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Research of Properties of Water and Oil Products Emulsions and Their Separation

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***Abstract*—The article provides the results of experimental research of the separation of water-oil emulsions of different composition, consisting of oil, fuel oil and water of different structure, chemical and ionic composition (river, sea, artesian). A method for separating oil-water emulsions using the introduction of sea salt ash is proposed.**

Keywords—water-oil emulsion; oil; fuel oil; river water; sea water; hardness salts; sea salt

I. Introduction

The stable oil-water emulsions are formed in the process of oil production as a result of intensive mixing with water pumped into the oil reservoir with the intensive turbulence of oil and water flows during transportation through pipelines, [1]. The presence of water in oil negatively affects the efficiency of its processing in order to obtain light fractions of hydrocarbon fuels. Since the water, contained in the oil, when it is heated, reduces the partial pressure of the vapors of petroleum products, the process of oil separation is unstable. Water contained in oil deactivates the catalysts used to increase the degree of conversion of hydrocarbons in the processes of its destruction to obtain light fuel fractions, solvents, individual hydrocarbons, products and semi-products of petrochemical synthesis.

While preparing oil for refining, electrical desalting plants generate significant amounts of oil-in-water emulsions, which are highly toxic and have a negative impact on the environment [2, 3].

So, the problem of oil-water emulsions separation is very relevant and in demand.

II. Results and discussions

While studying the properties and process of water-oil emulsions separation, it was found that with the introduction of sea salt ash into the emulsion, the intensity of its separation significantly increases [4, 5, 10].

To study the kinetics of water-oil emulsions separation, the following products were used:

A. Oil products:

1. Oil of JSC "Lukoil"

2. Fuel oil

B. Water structures:

1. Artesian water

2. River water (River “Polnoy Voronezh”)

3. Sea water (the Black Sea)

Chemical and ionic compositions of water of various structures used for the preparation of emulsions are analyzed. The results of studies of the composition of sea, river and artesian water are presented in Tables I-IV.

TABLE I. IONIC COMPOSITION OF SEA WATER.

Cations	mg/l	Equivalent. %	Anions	mg/l	Equivalent %
Na^{+}	10760	38.64	Cl^{-}	19353	45.06
Mg^{2+}	1296	8.81	SO_4^{2-}	2712	4.66
Ca^{2+}	412	1.69	HCO_3^{-}	141	0.20
K^{+}	399	0.84	Br^{-}	67	0.07
Sr^{2+}	8	0.01	-	-	-
Total:	12875	49.99	Total:	22273	49.99

TABLE II - CHEMICAL COMPOSITION OF SEA WATER

Salts	mg/l	% mass.
NaCl	about 27300	about78
$MgCl_2$	more than 3150	more than 9
$MgSO_4$	more than 2275	more than 6,5
$CaSO_4$	about 1225	about 3,5
KCl	about 700	about2
Hydrocarbonates	less than 350	less than 1

TABLE III - IONIC COMPOSITION OF RIVER WATER

Ion	Content, mg/l	Ion	Content, mg/l
Cl^-	2.5	K^+	0.5
SO_4^{2-}	8.9	Mg^{2+}	0.4
HCO_3^-	9.2	Ca^{2+}	0.6
Na^+	1.8		

TABLE IV - IONIC COMPOSITION OF ARTESIAN WATER

Substance	Content,mg/l	Substance	Content,
SO_4^{2-}	5.2	Mg^{2+}	1.2
Cl^-	1.9	HCO_3^-	15.4
Ca^{2+}	0.3	Na+	2.7

Fig. 1. Installation for emulsions preparation: 1– engine; 2 – container with emulsion.

For emulsions preparation, 50% of fuel oil or oil and 50% of (river, sea, artesian) water were used. Oil and water were placed in a container 2 and stirred with a paddle stirrer for 30 minutes at a speed of 100 revolutions per minute on the unit shown in Figure 1. The obtained samples of the emulsions were placed in measuring cylinders with a capacity of 200 ml and were precipitated.

The observation results of the emulsions separation process are presented in Figure 2; it is clear that the most complete separation occurred when used to prepare the emulsion of river and sea water. The smallest separation is observed when using artesian water.

In the study of the separation process of emulsions fuel oil-water, using water of various structures (artesian, sea, river), it has been found that the kinetics of separation of fuel oil emulsions with river water is most intense.

The content of salts and ions in the samples of water used in experimental studies shows that the low kinetics of the separation process of the oil-water emulsion obtained as a result of dispersion of artesian water in oil is affected by the high content of calcium and magnesium carbonate and carbonate salts in the water. The assumption is confirmed by the fact that the emulsion obtained by mixing sea water and oil is also difficult to separate. The kinetic characteristics of the separation of an oil product emulsion with river water containing a minimum amount of salts (Table III) have higher rates. When comparing the data of Tables I and II, it was found that the maximum salt content is in sea water. Salts that are dissolved in sea water have a different composition than salts contained in artesian and river waters. Their main mass is NaCl, which is in water in ionic form. The main share of salts contained in artesian water is hardness salts — carbonates and hydrocarbonates, which have a higher binding energy with the contact surface of any substance.

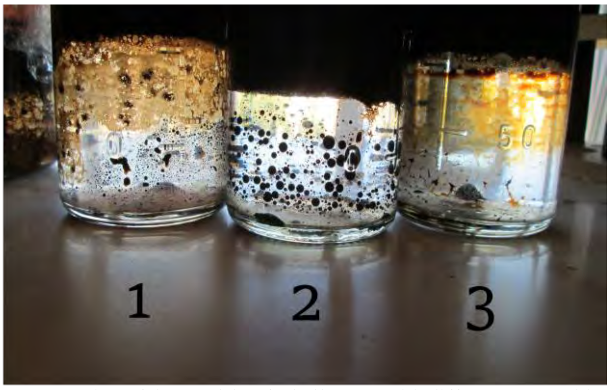

Fig. 2. Separation of the emulsion fuel oil-water with different composition
1 — emulsion fuel oil — sea water in the ratio of 1: 1; 2 — emulsion fuel oil — artesian water in the ratio of 1:1; 3 —emulsion fuel oil — river water in the ratio of 1:1

The hardness salts contained in artesian water, adsorbed on high molecular weight associates of oil, increase the binding energy of the globules of water and oil.

The kinetics of separation of water-oil emulsion of river water is higher in value, which is explained by the low content of carbonate and bicarbonate salts of calcium and magnesium in it, forming a chemisorption bond on the surface of high-molecular-weight hydrocarbons. The results obtained are confirmed by the results of experimental data presented in Fig. 2. The use of oil products of different fractional composition allows evaluating its effect on the kinetic characteristics of the process of demulsification using sea salt ash.

To increase the intensity of the process of separation of oil-water emulsions, the ashes of sea salt were introduced to neutralize the emulsifying effects of the salts present in the oil-water emulsion. Sea salt ash is obtained by burning in a muffle furnace at a temperature of 600 °C.

Fig. 3 provides samples of fuel oil-water emulsions. For the preparation of emulsions, fuel oil and distilled water were used in a ratio of 1: 1, stirred with a paddle stirrer at a speed of 100 rpm for 30 minutes. 0.5 grams of sea salt ash was added to sample No. 2. Figure 1 demonstrates an increase in the intensity of separation of the fuel oil-water emulsion with the introduction of sea salt ash particles into it. The ash structure of sea salt was analyzed for elemental composition by X-ray diffraction.

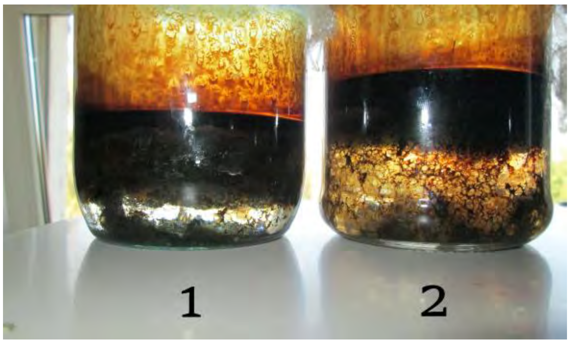

Fig. 3 Emulsion fuel oil-water: 1 — natural exfoliation; 2 — with the introduction of sea salt ash.

The elemental composition of sea salt ash is presented in Table V.

TABLE V. THE ELEMENTAL COMPOSITION OF SEA SALT ASH

Element	Amount, mg/kg	Element	Amount, mg/kg
1	2	3	4
Na	10436	Si	197
S	2850	Cl	2689
Mg	1230	I	568
Ca	450	Fe	679
K	385	Zn	146
C	123	Cu	234
O	318	Sr	14
Ba	56	F	1

The emulsion, prepared in the ratio of oil: water - 3: 1, was stirred with a paddle stirrer for 10 minutes at a rotation speed of the stirrer of 100 revolutions per minute. An increase in the intensity of the oil-water emulsion separation was observed when adding emulsions of different composition of sea salt ash particles in an amount of 0.3 grams to the samples.

To eliminate the influence of salts in waters of different structures on the process of demulsification oil-water emulsions, the following water structures condensates were used: sea water, river water, artesian water. 12 samples of emulsions were prepared: 6 — reference samples, 6 — samples with sea salt ash. The compositions of the samples are presented in Table VI.

TABLE VI. COMPOSITION OF THE SAMPLES OF WATER EMULSIONS IN OIL PRODUCTS

No.	Composition
1	2
1	Tap water condensate + oil
2	Sea water condensate + oil
6	River water condensate + oil
4	Artesian water condensate + oil + sea salt ash
5	Sea water condensate + oil + sea salt ash
6	River water condensate + oil + sea salt ash
7	Artesian water condensate + fuel oil
8	Sea water condensate + fuel oil
9	River water condensate + fuel oil
10	Artesian water condensate + fuel oil + sea salt ash
11	Sea water condensate + fuel oil + sea salt ash
12	River water condensate + fuel oil + sea salt ash

Fig 4. Formation of the phase boundary in the fuel oil emulsion - river water

The obtained emulsions were placed in graduated tubes with a capacity of 20 ml. In 7 days, the absence of a visible phase boundary in the samples of water-oil emulsions (condensates of sea, river, artesian water with oil and fuel oil) obtained by the above route without the addition of sea salt ash was noted. At the same time, the formation of a clear phase boundary between the oil — condensate of river water for sample No. 12 (Fig. 4) and oil — condensate of river water for sample No. 5 (Fig. 5) was observed.

After 2 weeks of sinking, separation of emulsions of oil-condensate of seawater with the introduction of sea salt ash was found (Fig.5).

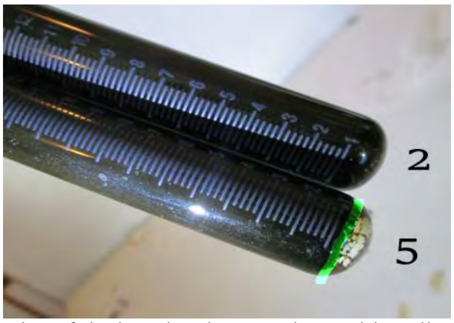

Fig. 5. Formation of the boundary between the emulsion oil and sea water condensate

Two weeks later, the thickness of the water layer at the bottom of the tube doubled. The separation of samples of oil-water emulsions without the addition of sea salt ash is not observed.

With sea salt ash particles, the kinetics of the water-oil emulsion separation process increases, which is accompanied by an increase in the diameter of water droplets and their deposition rate. The main part of the water is separated from the water-oil emulsion due to the gravitational forces with the difference between the densities of oil and water, and the separation of fuel oil and water is much easier.

Due to intensive turbulence in the oil and water flows during its production, when pumping through pipelines with high power pumps, an intermediate layer forms at the oil /

water intermediate layer (Fig.6), which is a highly dispersible emulsion that is difficult to separate.

Fig 6. Formation of an intermediate layer of oil - water.

The intermediate layer of oil contains a significant amount of water. The stability of water-oil emulsions consists of kinetic (sedimentation) and aggregative [3].

The kinematic stability of the oil-water emulsion is characterized by the inverse of the sedimentation rate (or ascent) of particles of the dispersed phase (water drops) [4]:

$$K_y = \frac{1}{w_r} = \frac{9v}{2\left(\rho_в - \rho_н\right) r^2 g},$$

where W_r – deposition rate of the dispersed phase, m/sec; r – dispersion phase radius, m; ($\rho_в$ — $\rho_н$) — difference between the densities of the dispersed phase and the dispersion medium, kg/m^3; υ — kinematic viscosity, m^2/sec; g – gravitational acceleration, m/sec^2.

With an increase in the viscosity of the dispersion medium and a decrease in the difference in the densities of the dispersed phase and the dispersion medium, the kinetic stability of the oil-water emulsion increases. This assumption is confirmed by the results of the separation of the emulsion of water and fuel oil, which has a greater rate than the emulsion of water and oil. The stability of the emulsion increases with increasing diameter of the oil globules. Based on the above, it can be concluded that with an increase in the degree of dispersion of media, the kinetic stability of the oil-water emulsion also increases [6, 7]. The globules of the dispersed phase during mutual collisions, as well as contact with the phase boundary under the action of molecular attraction forces (van der Waals forces), merge to form globules of larger diameter. As a result of a decrease in aggregative stability, sedimentation (kinetic) stability also decreases. Reducing the stability of the emulsion is an important requirement when preparing an oil well for field oil production [8, 9]. Oil-water emulsions are characterized by significant stability and are prone to long-term existence.

The forces of mutual attraction and repulsion stabilize the ratio and spatial orientation of water and oil droplets relative to each other. The water in the oil contains salts that are part of the formation water, which are emulsifiers of water droplets in the oil (Fig. 7).

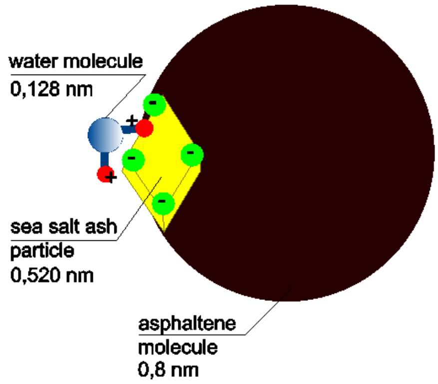

Fig 7. Scheme of adsorption of water molecules on the surface of a particle of sea salt ash

With the introduction of an additional amount of water under conditions of intensive mixing, the formed spatial bonds between the molecules of hydrocarbons of oil and water adsorbed on their surface are destroyed, and conditions for leaching of adsorbed salts are formed.

Introduction of sea salt ash particles into the oil-water emulsion forms energy centers around which solvated on the surface of the salt oil globule are stabilized (Fig. 8). When NaCl is formed in the ionic form in an aqueous solution, their mobility in the formation water increases. Ions of salts that are in the active state tend to take a more energetically favorable position, and they are moved from a zone with a low concentration, in which there are no forces of mutual attraction of charged particles to a zone with a high concentration. The energy center of the zone of high concentration of salts and their ions is the particle of sea salt ash in the water. These particles form in the volume of the liquid medium the movement of salt ions in the reservoir water. The effect obtained is observed in the case when the chemical composition of the salts of the produced water of oil is similar to the chemical composition of the ash particle of sea salt placed in a water-oil emulsion. The ions of salts dissolved in the formation water are adsorbed on the surface of the ash particles of sea salt, thus forming a more powerful surface of the salt structure, which forms a higher sorption energy for water droplets that are dispersed in the bulk of the oil product.

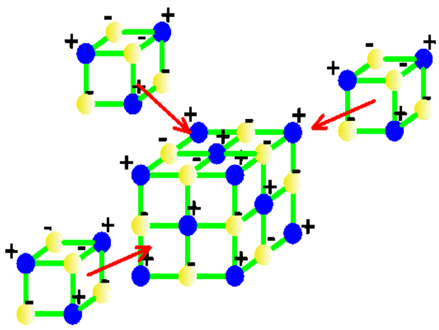

Fig. 8. Adsorption of particles of dissolved salts on the ash particle of sea salt.

So, at this energy center formed by the ash particles of sea salt, the crystal structure grows due to the movement of ions dissociated in water. In the presence of the energy centers of the ash particles of sea salt in an aqueous solution, conditions are formed for separating water from the emulsion in the oil product.

III. CONCLUSIONS

The result of experimental studies to determine the properties and parameters affecting the stability and speed of separation of oil-water emulsions proved that the introduction of sea salt ash particles into the emulsion increases the sedimentation rate of the aqueous phase from the emulsion by reducing the bonding energy of the oil globule - a drop of water. There is also an increase in the rate of fusion of drops of water dispersed in the bulk of the oil product.

The identified effects make it possible to increase the efficiency of separation of water-oil emulsions due to the introduction of ash particles of sea salt.

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