size and concentration on the synergistic UF membrane fouling by particles and NOM fractions, J. Mem. Science 446 (2013)1–9.
- [12] Frintrop P (2007) A change of the oil in produced water analysis reference method – why and its implications. In: A presentation made at TUV NEL’s OSPAR GC-FID method implementation session, Aberdeen, 18 September 2007
- [13] Myers, J.E., March 17-19. 2014, “Chevron San Ardo Facility Unit (SAFU) Beneficial Produced Water Reuse for Irrigation,” SPE 168401, presented at the SPE International Conference on

- Health, Safety, and Environment, March, Long Beach, CA,
- [14] Iqbal MF (2009) Produced water optimisation using visual processing technology. In: A paper presented at TUV NEL's 7th produced water workshop, 29–30 April 2009, Aberdeen, UK
- [15] Lambert P, Fingas M, Goldthorp M (2001) An evaluation of field total petroleum hydrocarbon (TPH) systems. *J Hazard Mater* 83: 65–81
- [16] Lendl B, Ritter W (2008) A new Mid-IR laser based analyser for hydrocarbons in water, a paper presented at TUV NEL's 10th oil in water monitoring workshop, Aberdeen, UK.
- [17] Martin T, Smith D, Schwarz T, Doucette L, Tripp CP (2008) A fast, solventless 'green' device and method for oil in water analysis using infrared spectroscopy. In: A paper presented at TUV
- [18] OSPAR Agreement (2006-6), Oil in produced water analysis – guideline on criteria for alternative method acceptance and general guidelines on sample taking and handling, [www.ospar.org](http://www.ospar.org)
- [19] Skeidsvoll J, OttoyMH, Vassgard EG, Oa JA (2007) Efficient produced water management through online oil in water monitoring. Case study: Statoil Hydro's Snore B. In: A paper presented at TUV NEL's produced water – best management practices, 28–29 November 2007, Abu Dhabi, UAE
- [20] Shell, 2015a. Shearwater field System Operations Oil Pollution Emergency Plan (OPEP), DECC reference 15062.
- [21] Yang M (2009) The problem of regulating on the basis of oil in water. In: A presentation made at OGP's Produced Water Discharges: Harm and Risk, 20–21 January 2009, Edinburgh, UK
- [22] Yang M, McEwan D (2005) oil-in-water analysis method (OIWAM) JIP, A JIP report for 10 organisations including 8 operators and 2 government bodies, TUV NEL Report No: 96.