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Oil-in-water Emulsion Breaking by Electrocoagulation in a Modified Electrochemical Cell

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Separation of oil from oil-in-water (O/W) emulsion using the electrocoagulation technique was investigated in an electrochemical cell employing new anode geometry. The anode was a horizontal coiled aluminum cylinder with an outer diameter of 1 cm and 0.5 cm gap between turns, the cathode was a horizontal Al disc placed at the bottom of the cell. The present anode geometry allows the use of the anode outer surface for electrocoagulation and the inner surface as a heat exchange facility to control the solution temperature. Variables studied are applied current density, electrolyte conductivity, initial pH of the electrolyte and initial oil concentration. Within the range of parameters studied, the % removal was found to increase with increasing current density, solution conductivity and initial pH in the range (3-8) with the increase in initial oil concentration has a negative effect on the % removal. In order to optimize (technical and economical) the parameters of the present study, electrical energy consumption (kW·h/m^3) was calculated at various operating conditions.

Keywords: Electrocoagulation; Wastewater; Emulsion; Oil removal

1. INTRODUCTION

Production of crude oil is usually associated with water. Water may be produced as it is injected into the reservoir to enhance the recovery of crude oil. Production of water with the crude oil reduces the productivity of the well and causes a serious corrosion problem. Therefore, water must be separated from petroleum crude. Water may be present as free water or emulsified water. Oil emulsions are mixtures of oil and water and can be defined as a mixture of two immiscible or partially miscible liquids, one of which is dispersed in the other in the form of droplets, and is stabilized by an emulsifying agent. There are many sources of oily wastewater in industries such as crude oil fractionation, thermal and catalytic cracking, and washing of tanks. Also, oil-water emulsions are widely used in metal industries in processes such as shaping, rolling and forging. Chemically stabilized oil-water emulsions present several environmental problems to water sources, including high BOD, odor, and turbidity. These problems affect the aquatic life and its severity depends on the source of waste. In petroleum industries emulsions can be difficult to treat and may cause several operational problems [1]. O/W emulsions typically contain from 100 to 1000 ppm of oil with drop diameter from 0.1 to 10 μm, while the allowable limit for oils and greases in wastewater discharged into open water streams is 10 ppm. Therefore, it becomes essential to remove oil from wastewater before it is discharged for final disposal [2-5]. Emulsion separation into oil and water can be done using several methods such as chemical, thermal, mechanical and electrical methods. The most common one is the chemical method where chemicals are added to neutralize the stabilizing effect of emulsifying agents. It may also require the use of electric field, heat and coalescers to completely break the emulsion. The promising methods based on electrochemical principals are electrocoagulation, electroflotation, electrodecantation, and others [6-14]. Electrocoagulation is receiving a great attention for removing organic pollutants from wastewater due to its advantages compared to the others. Electrocoagulation considered to be versatile and safety, no auxiliary chemicals required and do not produce waste and can be easily combined with other technologies.

In case of aluminum as an electrode material, the electrocoagulation process occurs via series steps and can be simply presented as follows:

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+}_{(aq)} + 3e^{-} \quad \text{(anode)} \qquad (1)$$

$$3\mathrm{H_2O} + 3e^{-} \rightarrow 3/2\mathrm{H_2} + 3\mathrm{OH}^{-} \ \text{(cathode)} \qquad (2)$$

The generated Al ions combine with water and hydroxyl ions to form corresponding hydroxides and/or polyhydroxides. The formed hydroxides and polyhydroxides remain in the aqueous medium as gelatinous suspensions, which can neutralize the colloidal charges, resulting in destabilization of the emulsion. Hydrogen bubbles formed at the cathode improves oil separation efficiency via (i) the rising bubbles assist in mixing of the anodically dissolved Al^{3+} ions with the bulk of the solution (ii) the hydrogen bubbles can adhere to the flocculated species and induces its floatation.

Electrocoagulation does not use expensive chemicals but, uses cheap scrap iron and aluminum; this in addition to the simple design of the electrocoagulation cell which makes the capital and operating cost of electrocoagulation much less than that of chemical coagulation and the process has been proven to be more efficient compared to other methods. The efficiency of electrocoagulation process in removing pollutants from water is affected by various parameters. The removal efficiency of EC to some different selected contaminants is shown in table 1.

Table 1. Removal efficiency of EC.

Contaminant	Before EC (mg/L)	After EC (mg/L)	% removal
Ammonia	49	19.4	60.41
Arsenic	0.076	<0.0022	97.12
Barium	0.0145	<0.001	93.1
Benzene	90.1	0.359	99.6
BOD	1050	14	98.67
Cadmium	0.1252	<0.004	96.81
Chlorieviphos (pesticide)	5.87	0.03	99.5
Cyanide (free)	723	<0.02	99.99
Mercury	0.72	<0.003	98.45
Nickel	183	0.07	99.96
Nitrate	11.7	2.6	77.78
Petroleum hydrocarbons	72.5	<0.2	99.72
Phosphate	28	0.2	99.28

Electrocoagulation as an efficient method for oil-water demulsification has received a growing attention by different authors in recent years, the authors used various anodes to improve the efficiency of the electrochemical cell such as fixed bed anode of iron Al cylinders [10], a block of vertically oriented Al parallel-plate electrodes in a continuous flow cell [15], horizontal intermeshing steel vanes [16], and rotating cylinder Al anode [17] etc.

The present work aims to study the effect of electrocoagulation parameters on the % removal of the oil from O/W emulsion in a new cell geometry consists of a spiral anode and a horizontal disc cathode. The cell geometry provides high surface area of electrode per unit volume of the cell and make a beneficial use of hydrogen evolution, which allow good removal efficiency at a low level of energy consumption. Besides, the inner side of the coiled tube can be used as a heat exchanger to control the temperature in the cell. The performance characteristics of the cell electrodes which can perform dual functions have been reported by different studies [18,19].

2. EXPERIMENTAL SECTION

2.1. Setup

The experimental setup used in conducting the experiments of the present work consists of a cell and an electrical circuit. The cell is made of a Plexiglas cylindrical container of 15 cm inner diameter and 25 cm height.

The cathode was a horizontal aluminum disc of 14.5 cm diameter resting on the container bottom while the anode was a horizontal spiral with an outer tube diameter of 1 cm, pitch (the gap between turns) was 0.5 cm. The vertical distance between the anode and the cathode was maintained at 1 cm. The electrical circuit consisted of 20 V D.C. power supply with a built-in voltage regulator and a multi-range ammeter connected in series with the cell to measure its current. A high impedance voltmeter was connected in parallel with the circuit to measure the actual cell voltage. Insulated copper wires were used as a current feeder to the cell electrodes.

2.2. Procedure

A stable synthetic emulsion was prepared to simulate the actual case. A known weight of the engine oil (SAE 15W-50 Mobile oil) was added to the emulsifier which is a mixture of equal volume of nonylphenol ethylate + castor oil soap. The mixture was stirred for at least 15 minutes and then an amount of water is added depending on the required oil concentration. The characteristics of the engine oil, nonylphenol ethylate, and castor oil are listed in tables 2, 3, and 4.

Table 2. General characteristics for the engine oil (SAE 15W-50 Mobile oil)

Test	Method	Result
Density @15.6 ˚C g/ml	ASTM D4052	0.87
Flash Point, ˚C	ASTM D92	232
Vapor Density (Air = 1)		> 2 at 101 kpa
Vapor Pressure		< 0.013 kpa (0.1 mm Hg) at 20 ˚C
Viscosity @ 100 ˚C	cSt ASTM D445	18
Viscosity, @ 40 ˚C	cSt ASTM D445	125
Viscosity Index		160
Pour Point		-47 ˚C (-53 ˚F)
Sulfated Ash, wt%	ASTM D874	1.21
SAE Grade		15W-50

Table 3. Characteristics of nonylphenol ethylate

Formula	$C_9H_{19}C_6H_4(OCH_2CH_2)n\ OH$
Viscosity at 25 ˚C (77 ˚F), cP	237
PH	6.3 (10% sol.)
Specific gravity	1.03 ± 0.01
Density at 20 ˚C (68 ˚F), g/mL	1.060
Surface Tension(: dynes/cm at 1% actives, 25 ˚C)	33
Pour Point (˚C)	6
Appearance	Pale yellow liquid
Flash point	94 ˚C

Table 4. Characteristics of castor oil

Ingredients	Vegetable Oil Triglycerides 100%
Boiling Point	313 ˚C
Melting Point	-10 ˚C
Specific Gravity	0.962 @ 15 C (Water = 1)
Solubility in Water	Insoluble

Before the start of each run the cell was filled with 2 L of a synthetic oil–water-emulsion, during electrolysis a sample of 5 cm^3 was taken from the bulk of the emulsion every 5 mins for oil analysis. Oil concentration in the emulsion was determined by means of a visible spectrophotometer (UNICO ® 1200) using a wavelength of 722 nm. A calibration curve (absorbance vs. oil concentration) was used to determine the oil concentration from the sample absorbance measured by the spectrophotometer.

The residual oil concentration was measured at different current densities, different initial pH of the emulsion, different initial oil concentration, and different electrolyte conductivity.

3. RESULTS AND DISCUSSION

3.1. Effect of initial concentration of the oil

The influence of the initial oil concentration on the % removal of oil is shown in Fig.1. The figure shows that the percentage removal decreased with increasing oil concentration. This may be explained by the fact that at a constant current density the anodically dissolved Al^{3+} and H_2 production rate are constant and distributed over a large number of oil droplets, thus the adsorption capacity of gelatinous aluminum hydroxide compounds is consumed. Also, the fixed anodically dissolved Al^{3+}diminishes the neutralized negative charges existing at the interface between the oil droplets and the aqueous phase which is important for emulsion breaking.

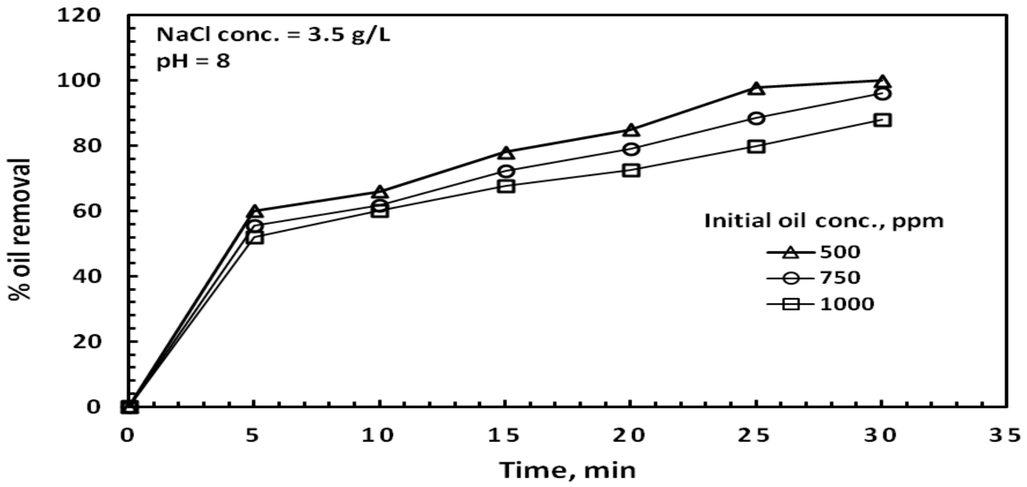

Figure 1. Effect of initial oil concentration on the % removal.

3.2. Effect of applied current density

The current density is related to the coagulant dosage formed at the anode and the bubble generation rate at the cathode which affect the extent of mixing within the cell and floatation of the sludge. The amount of metal dissolved is related to the current density by the equation (Faraday's law):

$$m = \frac{M}{Z \times 96500} \times i\ A\ t \qquad (3)$$

Where m is the mass dissolved per unit time, M is the molecular weight, Z is the valency, i is the current density, A is the active surface area of the electrode, and t is the operating time.

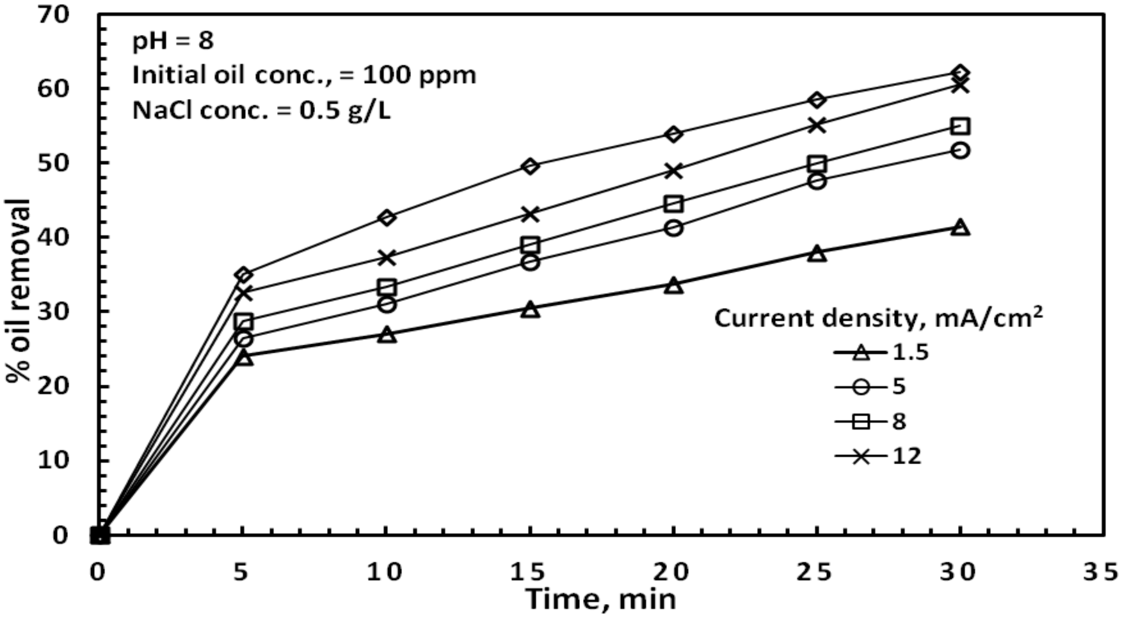

Figure 2. Effect of applied current density on the % oil removal.

Fig. 2 depicts that the % removal of oil increases as the current density increases. This is ascribed to: (i) the increase in the dissolved Al^{3+} according to equation (12) (ii) The increase in the cathodically generated small sized H_2 bubbles which are not only assist in mixing the anodically formed Al^{3+} with the oil/ water emulsion but also assist in floating the coalesced oil phase to the top of the dispersion. The coalesced oil drops adhere to the uprising H_2 bubbles to the top where a separate oil layer formed [13, 20-24]. (iii) increasing the electrophoresis of the negatively charged oil droplets towards the positively charged anode under the influence of increasing the current density increases the rate of demulsification via the neutralization of these droplets at the anode [12].

It should be noted that the selection of the optimum economical current density does not depend on the highest value, but the one corresponding to the minimum total operating cost and it is related to other operating parameters such as electrolyte temperature, pH, conductivity, and the hydrodynamic conditions of the solution in the cell to ensure a high current efficiency. Previous studies on oil separation from oil-water-emulsion reported that a current density between 20 – 25 A/m^2 is suggested to operate an electrocoagulation system continuously for a long period without maintenance [2-4].

3.3. Effect of electrolyte conductivity

Fig. 3 shows that the % removal of oil increases with increasing NaCl concentration (electrolyte conductivity). Increasing NaCl concentration from 0.5 to 3.5 g/L increased the % removal by a factor ranged from 1.31 to 1.51. Generally, the addition of NaCl plays two important roles, namely, (i) to increase the electrolytic conductivity, and (ii) during electrolysis active chloride will be produced, which will contribute to the water disinfection and also eliminates the formation of passive layer on the anode and improve the current efficiency [20, 25].

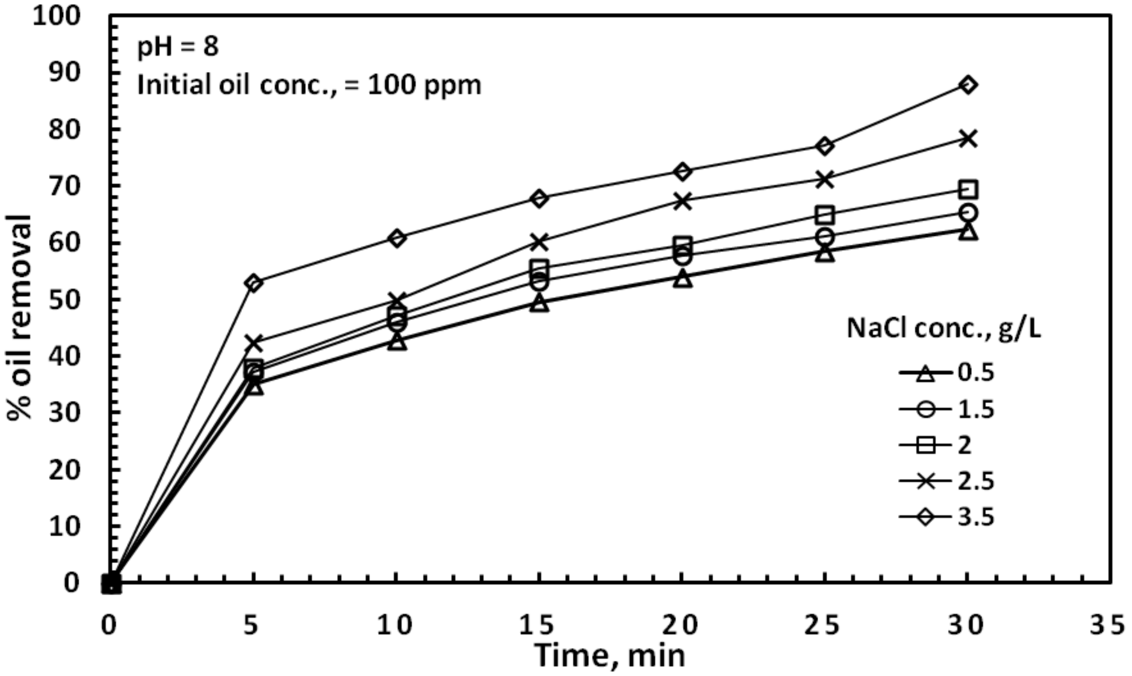

Figure 3. Effect of NaCl concentration on the % oil removal.

When the electrolytic conductivity is low a high applied potential is required which leads to the passivation of electrode, decrease the current efficiency and increase the treatment cost. The addition of Cl^{-} will also decreases the negative effect of CO_3^{2-} and SO_4^{2-}. The presence of CO_3^{2-} and SO_4^{2-}will lead to the deposition of Ca^{2+} and $Mg^{2+}$and formation of an oxide layer, which will decrease the current efficiency rapidly. It is therefore recommended that among the anions present, there should be 20% Cl^{-} to ensure a normal operation of electro-coagulation in water treatment. The high contents of NaCl have the advantage of lowering the voltage of the cell and lowering the energy consumption [25,26].

3.4. Effect of pH

Fig. 4 shows the effect of initial pH of the electrolyte on the % removal of oil. The data show that the process is highly dependent on pH and it has various effects. The % removal of oil increase with increasing pH in the range (3 – 8) and outside this range % removal decreased. The pH of solution plays an important role in electrochemical and chemical coagulation process [20]. Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of electrochemically dissolved Al^{3+}[27].

In the pH range of (3–8),$Al(OH)^{+2}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{+4}$, $Al(OH)_3$, and $Al_{13}(OH)_{32}^{+7}$, are formed. The surface of these compounds has large amounts of positive charge, which can lead to adsorption electrochemistry neutralization and net catching reaction [10].

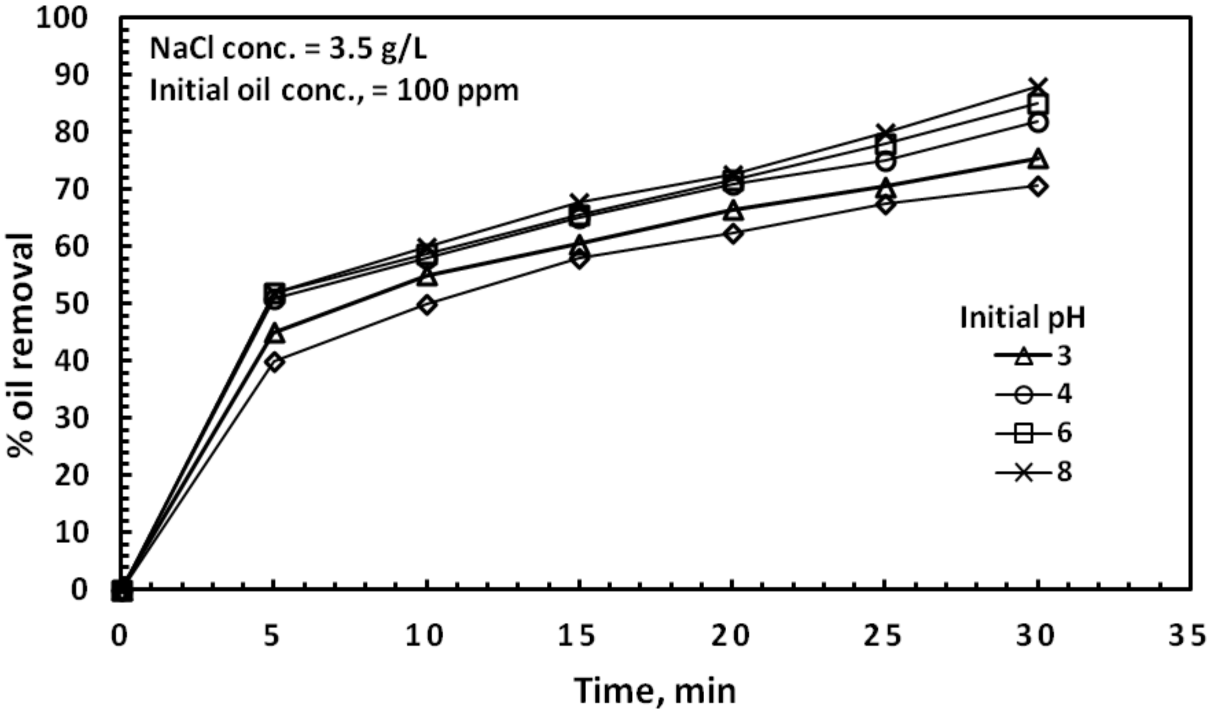

Figure 4. Effect of initial pH of the emulsion on the % removal at different operating times.

At (pH > 10), $Al(OH)_4^-$is dominant, and the coagulation effect rapidly decreases. At low pH, $Al^{3+}$is dominant, which has no coagulation effect.

3.5. Electrical energy consumption

To assess the economic feasibility of electrocoagulation in comparison with other demulsification techniques such as chemical coagulation and ultrafiltration, electrical energy consumption and Al metal consumption were calculated for 99% demulsification. Electrical energy consumption (E.C) in k.W.h/m^3 of the treated effluent was calculated from the formula:

$$EEC = \frac{E \times I}{1000 \times Q} \quad (4)$$

where E is the cell voltage, I is the cell current and Q is the volume of solution treated/hour. Electrical energy consumption was calculated for 99% demulsification of initial oil concentration of 500 ppm, under different conditions. The cell voltage fluctuated between 5 and 16 volts, while the 99% demulsification time ranged from 30 to 45 minutes. The average electrical energy consumption ranged from 3 to 9 kW·h/m^3 of treated emulsion. The amount of Al metal consumed in demulsification was calculated from Faraday’s law:

$$m = e \times I \times t = \frac{27}{3 \times 96500} \times I \times t \qquad (5)$$

where m is the amount of Al dissolved in grams; e is the electrochemical equivalent, I is the cell current; and t is the electrolysis time required to remove 99% of the oil. For the aforementioned case where the electrolysis time ranged from 30 to 45 min the amount of Al consumed ranged from 0.061 to 0.168 g/m^3 of treated emulsion.

4. CONCLUSIONS

A new electrocoagulation cell consists of a horizontal spiral aluminum anode and a horizontal disc aluminum cathode was used in oil/water emulsion breaking. The cell makes an efficient use of the hydrogen bubbles evolved at the cathode to improve the floatation ability of the cell and at the same time allows the use of the anode inner surface as a heat exchanger to control temperature and also provides a large electrode area per unit volume of the cell. The effect of various operational parameters on % removal of oil was investigated. The results showed that the % removal increases with the increase in current density, initial pH in the range (3-8) and electrolyte concentration. While the % removal decreases with the increase in oil concentration.

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