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Continuous De-emulsification of Crude Oil Using Packed Column Under Various Conditions

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Abstract

This research dealt with desalting of East Baghdad crude oil using pellets of either anionic, PVC, quartz, PE, PP or nonionic at different temperature ranging from 30 to 80 °C, pH from 6 to 8, time from 2 to 20 minutes, volume percent washing water from 5 to 25% and fluid velocity from 0.5 to 0.8 m/s under voltage from 2 to 6 kV and / or using additives such as alkyl benzene sulphonate or sodium stearate. The optimum conditions and materials were reported to remove most of water from East Baghdad wet crude oil.

***Keywords*: de-salting, de-emulsification, crude oil, packed column .**

Introduction

Crude oil consists mainly (by wt.) 84% carbon, 14% hydrogen, 1% sulfur and 1% nitrogen (1). Corrosive materials such as sulfur and hydrogen sulphides were removed, because these can cause corrosion. The wet Iraqi crude oil such as Kirkuk main pay and Zubair main pay in Basarah have to separate salt water from crude oil before pumping it to export. Different researchers (2-6) used different materials such as sulphonic acid with phenol to desalt water from crude oil. Other additives such as sodium sulphate, mixture of 0.5% sodium sulphate with 0.5% phenol, starch, were also studied.

During testing oil well production, after drilling has been complete, said removal, silt removal, and other debris removal are required to clean the well during initial well production. Desalting and dewatering are necessary to remove undesirable components from wet crude oil.

Oil containing water during oil well production, when the production well near oil-water contact, or when there is water conning from the aquifer or when there is water injection in the aquifer.

Crude oil from different reservoirs has different amounts of asphaltenes, wax, bituminous which affect de-emulsification (4-6).

Unremoved most of the salt and water from the crude oil will cause corrosion and fouling when deposited on the heated surfaces (7-8). Similarly refineries, separators, pipes, heat exchangers, etc will be subjected to corrosion during operation, if water in crude oil is not removed. Dissolved metals act as catalyst during crude refinery.

In order to remove salts and water, from crude oil, the crude oil washed with water and then demulsifier are use under electrostatic fields in order to break the emulsion (9-11).

Control pH by acid or alkaline is necessary in order to increase rate of de – emulsion. Water cut increased during well life oil production, since water injection was used to increase the pressure in the reservoir. The interfacial tension between two immiscible or partially miscible liquids reflects in the ability of a particular surfactant systems to solubilize materials include pH and pressure (12 – 14).

The solubility of a particular surfactant systems to solubilize materials which are Hydrophilic-Lipophilic in crude oil depends on pH, pressure, temperature. These long chain hydrocarbons (Lipophilic) with hydrophilic radicals are similar to surfactants. Using polymers as demulsifier will mix with those long chain hydrocarbons in crude oil making complex (10-12), since the polymer have wide range of different molecular weights. If the surfactant was used well below the critical concentration of the surfactant without using the polymer, the surfactant will solubilize the long chain hydrocarbon (6-11).

The East Baghdad wet crude oil was studied because it gives stable emulsion with very active radicals. Different behavior between polar radicals which exist in water and non – polar radicals which exist in crude oil resulting in forming different water layers around the oil drops (6-11). Separation and migration depend on hydrophilic – lipophilic balance which can be represented by equation shown below which relates polarity and non polarity and the pH of the solution. The effect of changes in the hydrophobic chain length on the effectiveness of surface tension reduction is minimum (6-11).

$$H.L.B. = \sum (hydrophilic\ \ group\ \ numbers) - m(group\ \ numbers\ \ per - CH_2 - group) + 7$$

If two oil drops are to coalesce and water of hydration must be displaced, the rate (Rate 1) of oil coalescence will be expressed by

$$Rate\ \ 1 = C_1 \exp\left[\frac{-0.24 y_o^2 - q\sum E_h}{RT}\right]$$

If two water drops are to coalesce and separated by non-polar oil, the rate (Rate 2) of water coalesce will be expressed by

$$Rate\ \ 2 = C_2 \exp\left(\frac{-600mq}{RT}\right)$$

The hydrophilic groups contain mainly 70% of anionic groups such as carboxylic acid, alkyl aromatics sulphonic acid, alkane sulphonic acid, sulphuric acid. While cationic groups contain amine salt, quaternary ammonium compounds.

The formation of small droplets requires that the system overcome both the adverse positive interfacial free energy between the two immiscible phases working toward drop coalescence and bulk properties of the dispersed phase such as viscosity (15 – 19). The possible sizes of the dispersed phase units range from the molecularly dispersed solution where "droplet" sizes are on the order of a few nanometers to macro emulsions with droplet diameters of hundreds or thousands of nanometers (8 – 11).

Experimental Work

The available properties of formation water is specific gravity= 1.12, viscosity= 0.65 cp, formation volume factor= 1.044 vol./vol., and compressibility factor= 2.077î 10-6 Psi-1 (from Iraqi National Oil Co., reservoir report (PVT analysis)). Water salinity is around 23% which contains mainly cations of Na, Mg, Ca, K, Fe and anions of Cl, HCO3, CO3, SO4 *, (3).

In the experiments, an artificial water had been formulated which consisted from 70% by vol. of 20 g/l NaCl, 20% by vol. of 20 g/l MgCl2, and 20% by vol. of 20 g/l CaCl2. Used water content in crude oil was 5% by volume with salt concentration of 2% making total salt content in crude oil to be 1000ppm.

Fig. (1) illustrates the used Electrostatic packed column which consists of about 10 liters vessel packed with packing materials and subjected to 3 kV DC, with continuous circulation of the wet crude blend oil. The packed column is connected to settler, pumps, control valves, and about 20 liters tank which contains stirred wet crude blend oil.

Initially the stability of emulsion was investigated by bottle test, using 20% volume containing 2% wt. NaCl at different temperature, pH, mixing speed, % wash water, mixing time. Variable electrical mixer was used for 20 minutes with speed 2000 rpm at 60°C. The studied demulsifer (concentration ranges from 0.4% up to 1.4% by wt.) was added to the mixture and shaken vigorously for about 7 minutes.

Then the mixture was left for different periods of time (ranges from 10 mins. up to 120 mins.) into the settling tank in order to separate water from oil. The studied surfactant concentration varies from 1 ppm to 8 ppm.

East Baghdad crude oil contains a high percentages of asphaltenes (about 6.2% by wt.) and it also contains metallic impurities such as 76ppm Vanadium, 15 ppm Iron, 30ppm Nickel and has conductivity of 4.5î 10-8 (O.m)-1. East Baghdad crude has specific gravity= 0.9 and kinematic viscosity of 60 centistoks at 26.7°C

Additives were added to the crude oil in the mixing tank at constant temperature for certain period of time and then the mixture is pumped at specified rate into the packed tower at proposed temperature and time. Then the mixture was left for different period of times ranging from 20 mins. up to 120 mins. into the settling tank to separate salt water from the oil.

The studied parameters were packing of either ionic pellets, PVC pellets, quartz pellets, polyethylene pellets, non – ionic pellets at different temperatures from 30 °C up to 80 °C, at pH from 6 up to 9 for time from 2 to 20 minutes, and under voltage from about 2 – 6 kV using 2 ppm of either alkyl benzene sulphonate or 2 ppm of sodium stearate. This work was carried out in order to desalt water from East Baghdad wet crude oil. Using hydrophilic anions groups demulsifier in PVC packed bed.

Results and Discussion

Different experiments were conducted in order to obtain the optimum variables to get higher water separation from East Baghdad wet crude oil. The study was carried by keeping constant all variables and varying only one parameter, so that the optimum conditions was used to study the shortest time required for separation using packed bed.

Packing gave a good separation at low retention time. Therefore, these experiments were conducted at optimum previous experimental measurements. Table (1) illustrates the experimental measurements of each variable, while, Table (2) shows the studied parameter at constant other reported parameters. Each figure has constant specified parameters except the parameters which have been plotted. Figure (1) shows the percent water removal from wet crude oil versus retention time using 2 ppm of either alkyl benzene sulphonate or sodium stearate at constant other variables as shown in Table (2). pH influences percent water removable at constant other variables and using 2 ppm of alkyl benzene sulphonate as shown in Figure (2) and Table (2). Figure (3) illustrates the affects of voltage on percent water removal from wet East Baghdad crude oil at constant other conditions. Figure (4) and Table (2) show the effects of temperature of crude on the percent water removal under specified conditions, while, Figure (5) points the affects of using washing water on the percent water removal from wet crude oil at given conditions at shown in Table (2). Crude oil circulation velocity affects percent water removal as shown in Figure (6) and Table (2). Different types of packing such as anionic, PVC, quartz, polyethylene (PE), polypropylene (PP), non ionic pellets all affects rate of water removal from East Baghdad wet crude oil as shown in Figure (7) and Table (2). PVC pellets were easily available and gave good water separation and therefore, PVC pellets were used through all the experimental studies. The optimum findings of the studied variables at constant of other conditions were reported in Table (3).

Percent water removal increases steeply with retention time using 2ppm additives giving a high percent water removal within 15 minutes. Similarly, pH of 7.2 gives a good percent water removal and then water removal decreases with pH. A higher voltage applied on the crude will give a high water removal from wet crude oil. PVC packing with 3 kV voltage applied is recommended to remove almost most of water from wet crude oil. The results indicate high temperature increases water removal up to 65°C, and after that higher temperature above 65°C will decrease water removal from wet crude oil. Increasing volume of washing water will increase water removal from crude oil, while decreasing circulation crude oil velocity decreases water removal. The experimental results indicate ionic packing has tendency for high water removal as indicated by PVC which is better water removal than PP or PE which are non – ionic packing. Separation depends on the interfacial phenomena between the packing, crude oil, salty water content, polarity, temperature, retention time and pH of the water phase.

Under current potential, the water layers segregate into lower phase leaving oil in the upper phase. Phase separation depends on the structure configuration of the additives and their polarity. The packing increases the surface area between the two fluid phases which accelerate phase separation with efficiency. The studied parameters such as temperature increase active energy and hence increase the migrations and separations of water from the oil. Hydrophilic anionic polar group in PVC will accelerate the separation of water from oil phase due to the chloride ions impeded in the PVC and under voltage will give rise to negative ion charges in the water molecules, even through there is low DC voltage and low % vol. washing water due to formation and rupture of tensio-active film (20-21).

High viscosity of East Baghdad crude oil will slow down water coalescence due to the high molecular weight of oil components. But having a high concentration of hydrophilic anionic polar groups will accelerate water coalescence.

The existence of dissolved salts in water phase which is present in crude oil tends to form drops of water molecules dispersed in oil phase. The Lipophilic hydrocarbon will dissolve in hydrocarbon oil phase and the hydrophilic radicals will dissolve in water phase, due to ionic polar radicals. The present of ionic polar radicals in the packed bed (such as PVC) will accelerate water separation from oil and hence water removal from oil.

Table (1) Experimental measurements for each condition

	Variable condition	Reading measurements
1	Time, min (for used additives)	2, 4, 6, 8, 10, 12, 14, 16, 18, 20
2	pH	6.0, 6.5, 7.0, 7.5, 8.0
3	Voltage, kV	2, 3, 4, 5, 6
4	Temperature, °C	30, 40, 50, 60, 70, 80
5	% vol. washing	5, 10, 15, 20, 25
6	Fluid velocity, cm/s	0.5, 0.55, 0.6, 0.65, 0.70, 0.75, 0.8
7	Packing (Anionic, PVC, Quartz, PE, PP, Non ionic)	2, 4, 6, 8, 10, 12, 14, 16, 18, 20 (min)

Table (2) Varying one operating condition while keeping other variable conditions constant

Variables	pH	Voltage (kV)	Temperature (°C)	% vol. washing	Fluid velocity (cm/s)	Type of Packing	Additives (2ppm)	Retention time (mins.)
pH		3	65	15	0.5	PVC	ABS	20
Voltage (kV)	7.2		65	15	0.5	PVC	ABS	20
Temperature (°C)	7.2	3		15	0.5	PVC	ABS	20
% vol. washing	7.2	3	65		0.5	PVC	ABS	20
Fluid velocity (cm/s)	7.2	3	65	15		PVC	ABS	20
Packing	7.2	3	65	15	0.5		ABS	
Additives (2 ppm)	7.2	3	65	15	0.5	PVC		

Table (3) The optimum studied conditions

	Variables	Optimum
1	Time, min	15
2	pH	7.2
3	Voltage, kV	3
4	Temperature, °C	65
5	% vol. washing	15
6	Fluid velocity, cm/s	0.5
7	Anionic, PVC, Quartz, PE, PP, Non ionic	Anionic or PVC
8	Alkyl Benzene sulphonate (2 ppm), Sodium stearate (2 ppm)	Alkyl Benzene sulphonate (2ppm)

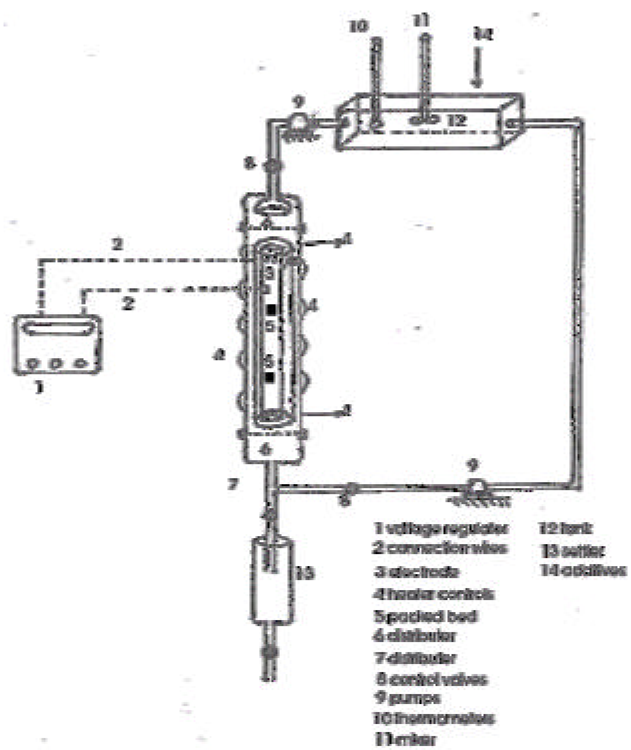

Fig (1) Electrostatic Packed Bed Units

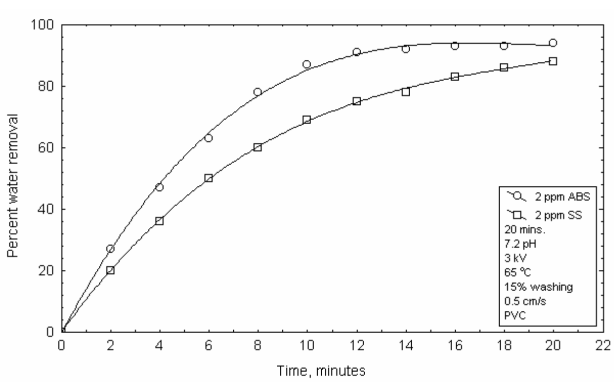

Figure (2) Water removal versus retention time

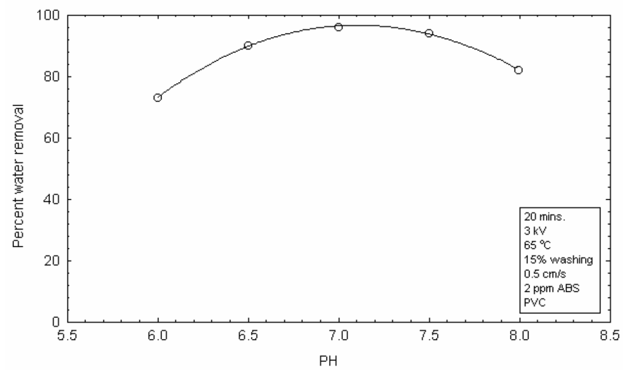

Figure (3) Water removal versus pH

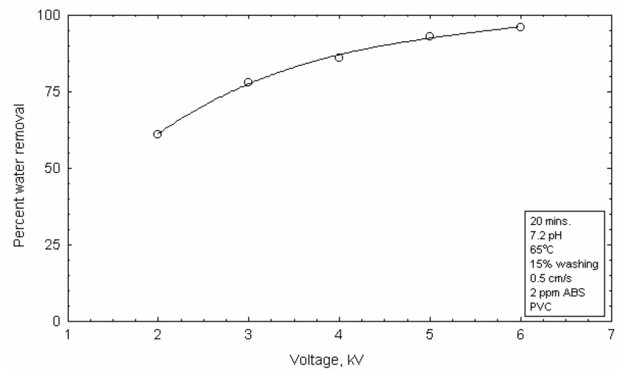

Figure (4) Water removal versus voltage

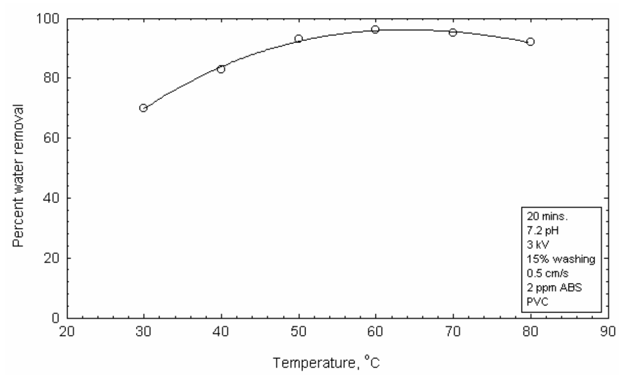

Figure (5) Water removal versus temperature

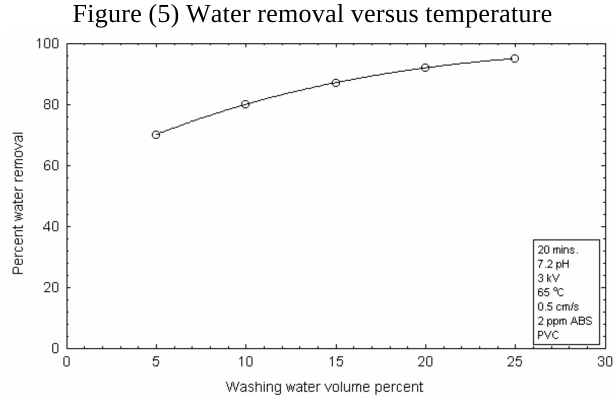

Figure (6) Water removal versus washing water volume percent

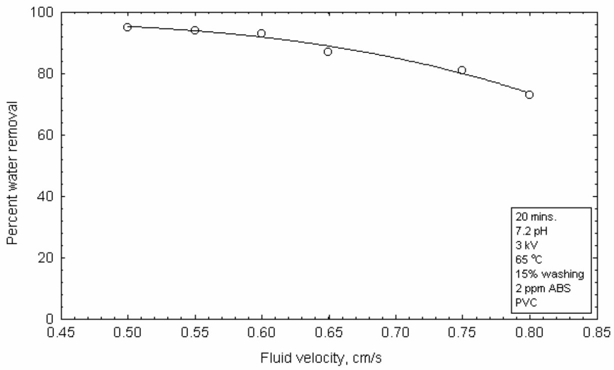

Figure (7) Water removal versus fluid velocity

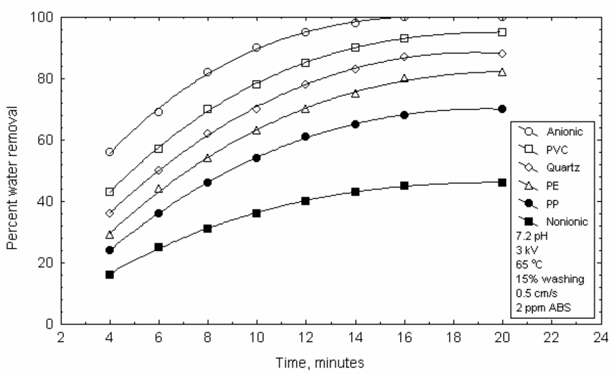

Figure (7) Water removal versus retention time

Conclusions

The following points were obtained from experiments for desalting and dewatering of East Baghdad wet crude oil:

1. 2 ppm alkyl benzene sulphonate removes almost 100% of salty water from the wet crude oil after 15 minutes. 2 ppm of sodium stearate removes salty water with slightly lower efficiency.
2. Packing pellets indicate that anionic pellets and PVC pellets remove almost 100% of water from wet oil.
3. The best parameters used to obtain an efficient water removal from crude oil are, temperature of 65 °C, fluid velocity of 0.5 cm/s, pH of 7.2, 15% by volume washing water under 3 kV voltage for 15 minutes.

Nomenclature

Symbols	***Meaning***
ABS	Alkyl Benzene Sulphonate
C1	Collision factor for oil drops
C2	Collision factor for water drops
CMC	Carboxymethyl cellulose
cp	Centi poise
Eh	Free energy of displacement of hydrated layer at a "deep" surface
HLB	Hydrophilic-Lipophilic Balance
m	Number of –CH2– groups involved in adsorption
PE	Poly ethylene
PP	Poly propylene
PVC	Poly vinyl chloride
R	Gas constant 1.986 cal.mole-1.(c)-1
Rate 1	Rate of oil coalescence
Rate 2	Rate of water coalescence
S.S	Sodium Stearate
T	Temperature (°K)
q	The fraction of the interface covered
y_o	Electrostatic potential in interface relative to the adjacent conducting phase (mv)

References

1. Campbell, J.M. "Gas conditioning and processing", 2nd ed., Campbell Petroleum Series, USA, (1972).
2. Al-Jassim, A.S., "De-emulsification of different Iraqi Crude Oil Emulsions", M.Sc. Thesis, Baghdad University, (1998).
3. Hassan, H.A., Slaiman, Q.J.M., Abu-Al-Gayd, A.K., "Properties of Petroleum and Natural Gas", Iraq, (1985).
4. Salager J.L., "The fundamental basis for the action of a chemical dehydrant: Influence of the physical and chemical formulation on the stability of an emulsion", *Int. Chem. Eng.*, **30** (1), 103 – 106 (1990).
5. Sanford, E., *Can. J. Chem. Eng.*, **62**, 258 (1985).
6. Davies J.T., "Interfacial phenomena", 2nd Ed., Academic Press (1963).
7. Karine B.B. Capabli A., Lamesa, "Polymer – surfactant interactions", *Phys. Chem.*, **3**, 2872 – 2878 (2001).
8. Nordi K.G., Sjöblom, J., and Stenius, P., "Water in crude oil emulsions: Monolayer study of model polymer", *Coll. & Surf.*, **63**, 241–251 (1992).
9. Menon V.B. Wassan, D.T., "Characterization of oil – water interfaces containing: Finely divided solids with application to the coalescence of water in oil emulsion", *Coll. & Surf.*, **29**, 7–27 (1988).
10. "Surfactants general information", *Clean Rti. Org.*, (2005).
11. Adamson A.W., "Physical chemistry of surfaces", 3rd ed., John Wiley & sons (1976).
12. Lemanceau B., *Adv. in Coll. & Int. Sci.*, **20**, 167 (1984).
13. "Polymers wikipedia", *Eng. Org.*, July (2005).
14. Layman P.L., *Chem. Eng. News*, **62** (4), 17 (1984).
15. Jersy K. Stenius, P., Sjöblom, J., Nordi, K.G., "Water in crude oil emulsions from Norwegian continental", **63**, 241 – 251 (1992).
16. "Surfactant", Creative developments limited (2005), www. Creative developments Co., June (2005).

17. Staiss F. Bohm R., Kupfer, R., "Improved demulsifier chemistry", *SPE Prod. Eng.*, 334 – 338 (1991).
18. Mitchell D. J., *J. Chem. Soc. Faraday Trans.*, **77** (2), 601 (1981).
19. Florence A.T., *J. Coll. Int. Sci.*, **79**, 243 (1981).
20. Kenneth, W.W., and Gary W.S., "The roles chemical screening and electrostatic field selection in desalting" NATCO, (2003).
21. Waterman, C., "Operation and maintenance manual for desalter" Petrolite Co., (1982).