

The effectiveness of chemicals used in the process of transmitting crude oil from the well to the processing plant

Efektywność środków chemicznych stosowanych w przesyłce ropy naftowej z odwiertu do instalacji procesowych

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ABSTRACT: Chemicals are added to crude oil to ensure that it flows from the well to the processing plant. Depending on the composition of the reservoir fluids being extracted (crude oil, reservoir water, natural gas), paraffin may be separated from the crude oil, hydrates may be formed from reservoir water and natural gas, and the combination of reservoir water and crude oil may form an emulsion. Those situations should be avoided to ensure continuous flow from the wellbore to the processing plant. To this end, chemicals, paraffin inhibitors, hydrate inhibitors, and demulsifiers are used. Based on the literature on the subject and on the author's own experience from observing technological processes, research methods were proposed to assess the effectiveness of chemicals used to ensure the continuity of crude oil flow. The crude oil selected for the tests was characterised by a high content of paraffins, asphaltenes, chloride ions, and water. To determine the onset of paraffin precipitation, tests were conducted based on a change in viscosity and a coupon method – determining the weight gain on a coupon to check the effectiveness of a paraffin inhibitor. The rate of emulsion separation was evaluated in separating funnels. The water released from crude oil often leaches the salt contained within it. Various demulsifiers were used to investigate the separation of emulsions and the purification of oil from salts; silicone demulsifiers in particular were considered. To determine the change in the amount of salt in crude oil, a conductometric measurement was performed. The amount of demulsifier used for phase separation was determined by changing the surface tension. The proposed solution for the use of chemicals to transport and purify crude oil yields tangible economic benefits. The article summarises the research procedures and presents the results for selected crude oil and chemicals.

Key words: oil transportation, paraffin inhibitors, demulsifier, removal of salt from oil.

STRESZCZENIE: Dodawanie środków chemicznych do ropy naftowej ma zapewnić jej przepływ między odwiertem a urządzeniami procesowymi kopalni ropy naftowej. W zależności od składu wydobywanych płynów złożowych (ropa naftowa, woda złożowa, gaz ziemny) z ropy naftowej może wydzielać się parafina, z wody złożowej i gazu ziemnego mogą powstawać hydraty, a z połączenia wody złożowej i ropy naftowej może powstawać emulsja. Aby zapewnić ciągłość przepływu z odwiertu do instalacji procesowych, należy stosować środki chemiczne przeciwdziałające tym zjawiskom: inhibitory parafinowania, inhibitory hydratów i demulgatory. Na podstawie doniesień literaturowych oraz własnych doświadczeń opartych na obserwacjach procesów technologicznych w instalacjach procesowych – zaproponowano metody badawcze w celu oceny efektywności środków chemicznych stosowanych do zapewnienia ciągłości przepływu ropy naftowej. Do badań wybrano ropy naftowe, które cechowały się dużą zawartością parafin, asfaltenów, jonów chlorkowych oraz wody. W celu określenia początku wytrącania parafiny przeprowadzono badania oparte na zmianie lepkości. Metodą kuponową określono przyrost masy na kuponie dla sprawdzenia skuteczności inhibitora parafiny. Szybkość rozdziału emulsji oceniono w szklanych rozdzielaczach. Wydzielająca się woda z ropy naftowej niejednokrotnie wymywa sól w niej zawartą. Do badań rozdziału emulsji i oczyszczania ropy z soli użyto różnych demulgatorów jonowych i niejonowych, a w szczególności zwrócono uwagę na silikonowe demulgatory. W celu określenia zmiany ilości soli w ropie naftowej zastosowano pomiar konduktometryczny. Ilość użytego demulgatora do rozdziału faz określono za pomocą zmiany napięcia powierzchniowego. Zaproponowane rozwiązania użycia środków chemicznych do transportu i oczyszczania ropy naftowej przynoszą wymierne skutki ekonomiczne. W artykule zebrano procedury badawcze oraz przedstawiono wyniki badań dla wybranych wysokoparafinowych ropy naftowych oraz środków chemicznych.

Słowa kluczowe: transport ropy, inhibitory parafiny, demulgator, usuwanie soli z ropy.

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Article contributed to the Editor: 03.08.2020. Approved for publication: 02.11.2020 r.

Introduction

The process of separating paraffin from reservoir fluids, particularly during the flow of crude oil from a well to a processing plant, is often the reason for interrupting extraction (Pauly et al., 2004). To prevent this, paraffin inhibitors are applied (Guo et al., 2004; Jang et al., 2007; Jafari et al., 2013; Chi et al., 2017). When developing a laboratory test programme to assess the effectiveness of inhibitors in preventing paraffin precipitating from crude oil whilst flowing, it is necessary to determine the deposition conditions of the temperature-dependent solid phase (wax appearance temperature [WAT]) (Pedersen and Rønningsen, 2003; Kelland, 2009; Japper-Jaafar et al., 2016). Establishing the temperature at which the first paraffin crystals begin to appear under given conditions is necessary in order to determine the effectiveness of the paraffin inhibitor and the amount required (Beben, 2010).

High-molecular-weight paraffin containing 18 to 60 carbon atoms per molecule is the main issue when paraffin crude oil is transferred through a pipeline. Crude oil is a mixture of paraffins, aromatic compounds, naphthenics, asphaltenes, and resins (Ribeiro et al., 1997; Loskutova et al., 2015). High-molecular-weight paraffins (linear chain n-paraffin and branched chain paraffin isopine) and asphaltenes are mainly responsible for the issues related to ensuring flow during transfer (De Souza Mendes and Thomson, 2012). During the flow of crude oil, the pressure and temperature change; the paraffin molecules then crystallise into solids, which build up in larger agglomerates, adhering to the pipeline walls and reducing the flow (Tinsley and Prud'Homme, 2010). The formation of paraffin crystals occurs in three stages: 1) nucleation – the formation of small particles of crystallised material from which the first paraffin crystals will grow; 2) growth – the transport of solution mass towards the nuclei formed during the nucleation stage; 3) agglomeration – the formation of the growing crystals into larger crystals (Vieira, 2008).

The process plant inlet temperature is usually much lower than that of the production well. Paraffin crude oil which is below the paraffin precipitation temperature stops flowing in the pipeline (El-Gama, 1998). Therefore, in order to allow paraffin crude oil to flow, inhibitors are used to lower its solidification point (Pedersen and Rønningsen, 2003; Vieira, 2008).

Crude oil is extracted with highly mineralised reservoir water; therefore, it contains large amounts of salt in the form of stable emulsion and colloidal crystals ($< 1 \mu\text{m}$). Separating the brine from the crude oil results in difficulties, particularly when it forms stable emulsions, stabilised by asphaltenes, resins, and water-insoluble salts from the crude oil. Saline crude oil poses a significant technical and economic challenge, as oil in such a form is highly corrosive to the equipment

used in refineries, such as distillation towers, heat exchangers, or condensers; thus, such oil has a low market value. Depending on the stability of the emulsion, it is separated in separators and heated to a temperature of about $50\text{--}60^\circ\text{C}$ and the emulsion is broken in high-speed centrifuges or in an electric field. The latter method is the most effective. It is based on the presence of electric charges on the surface of the emulsion droplets.

These emulsion separation processes can be accelerated by using an appropriate demulsifier. Demulsifiers are surfactants which reduce the surface tension at the crude oil–water molecular interface. For the separation of such an emulsion, non-ionic surfactants with both lipophilic and hydrophilic groups are mainly used.

Simple methods are known for dosing the demulsifier into the reservoir fluid at the wellhead zone to the pipeline, after pressure reduction, where the reservoir fluid whilst flowing through the pipeline achieves an appropriate contact time of the reservoir fluid–demulsifier interface, followed by the water phase separation together with contained salts in a separator (Beben, 2010). By so doing, crude oil's salinity can be reduced to less than 10 mg/dm^3 , while requires 35 mg/dm^3 .

Samples and methods

Study material

Crude oil from wells in the north-west of Poland (A-1, A-2, and A-3) were selected for the study.

The paraffin inhibitors and demulsifiers tested were as follows:

- A50 ion paraffin inhibitor containing polyolefin copolymer, ethylene glycol, potassium oil, and vinyl acetate.
- A10 non-ionic paraffin inhibitor containing ethylbenzene, xylene, benzene sulphonic acid, C_{10} aromatic hydrocarbons, naphthalene hydrocarbons, $\text{C}_{10}\text{--}\text{C}_{14}$ n-alkanes, and didecyl dimethyl ammonium chloride.
- Demulsifier A: block copolymer, ethylene, and propylene oxide + acid and amine derivatives, (amine salts) non-ionic + ionic at a ratio of 50%:50% (m/m).
- Demulsifier B: silicone oil dissolved in aliphatic hydrocarbons at a ratio of 50%:50% (m/m).
- Demulsifier C: silicone oil dissolved in toluene + acid and amine derivatives. This chemical is prepared at Oil and Gas Institute – NRI. It is a demulsifier based on a typical emulsifier for preparing silicone emulsions with added acid and amine derivatives (the emulsifiers have hydrophobic and hydrophilic parts in their structures. The hydrophobic part is orientated towards polydimethylsiloxane, a component of silicone oil, and the hydrophilic part towards water).

Table 1. Physiochemical properties of crude oil samples

Tabela 1. Właściwości fizyko-chemiczne próbek ropy naftowej

Well Designation	Unit	A-1	A-2	A-3
Density	g/cm ³	0.812	0.809	0.797
Water cont.	% _{vol.}	0.670	0.210	0.205
Cl ⁻	mg/dm ³	138.10	120.10	158.40
Viscosity	mPa · s	34.700	13.400	6.89
Paraffin	% _{wt}	7.100	5.500	2.200
Oils	% _{wt}	49.300	50.200	22.400
Resins	% _{wt}	3.900	3.300	1.200
Asphaltenes	% _{wt}	2.600	0.700	0.550
Mechanical impurities	mg/dm ³	0.292	0.151	0.111

Table 2. Composition of reservoir waters accompanying the crude oil

Tabela 2. Skład wód złożowych towarzyszących ropy naftowej

Well	Density [g/cm ³]	pH	Ion content [g/dm ³]				
			Ca ²⁺	Mg ²⁺	K ⁺	Cl ⁻	HCO ₃ ⁻
A-1	1.183	6.00	21.500	1.87	4.80	170	3.57
A-2	1.110	6.60	9.16	2.30	5.20	131	7.23
A-3	1.268	5.20	33.90	47.80	10.00	255	1.79

In the crude oil from well A-1 in the north-west of Poland, the paraffin content was determined to be approximately 7.1%, which can cause some difficulties related to the separation of paraffin-asphaltene deposits during the process of extraction and transfer through pipelines.

Viscosity test to determine the temperature at which paraffin deposits separate from crude oil (wax appearance temperature [WAT])

In order to determine the temperature at which paraffin deposits begin to separate from crude oil (WAT), the method of viscosity change vs temperature was adopted. A set of linear, logarithmic, polynomial, and exponential functions was analysed, out of which the most relevant is the linear function that best reflects the properties of the paraffin precipitation point. It is assumed that for Newtonian fluids, the viscosity log μ remains in a linear relationship to the inverse of 1/T temperature according to the Arrhenius equation (Hamouda 1993):

$$\mu = C \exp E_a / R T \tag{1}$$

where:

- C – constant dependent on entropy stimulating the flow,
- E_a – activation energy in J/mol,
- R – universal gas constant, 8.314 J/mol·K; and
- T – temperature in K.

As the temperature drops below the paraffin precipitation point, a suspension appears in the crude oil, the fluid becomes non-Newtonian, and the dependence of viscosity on temperature loses its linear character. This viscosity curve deflection is used to identify the paraffin precipitation temperature. The point of the curve deflection in the viscosity–temperature relationship determines the temperature at which paraffin precipitation begins. In order to observe the changes in viscosity, it is necessary to precipitate a certain number of paraffin particles; thus, slightly lower results are obtained with this method. All the resulting paraffins contain an equal number of individual molecules (homodispersity). In fact, the transition from single molecules to deposits occurs

in a certain quantity range, so the physical properties do not change abruptly near the WAT. As mentioned before, the usefulness of the chosen measurement method also depends on the quantity range of separated paraffin particles below and above WAT at which the measurements were performed. If the resulting points lie on straight lines, the WAT measurement will be clearly visible where straight lines going through the points intersect. In the study, straight lines described by the y = ax + b equations were drawn through the measurement points, and the point of intersection determined the minimum temperature of paraffin precipitation, and thus the minimum dose which will prevent paraffin formation.

The point at which the straight line reflecting rapid changes in viscosity values is determined by WAT can be found as follows:

If the straight-line equation for rapid changes takes the form of

$$y_1 = a_1x + b_1 \tag{2}$$

and the straight-line equation for slow changes takes the form of

$$y_2 = a_2x + b_2 \tag{3}$$

then the two lines intersect at the point corresponding to the separation of paraffin, which was calculated from the formula

$$WAT = (b_2 - b_1) / (a_1 - a_2) \tag{4}$$

The crude oil was prepared for the study by preheating it to evaporate hydrogen sulphide (H₂S) and leaving the oil for several hours to stabilise under atmospheric conditions at ambient temperature. It was then subjected to tests which characterise the changes in viscosity with temperature at different shear rates. A Brookfield DV-II + Pro viscometer was used to measure crude oil viscosity at a given temperature (using a Huber CC705 thermostat) at different shear rates.

Paraffin separation test (coupon method)

This test consists in assessing the effectiveness of the paraffin inhibitor using the coupon method to determine the mass gain on a coupon.

The crude oil was preheated to 60°C before adding the inhibitor. After reaching this temperature, 80 ml of crude oil was poured into a 100 ml flask. The paraffin inhibitor was then dosed so as to achieve the following concentrations: no inhibitor or 500, 1000 and 1500 mg/kg. Three crude oil samples were tested for each concentration of paraffin inhibitor. Then, a previously weighed metal plate measuring 68 × 18 × 1 mm was immersed in the oil. The plate was fixed so as to be fully immersed in the middle of the liquid. The kit prepared in this fashion was left in the laboratory at 20°C for 24 hr. After that time, the plate was removed and allowed to drain for 15 min and then weighed. The result of the test is the difference in weight of the metal plate immersed in crude oil without the paraffin inhibitor and with the concentrations of the inhibitor being tested.

Selection of surfactants in the process of crude oil purification from water and chlorides

There are numerous ways to carry out the separation of crude oil vs. reservoir water phases. The most cost-effective one is to add surfactants to reduce surface tension at the phase interface, the goal of which is to cause water molecules to aggregate into larger molecules, followed by deposition (Saad et al., 2019). The purpose of adding chemicals is to accumulate molecules at the phase interface in order to change the properties of the fluid. The action of chemicals has been described in many publications and depends on many factors (composition of crude oil, amount of water, temperature, type of chemical used, time, and pH) (Rondón et al., 2006; Pereira et al., 2011; Balsamo et al., 2015; Hajivand and Vaziri, 2015). Therefore, tests should be carried out to separate the emulsion.

Surfactants added to crude oil containing reservoir water at a concentration higher than the critical micellar concentration are divided between crude oil and reservoir water reaching equilibrium, while excess compound forms micelles. Note that surfactants in excess in micelles can change critical micellar concentration. The “P” partition coefficient is determined by measuring the critical micellar concentration of CMC (Nakada et al., 2010; Hutin et al., 2016).

Having read the literature, the author decided to study the water–crude oil partition coefficient depending on the type and concentration of the surfactant using the PAT-1 tensiometer by changing the surface tension of a droplet. The test allows the researcher to select the critical demulsifier concentration. Crude

oil contains a number of compounds which affect the action of the surfactant, so it is difficult to calculate the partition coefficient and it seems justified to determine that value experimentally. Crude oil from the Polish Lowlands was selected for the study. Considering the effect of the demulsifier concentration on that coefficient, it was decided to carry out tests at various concentrations.

The conductometric method for the determination of chlorides in crude oil consists in reading the potential difference on two flat metal electrodes immersed in crude oil, with given known parameters, in accordance with the standards (ASTM D 3230). With the use of the Petrotest 2100 apparatus the salinity in crude oil and in hydrocarbon condensate in concentrations ranging from 0 mg/dm³ to 2.850 mg Cl/dm³ can be determined.

Results

The temperature at which the precipitation of paraffin deposits from reservoir fluids (WAT) begins must be known in order to determine the optimal method for the given conditions to counteract the formation of solid paraffin particles blocking the flow of reservoir media. During the precipitation of paraffins, the particles are dispersed in crude oil and appear in a non-crystalline semi-solid phase. Consequently, the suspension appears in the crude oil volume, increasing its viscosity.

Viscosity tests to determine the temperature of the beginning of paraffin deposit precipitation from crude oil (WAT)

The purpose of this study is to evaluate and compare three types of crude oil, with high and low paraffin contents, by measuring the crystallisation temperature and changing viscosity vs. temperature (Figures 1-3).

In order to assess the effectiveness of paraffin inhibitors for selected groups, their action was studied by determining the change in viscosity as a function of temperature. The crude oil samples differed as to the temperature of paraffin precipitation. Crude oil A-1 had a temperature of 21.8°C, crude oil A-2 was 19.3°C, and crude oil A-3 was 13.5°C. The test was designed to check by how many degrees centigrade the paraffin crystallisation temperature was lowered. The results demonstrated that the non-ionic A10 inhibitor lowered the paraffin precipitation temperature the most for the tested crude oils. For A-3 crude oil, it was able to lower it by 8.3°C and for A-1 oil by 6.1°C. The tests are summarised in table 3. These studies show that a non-ionic inhibitor reduced the viscosity of the crude oil types tested. It is a relatively important indicator, as the less viscous the oil is, the smaller the pressure drops are in transfer.

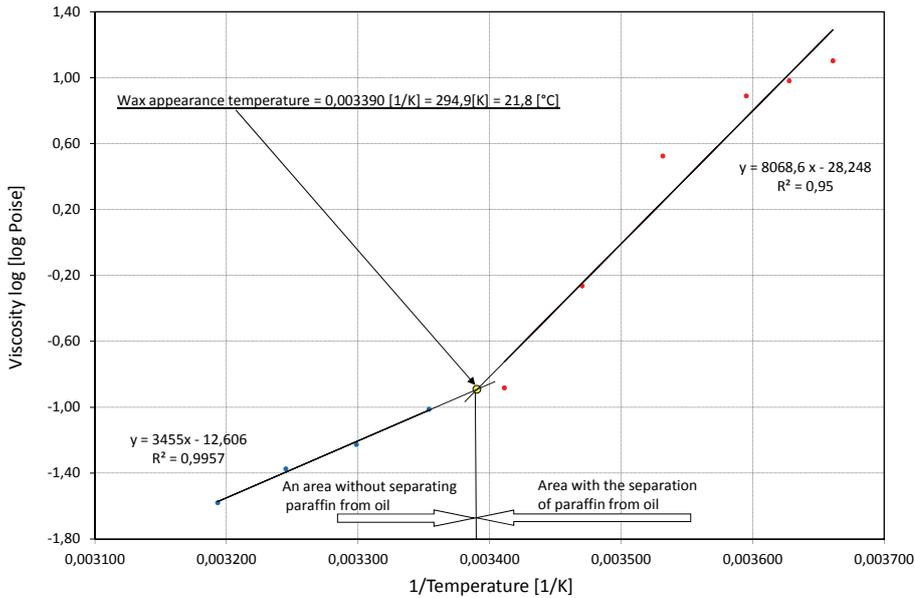


Fig. 1. Determination of the temperature at which paraffin begins to be released from the crude oil sampled from well A-1, based on the logarithmic viscosity curve deflection vs the inverse temperature

Rys. 1. Określenie temperatury początku wydzielania się parafiny z ropy naftowej pobranej z odwiertu A-1 w oparciu o zjawisko załamania się krzywej logarytmicznej lepkości w funkcji odwrotności temperatury

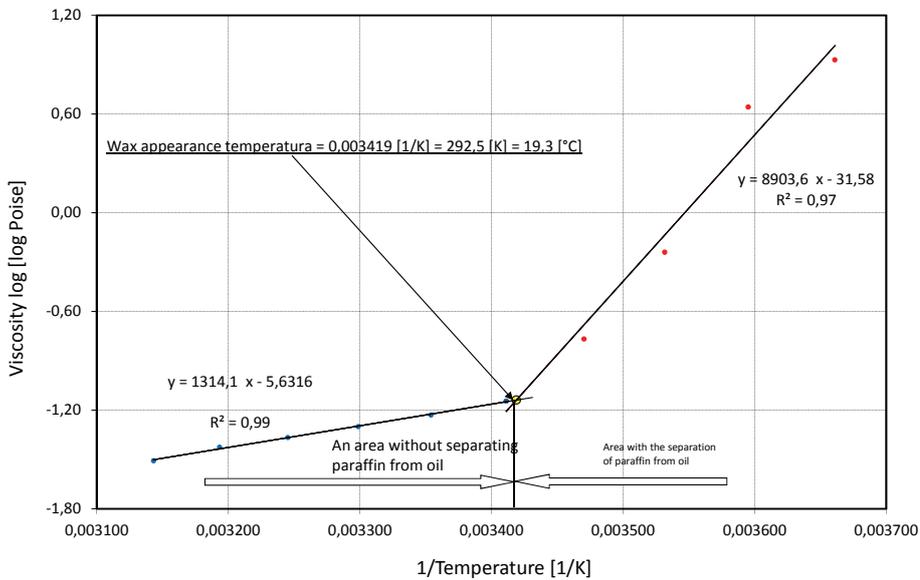


Fig. 2. Determination of the temperature at which the paraffin begins to be released from the crude oil sampled from well A-2, based on the logarithmic viscosity curve deflection vs the inverse temperature

Rys. 2. Określenie temperatury początku wydzielania się parafiny z ropy naftowej pobranej z odwiertu A-2 w oparciu o zjawisko załamania się krzywej logarytmicznej lepkości w funkcji odwrotności temperatury

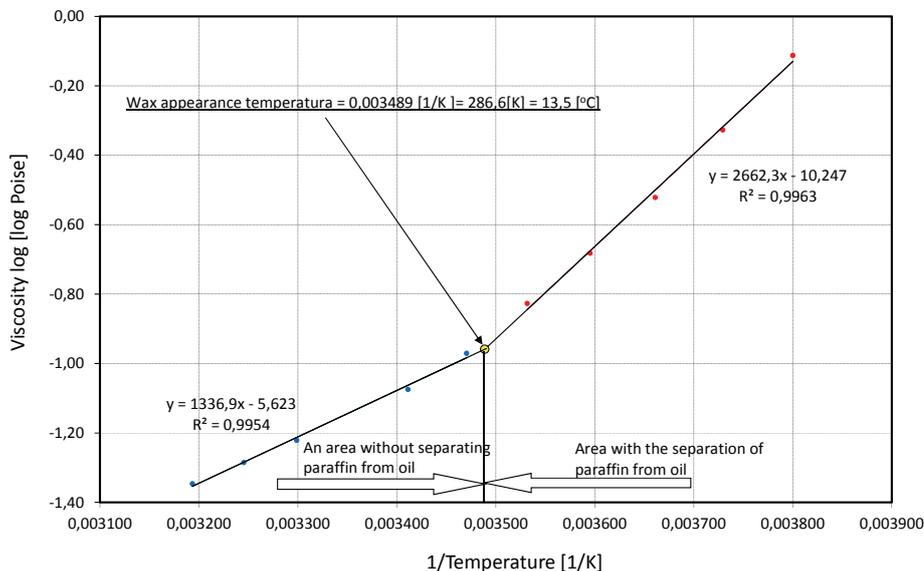


Fig. 3. Determination of the temperature at which paraffin begins to be released from the crude oil sampled from well A-3 based on the logarithmic viscosity curve deflection vs the inverse temperature

Rys. 3. Określenie temperatury początku wydzielania się parafiny z ropy naftowej pobranej z odwiertu A-3 w oparciu o zjawisko załamania się krzywej logarytmicznej lepkości w funkcji odwrotności temperatury

Table 3. Determination of the temperature where paraffin precipitates from crude oil with the addition of different amounts of paraffin inhibitor

Tabela 3 Określenie temperatury wytrącania parafiny z ropy naftowej z dodatkiem różnej ilości inhibitora parafinowania

Inhibitor Crude oil	WAT [°C]	500 mg/kg		750 mg/kg		1000 mg/kg		1500 mg/kg	
		[°C]		[°C]		[°C]		[°C]	
		A10	A50	A10	A50	A10	A50	A10	A50
A-1	21.8	21.3	21.2	20.1	20.5	18.8	19.5	15.1	16.2
A-2	19.3	18.8	19.0	17.9	18.5	15.8	16.8	13.1	14.2
A-3	13.5	12.1	13.0	11.2	12.3	8.8	10.5	5.2	7.1

Paraffin precipitation test (coupon method)

Table 4 shows the amount of protection in per cent from paraffin precipitation depending on the amount of inhibitor used. Test inhibitors reduced the amount of paraffin precipitated on coupons. The general rule that can be noted here is that the more paraffin crude oil contains, the more deposits there are on the coupon. The non-ionic inhibitors also behaved similarly. Inhibitor A10 was more efficient in protecting against the formation of deposits than inhibitor A50. This test is quite important because it can determine whether paraffin will be released during transfer through a pipeline. The precipitated paraffin can block the flow, so a properly selected inhibitor should ensure continuity of flow from the well to the mine.

Table 4. Paraffin deposition test on coupons

Tabela 4. Test wytrącania osadów parafinowych na kuponach

Crude oil	Inhibitor amount	500 mg/kg	1000 mg/kg	1500 mg/kg
		Protection of paraffin release [%]	[%]	[%]
A-1	A50	22.31	32.17	41.32
	A10	24.11	36.41	48.76
A-2	A50	14.21	21.35	28.07
	A10	14.99	25.54	36.76
A-3	A50	31.15	45.95	63.52
	A10	32.57	46.41	64.06

Surface tension tests to determine the critical concentration of demulsifiers (CMC)

For further study, the author selected crude oil from well A-1, since that oil was rich in paraffins, asphaltenes, chloride ions, and water.

Studies on the separation of emulsions using demulsifiers were preceded by determining the effect of the extracted substances on the critical micellar concentration of demulsifiers.

In aqueous micellar solutions, the presence of organic components can affect the structure of the micelles' incorporation between the molecules, which form micellar aggregates. The demulsifiers, as organic substances, then act as co-surfactants. The incorporation of chemical compounds into the micelles' structure may cause a change in CMC.

In the first phase of the selection of a surfactant for the purification of crude oil from the Polish Lowlands,

the critical micellar concentration was determined for emulsions prepared with a 2%, 4%, and 6% brine content.

Figure 4 shows the relationships between surface tension and the concentration of emulsion with the addition of the demulsifier A.

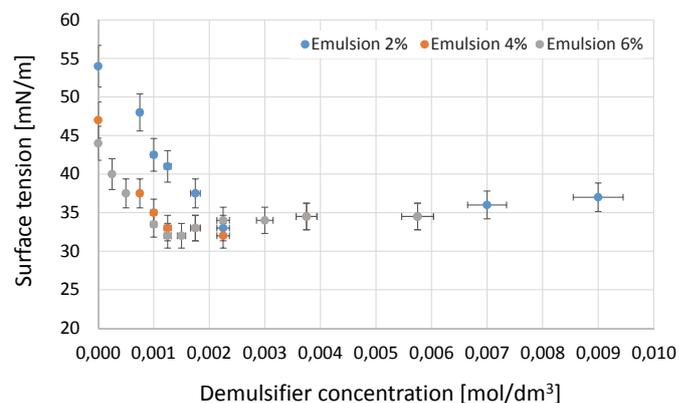


Fig. 4. Effect of brine concentration in emulsion on surface tension depending on the concentration of demulsifier A

Rys. 4. Wpływ stężenia solanki w emulsji na napięcie powierzchniowe w zależności od stężenia demulgatora A

The emulsion was made from brine and crude oil from well A-1. Noticeably, the surface tension changes the line deflection point, when the demulsifier concentration changes, shifting towards lower demulsifier concentrations for the increasing brine concentration. The dependence of CMC values (inflection point) read from this graph on the total concentration of the demulsifier in the 4% emulsion is shown in Figure 6. In the range of demulsifier concentrations studied, a decrease in surface tension at the CMC point and a three-fold decrease in the CMC value were observed. Figures 5 and 6 present analogous relationships for demulsifiers B and C.

Based on Figure 6, it can be concluded that demulsifiers C and B reduce the surface tension and CMC value more effectively than demulsifier A. Figure 7 presents the critical micellar concentration of the 4% emulsion of the concentration function of the demulsifiers tested.

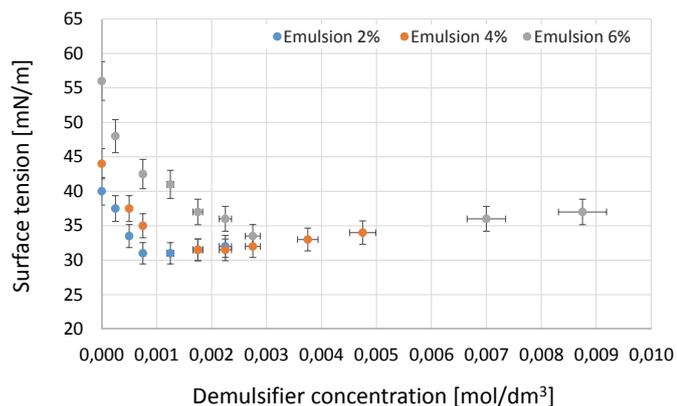


Fig. 5. Effect of brine concentration in emulsion on surface tension depending on the concentration of demulsifier B

Rys. 5. Wpływ stężenia solanki w emulsji na napięcie powierzchniowe w zależności od stężenia demulgatora B

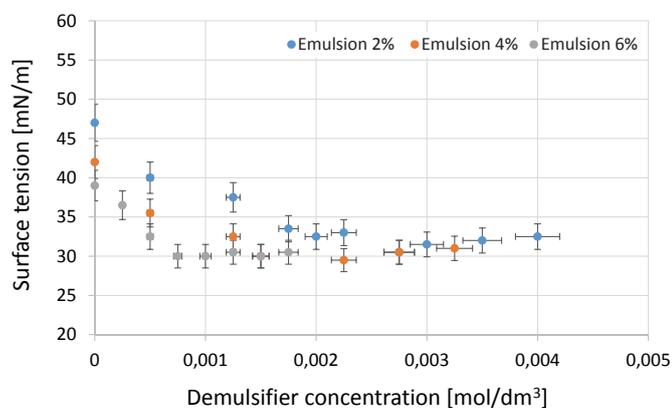


Fig. 6. Effect of brine concentration in emulsion on surface tension depending on the concentration of demulsifier C

Rys. 6. Wpływ stężenia solanki w emulsji na napięcie powierzchniowe w zależności od stężenia demulgatora C

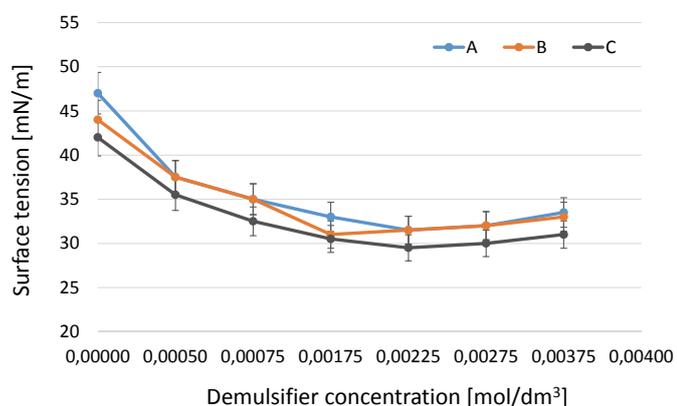


Fig. 7. Values of the change in surface tension (critical micellar concentration) of the 4% emulsion vs the concentration of the demulsifiers studied

Rys. 7. Wartości zmiany napięcia powierzchniowego (krytycznego stężenia micelnego) emulsji 4% w funkcji stężenia badanych demulgatorów

Demulsifier C is also present at the interface between phases and has a larger volume than demulsifiers A and B.

The tests also proved that the decrease in surface tension at the CMC point for high concentrations of the tested demulsifiers was low.

Studies of the emulsion–demulsifier relationship demonstrated that the partition coefficient values when using demulsifier can be defined as the quotient of equilibrium concentrations in the crude oil phase and separated water.

The decrease in the partition coefficient is greatest when dosing hydrophobic demulsifiers.

The factor which determines the ability for phase separation are hydrophobic interactions between the demulsifier and water.

Based on the above tests, it can be concluded that demulsifiers effectively reduce surface tension and that determining the CMC values is possible. The CMC value obtained in the tests confirms that the hydrophobic compound lowers the surface tension value for ion demulsifiers more effectively.

After testing the emulsion separation, the chloride content in the crude oils was checked.

An effective action of a demulsifier requires very good mixing in the entire volume of oil so that the stage of emulsion destabilisation is significantly accelerated (Bęben, 2018). The process requires the use of a demulsifier which, in a given highly dispersed medium, will reach the largest possible amount of water particles contained in crude oil, causing those water particles to aggregate in sizes at which gravity will overcome the force holding them in suspension (emulsion), leading to deposition.

The determination of chlorides in the crude oils under study was carried out by means of the conductometric method for chloride content measurement in petroleum selected previously by the author (Bęben, 2011).

Determination of chlorides in crude oil using demulsifiers

The positive results of the use of demulsifiers for phase separation were the basis for basic laboratory tests to separate the crude oil–reservoir water emulsion with a demulsifier. Further testing in this study was aimed at determining the suitability of surfactants for the purification of crude oil of various compositions.

Standards with different chloride content were used at first to document the correctness of individual control tests on the ASTM D-3230 reference material.

In order to perform correct analyses, the apparatus was calibrated using an external standard. In addition to that, a mixture of alcohol solvents was used to reduce surface ten-

Table 5. Results of chloride content analysis in a 100.8 mg/dm³ standard
Tabela 5. Wyniki analiz zawartości chlorków we wzorcu 100,8 mg/dm³

No.	Measurement [mg/dm ³]	Standard deviation (absolute value deviation)
1	102.1	0.47 (0.466%)
2	101.8	
3	100.5	
4	100.4	
5	101.3	
6	100.9	
7	102.1	
8	101.6	
9	100.9	
10	101.9	
11	101.1	
12	100.2	
13	101.8	

Table 6. Measurement of chloride content in the tested crude oil types

Tabela 6. Pomiar zawartości chlorków w badanych ropach naftowych

Crude oil	Measurement	Average
	[mg/dm ³]	[mg/dm ³]
A-1	138.2	138.1 ± 0.1
	138.1	
	138.1	
A-2	120.1	120.1 ± 0.2
	120.0	
	120.2	
	294.4	
A-3	158.3	158.4 ± 0.2
	158.4	
	158.5	

sion and achieve homogeneity of the sample being studied. In accordance with the recommendations of ISO procedures, the verification of calibration curves and their correction was performed using the standard ASTM D 3230. The calibration curves are the mathematical relationships between the magnitude of the chloride determination signal processed by the apparatus' measuring system and the concentration of chloride in the sample being tested. The results obtained from the standard tests are summarised in Tables 5 and 6. These tables summarise the average results of the measurements obtained, the standard deviation calculated, and the absolute deviation from the standard value.

The results obtained from testing various crude oil types are summarised in Table 6.

Table 7 summarises the determination of chloride content in the tested emulsions of 2%, 4%, and 6% water in crude oil using various types of demulsifiers.

The demulsifiers had different degrees of separation between the water and crude oil phases, allowing for a better degree of destabilisation and effective separation of the emulsion. For all the crude oil types tested, it was apparent that the amount of water in oil increases as the chloride content in oil decreases. However, note that introducing an incorrect concentration of demulsifiers into the crude oil may stabilise the emulsion or create a new type of emulsion that may be difficult to separate (Zolfaghari et al., 2016). It should be borne in mind that any salts contained in crude oil stabilise emulsions (Fortuny et al., 2007; Moradi et al., 2011).

Silicone emulsifiers are intended to support the creation of emulsions, which are used in the cosmetics industry. Therefore,

the author decided to add ionic compounds to silicone emulsifiers in order to form demulsifier C. As demonstrated in the study, that demulsifier effectively separated water from crude oil whilst reducing the chloride content in the tested petroleum most effectively.

Table 7. Summary of chloride content measured in the tested emulsions after using 0.00225 mol/dm³ of demulsifiers

Tabela 7. Zestawienie oznaczonych zawartości chlorków w badanych emulsjach po użyciu 0,00225 mol/dm³ demulgatorów

Crude oil	Emulsion	Demulsifier A	Demulsifier B	Demulsifier C
	[%]	[mg/dm ³]	[mg/dm ³]	[mg/dm ³]
A-1	2	60.2	55.8	58.1
	4	22.5	19.4	15.4
	6	13.2	10.6	6.1
A-2	2	48.6	36.5	31.4
	4	19.8	12.5	8.8
	6	7.7	3.5	1.8
A-3	2	87.4	61.5	38.1
	4	58.2	33.4	21.5
	6	41.2	10.5	2.0

Conclusions

This article presents an overview of some methods generally used for testing the temperature at which paraffin separation, water separation from crude oil, or salt removal begin. The impact of the use of surfactants on the precipitation of paraffin or the purification of crude oil from water and the salts contained was studied. In the research, the positive or negative

impact of variables such as temperature, salinity, and paraffin content on the process of transporting or purifying crude oil were found. In all processes used in the petroleum industry both efficiency and speed are essential, which is why the main focus of why proposed is to select the best chemical agent to ensure continuity of flow.

The results presented herein demonstrated that the non-ionic A10 inhibitor lowered the paraffin precipitation temperature the most for the crude oil types tested. For crude oil A-3, it was able to reduce it by 8.3°C, and by 6.1°C for A-1. It also reduced viscosity, which is an important parameter during crude oil transfer through a pipeline.

The studies demonstrated that the non-ionic demulsifier separates the crude oil–water phases better at lower concentrations in comparison to the ionic demulsifier.

It was found that the silicone demulsifier with added ionic compounds purified the tested crude oil from chlorides most effectively, reducing their content from 158.4 mg/dm³ to 2.0 mg/dm³ in crude oil A-3 (low paraffin content). For a high paraffin content in crude oil, demulsifier A-1 caused a reduction of the chloride content from 138.1 mg/dm³ to 6.1 mg/dm³.

The results of laboratory tests indicate that the use of a demulsifier with a mixed composition of ionic and non-ionic active agents is effective at removing chlorides from paraffinic crude oil. Compared to the demulsifiers tested, the proposed mixture of a demulsifier with added ionic compounds effectively cleans crude oil from chlorides.

Laboratory research on the selection of chemicals affects the efficiency of crude oil transport and they can be used during the flow from the well to the processing plant. They help ensure the continuity of flow of crude oil with a high paraffin content, they improve the separation of water and, at the same time, they clean salt from the oil. The solution of adding chemicals for the transport and purification of crude oil has tangible economic effects.

Acknowledgements

The authors would like to thank Brenntag Polska Sp z o.o. for help in carrying out the research for this work.

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Legal and normative acts:

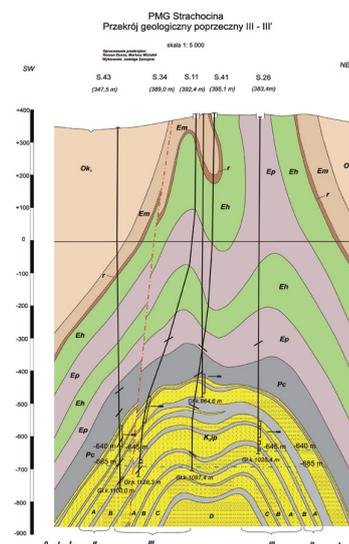
ASTM D 3230 Standard Test Method for Salts in Crude Oil (Electrometric Method).



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OFERTA BADAWCZA ZAKŁADU PODZIEMNEGO MAGAZYNOWANIA GAZU

- analiza struktur geologicznych złóż gazu ziemnego, ropy naftowej oraz obiektów zawodniomych, pod kątem możliwości ich przekształcenia w PMG;
- szczegółowa analiza warunków geologiczno-złożowych, ocena dotychczasowej eksploatacji złoża, warunków hydrodynamicznych, zdolności wydobywczych odwiertów;
- ocena stanu technicznego istniejącej infrastruktury w aspekcie jej wykorzystania w pracy PMG;
- wykonywanie cyfrowych modeli geologicznych PMG, złóż gazu ziemnego i ropy naftowej;
- wykonywanie projektów budowy PMG;
- analiza dotychczasowej pracy istniejących PMG w celu optymalizacji parametrów dalszej eksploatacji magazynów na bazie symulacji komputerowej;
- opracowanie projektów prac geologicznych, dotyczących poszukiwania i rozpoznawania złóż gazu ziemnego i ropy naftowej;
- opracowanie dokumentacji geologicznych złóż ropy naftowej i gazu ziemnego;
- opracowanie programu optymalnej eksploatacji złoża, wydajności poszczególnych odwiertów, tempa szczyptywania itp.



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