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SCREENING FOR EFFICIENT AGENTS FOR TRANSPORTATION AND TREATMENT OF OIL OF SOUTH-KHYLCHUIU FIELD

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ПОДБОР ЭФФЕКТИВНЫХ РЕАГЕНТОВ ДЛЯ ТРАНСПОРТА И ПОДГОТОВКИ НЕФТИ ЮЖНО-ХЫЛЬЧУЮСКОГО МЕСТОРОЖДЕНИЯ

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Oil of most of domestic and abroad fields is produced by a flooding of oil-bearing formations method. That leads to intensive mixing of oil and formation water and unavoidable formation of persistent water-oil emulsions. Demulsifiers are used to destroy water-oil emulsions and obtain commercial oil in gathering, transportation and treatment systems. In case of high water cut and certain modes of transportation demulsifiers can be a reason of free water formation. Due to its aggressive behavior water can lead to corrosion of a lower part of pipeline system. Therefore, along with demulsifiers a corrosion inhibitor is injected into systems of well fluid transportation. But some demulsifiers, having good washing properties, wash off from internal walls of pipes both an oil film and protective film of corrosion inhibitor adsorbed on them. In turn, some corrosion inhibitors can be emulsifiers, and adding them to a system of intratubular demulsification can have a negative effect on the processes of separation of water from oil. In this regard, compatibility of demulsifiers and corrosion inhibitors is very relevant question. A solution for such problems needs to screen agents that will not reduce demulsifying and protective properties of each other.
Oil of South-Khylchuiu field has high paraffin content and positive pour point. So, during transpiration it is needed to take into account that at low temperatures oil reveals non-Newtonian properties. Stop in transportation will possibly show formation of paraffin structures. That can lead to decrease in rate capacity of pipeline and significantly complicate operation.
Studies, carried out in the field of transportation of oil with high paraffin content, revealed that in order to improve transportation of high-hardening oil and heavy oil products it is possible to use substances such as flow stimulators (depressant additives). This method does not require large additional capital costs. With a sufficiently wide development of production of additives it can be economically more profitable compared to other methods of transportation.

Ключевые слова:
высокопарафинистая нефть, водонефтяные эмульсии, реологические характеристики нефти, деэмульгаторы, депрессорные присадки, ингибиторы коррозии, взаимовлияние и совместимость реагентов.

На большинстве месторождений в нашей стране и за рубежом добыча нефти осуществляется методом заводнения нефтяных пластов. Это приводит к интенсивному перемешиванию нефти и пластовой воды и неизбежному образованию стойких водонефтяных эмульсий. Для их разрушения и получения нефти товарного качества в системах сбора, транспорта и подготовки нефти применяют реагенты-деэмульгаторы. За счет их действия при высокой обводненности нефти и определенных режимах транспорта в трубопроводе может образовываться свободная вода, которая за счет агрессивности приводит к коррозии нижней части трубопроводной системы. Поэтому на промыслах по системам транспорта продукции скважин одновременно с реагентом-деэмульгатором вводят ингибитор коррозии. Но некоторые деэмульгаторы, обладая хорошими моющими свойствами, смывают с внутренних стенок труб не только пленку нефти, но и защитную пленку адсорбированного на них ингибитора коррозии. В свою очередь, некоторые ингибиторы коррозии могут являться эмульгаторами, и добавка их в систему внутритрубной деэмульсации может оказать негативное воздействие на процессы отделения воды из нефти.
В связи с этим весьма актуален вопрос совместимости реагентов-деэмульгаторов и ингибиторов коррозии. При решении таких проблем целесообразно подбирать реагенты, которые не будут снижать деэмульгирующие и защитные свойства друг друга.
Поскольку нефть Южно-Хыльчуюского месторождения высокопарафинистая и имеет положительную температуру застывания, при организации транспорта необходимо учитывать, что при низких температурах она проявляет резко выраженные неньютоновские свойства, а при остановке процесса перекачки возможно образование парафиновых структур. Это может привести к снижению пропускной способности нефтепровода и значительно усложнит эксплуатацию.
Исследования, проведенные в области перекачки высокопарафинистой нефти, выявили возможность использования для улучшения транспорта высокозастывающей нефти и тяжелых нефтепродуктов веществ – стимуляторов потока, так называемых депрессорных присадок. Этот способ не требует больших дополнительных капитальных затрат и при достаточно широком освоении производства присадок может быть экономически более выгодным по сравнению с другими способами перекачки.

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Introduction

Increase in a share of unconventional oil reserves is one of the features of modern oil production. That reserves include heavy, high viscosity and with high paraffin content oil of pour point temperature above the zero degrees Celsius. The volume of such oil in Russia is around 55 % out of total volume of reserves [1]. Such reserves include oil of north European fields.

There are techniques of transportation of heavy oil and oil of high pour point known worldwide that are as follows:

– preheating («hot pumping»);
– following heating (including skin-effect);
– after heat treatment;
– low viscosity diluters;
– oil saturated by gas;
– water solutions of surface active agents (surfactants);
– pour-point depressants.

Pumping technique is chosen based on a feasibility study.

Today, there are two main directions of oil pumping prevail. Those are conventional techniques of oil pumping with heating and using depressors to reduce the viscosity and oil pour point.

Use of chemical depressors during pumping of oil and oil products causes decrease in viscosity of pumped liquid and temperature of pour point of liquid with paraffin. Polymer additives whose molecules are characterized by high strength and high molecular weight reduce frictional losses, thereby increase pipeline throughout capacity.

Thus, use of depressant additives increases productivity of oil pipelines, guarantees reliability of start after long stops, improves work of wells and collection oil pipelines in fields and reduces paraffin deposition on walls of a pipeline and in reservoirs etc.

Use of polymer depressant additives allows solving many practical problems of pipeline transportation such as to reduce energy consumption for pumping and fuel consumption for oil heating; reduce capital costs in a linear part and heating points; increase productivity and throughput of oil pipelines; increase the efficiency and reliability of operation of oil pipelines under difficult climatic conditions [2–13].

Nowadays, the major amount of oil is extracted using techniques of flooding of productive formations by surface and mineralized wastewater from oil fields to maintain reservoir pressure. Over the time reservoir water-cut increases and a stable water-oil emulsion is obtained during production. That is also caused by natural demulsifiers presented in oil [14]. Therefore, it is almost impossible to destroy an oil emulsion without additional methods of dehydration used.

At the moment, there are many technological methods and technical devices that allow to completely destroy oil emulsion by certain effects. Thermal method with various demulsifiers is the most efficient one [15].

Location of demulsifier input in a system should be selected as to ensure good mixing and long time of an agent to be in contact with emulsion. To increase contact time of a demulsifier with an emulsion and to ensure that an emulsion is prepared to delamination a so-called track demulsification or pipe demulsification is used. For that a demulsifier is input to a system at a considerable distance from a unit of initial water separation unit (IWSU) or oil treatment unit (OTU), for example, at a well head of production well, at a group metering unit or at an initial pipeline section [16-19].

During choosing a demulsifier much attention is paid to its speed, which ensures a rapid initial separation of water from an emulsion and its subsequent deep separation.

The studies are dedicated to choose the most efficient demulsifiers for dehydration of oil of South-Khylchuiu field.

Laboratory studies dedicated to choose an efficient demulsifier for oil of South-Khylchuiu field

South-Khylchuiu field is located in the north of the European part of Russia on territory of Nenets Autonomous District of Arkhangelsk Region in an area of distribution of perennial frozen soils with a subarctic climate. Annual temperature fluctuations range from –46 to +30 °C. A hydrographic network is represented by a number of lakes, small rivers such as Khylchuyu, Dresvyanka, Serebryanka that have numerous tributaries.

Oil of South Khylchuyu field is light (density is equal to 849 kg/m^3 at 20 °C), low-viscosity (7.46 mPa·s) with high paraffin content (6.72 % by weight) and has a pour point at +5 °C.

For the period of work performance, water-cut of oil emulsions of the field was 27.0 %. Temperature of oil transport through filed oil pipelines to an oil treatment unit in wintertime is –30 °C. Values of dynamic viscosity of an emulsion at such transportation temperature is low (Fig. 1). Viscosity of an emulsion did not exceed 0.08 Pa·s at water cut of 70 %. It is not necessary to supply demulsifiers through the collection system. But in order demulsification to be performed at an OTU it is necessary to supply a demulsifier to obtain commercial 1st grade of oil in accordance with GOST R 51858-2002 [20].

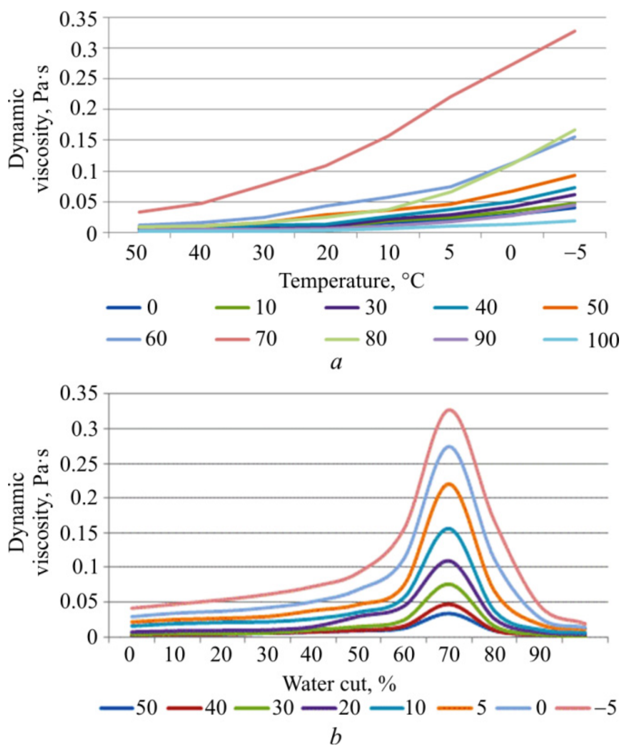

Fig. 1. Function of dynamic viscosity of oil emulsions of South-Khylchuiu field versus temperature (*a*) and water cut (*b*)

Processes of transportation and treatment of oil from South-Khylchuiu field were studied in order to select the most efficient demulsifier.

Laboratory tests directed to assess the efficiency of demulsifiers were performed by conventional Bottle Test with use of an 30 % oil emulsion under almost real conditions of transportation and treatment of oil of South-Khylchuiu field [21]. The agent Separol WF-41 was used as a reference one. Demulsifiers were input in the same amount as those of the base agent. Temperature of laboratory tests was chosen based on average temperature of transportation of well production in winter and temperature of oil treatment at South Khylchuyu TOU.

Conditions of laboratory tests:

– time of emulsion aging – 1 h;

– time of mixing of an oil emulsion with an agent – 5 min;

– intensity of mixing of an oil emulsion – 120 double strokes/min;

– temperature of mixing of an emulsion with an agent – 30 °C;

– temperature of oil demulsification process – 30 and 65 °C;

– duration of demulsification process is 1 hour at each temperature.

Results of the tests performed are shown in Fig. 2.

The Fig. 2 presents comparison of demulsifiers such as RP-6522; Separol WF-41 of Baker Petrolite; KhPD-005, KhPD-001 (5), KhPD-011 (P), KhPD-004 (KG) of ZAO kogalymskiy zavod khimicheskikh reagentov; Recod 752A of ZAO Agentstvo tekhnologiy i operativnoy nauki (ATON) (Kazan); FLEK-D-005 b of OOO FLEK (Perm).

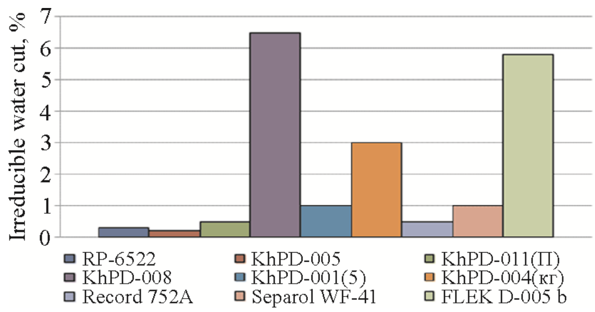

Fig. 2. Comparative efficiency of demulsifiers during demulsification of oil from South Khylchuiu field

The results of the Bottle Test were used to select the most efficient demulsifiers. Next, their consumption were adjusted during simulation in accordance with a technological scheme and the main parameters of an OTU operation.

Well production enters separators of IWSU and TFS at OTU and the first stage of oil separation from gas is carried out. Then water-oil emulsion goes to an IWSU for preliminary separation of water. The temperature of a process is 30-40 °C. Before the IWSU an agent-demulsifier is supplied. Consumption of an agent is 10 g/tonne (to prepare production of wells for a demulsification process a demulsifier in the amount of 30 g/tonne is an input to a collection system). At the outlet from IWSU apparatus an oil emulsion has a water cut of no more than 5 %. Then, partially dehydrated oil goes to the stage of deep dehydration and desalination through heating furnaces. A demulsifier and hot fresh water are input before that units. Temperature regime on a dehydration and desaltation unit is 65-70 °C. Commercial oil with water content of no more than 0.5 % after desalination apparatus and hydrogen blowing column enters commercial oil tanks. From tanks oil is transported by main pumps through a pipeline of around 160 km in length to a coastal tank battery of the Varandey oil terminal. Water separated at all the stages of oil treatment of an OTU is sent to a water treatment unit for cleaning and further use in a reservoir pressure maintenance system of South Khylchuiu field.

Screening for demulsifiers and adjustment of their consumption were carried out for emulsions that have water cut of 28 % (current period). Efficiency of agents was assessed by both the speed, depth of dehydration [21] and quality of separated water at the stage of preliminary separation (concentration of oil products) [22].

Parameters of transportation processes and oil treatment in laboratory conditions corresponded to real ones and were as follows:

– consumption of demulsifiers by a collection system – 30 g/tonne;

– emulsion transportation temperature – 30 °C;

– duration of transportation – not less than 1.0 h;

– dosage of demulsifiers before the input to a unit – 10 g/tonne;

– duration of mixing of emulsion with an agent – at least 10 min;

– water pre-separation temperature – 30 °C;

– process duration – 1,0 h;

– thermochemical dehydration temperature – 65 °C;

– additional demulsifier supply – 10 g/tonne;

– process duration – 1,0 h;

– volume of fresh water for desaltation process – 7 %;

– mixing of oil with hot (70 °C) fresh water – 10 min;

– process duration – 1,0 h;

– desaltation temperature – 60 °C.

After treatment processes were completed residual oil and the concentration of chloride salts in oil were determined using methods described in [23, 24].

Table 1

Results of modeling of oil treatment processes at South Khylchuyu OTU

Agent	Water cut of initial emulsion , %	Agent consumption of a collection system, g/tonne	Initial separation stage (IWSU), temperature 30 °C			Thermochemical dehydration of oil at temperature of 65 °C		Desaltation of oil at temperature of 60 °C		
			agent consumption g/tonne	water content at the outlet from the IWSU, %	concentration of oil products in water, mg/dm^3	additional input of an agent, g/tonne	quality of oil after the end of the process, %	volume of fresh water, %	water content according to Dean-Stark, %	concentration of chloride salts, mg/dm^3
RP-6522 (Baker Petrolite)	27.7	30	10	4.5	86.4	10	0.5	7	0.03	40.16
KhPD-005		30	10	6.5	303.4		1.4		0.06	104.56
KhPD-011(P)		30	10	5.0	139.3		0.9		0.06	125.38
Separol WF-41		30	10	4.5	215.7		1.0		0.06	98.71
Recod 752A		30	10	6.0	217.2		0.5		0.03	69.5
FLEK D-005 b		30	10	6.5	162.5		1.2		0.09	162.5

Results of simulation are given in the Table 1. According to the table, it is clear that the best results on the quality of commercial oil are obtained with demulsifiers such as RP-6522, Separol WF-41 and Recod 752A. The same agents also showed their speed. Almost all of the water was released at each stage in the first 0.5 h. Agents Recod 752A and Separol WF-41 showed worse quality of separated water. So, concentration of oil products was 217.2 and 215.7 mg/dm^3 [25–27].

Laboratory studies for determination of compatibility of demulsifiers and corrosion inhibitors

According to analysis of production of wells associated gas along with oil from a reservoir P1a+s (the main development reservoir at the field) contains components of harsh corrosion environment (except for light and heavy hydrocarbons) such as hydrogen sulphide and carbon dioxide. The content of X_2S reaches 2.7 % mole, CO_2 reaches 4.8 % mole. On average, concentration of these components in in the field is 1.48 and 2.51 % mole respectively. Moreover, presence of large amounts of H_2S or CO_2 in a transported liquid leads to increase in hydrogenation of steels, which facilitates their embrittlement and a sharp decrease in strength properties.

That means that there is a huge probability of failure in the first years of operation if no corrosion protection methods are used to protect field pipelines and equipment made of carbonaceous unalloyed steels. Therefore, there is an input of corrosion inhibitor CRW-82275 of Baker Petrolite at a flow rate of 25 g/m^3 in the collection system.

However, it is necessarily to evaluate effect of corrosion inhibitors that are input to an oil collection system on demulsifying ability of agents.

The effect of the combined action of a corrosion inhibitor and a demulsifier may in some cases be enhanced, but in others it may be decreased. That is caused by the fact that there are reactions occur with formation of new intermediate products that directly or indirectly influence the technological process. Those reactions occur when mixing organic and inorganic agents in presence of various chemical compounds in mineralized water, production of wells, formation rock and communications [28, 29].

The interaction of agents was studied by comparing the action of a demulsifier in the mixture with a corrosion inhibitor and without it by volume of water phase released during the simulation of initial water discharge (Table 2).

The conducted researches allow to draw a conclusion that inhibitor CRW-82275 together with RP-6522 demulsifier used for corrosion protection has no negative effect on the oil treatment process. Residual water cut of oil remained approximately at the same level. In addition, concentration of oil products in separated water has not increased.

There is in experiments with demulsifiers Separol WF-41 and Recod 752A with corrosion inhibitor CRW-82275 after demulsification an increase in water content of oil has shown. Concentration of oil products in separated water with all the agents remained approximately at the same level as is given in the experiments above.

Thus, demulsifier RP-6522 (Baker Petrolite) showed the greatest efficiency in treatment of oil of South Khylchuiu field in comparison with other studied.

Table 2

Results of laboratory studies of interinfluence of demulsifiers and a corrosion inhibitor on treatment process of oil of South Khylchuiu field.

Agent	Water cut of the initial emulsion,%	Consumption of a demulsifier along a collection system, g/tonne	Consumption of an inhibitor along a collection system, g/m^3	Initial water separation stage (IWSU), temperature 30 °C		
				consumption of demulsifier, g/tonne	water content at the outlet of an IWSU, %	concentration of oil products in water, mg/dm^3
RP-6522 (Baker Petrolite)	27.7	30	25	10	4.0	80.62
Separol WF-41		30	25	10	7.0	243.24
Recod752A		30	25	10	9.5	196.83

Rheological studies of oil and screening for depressant additives

External transportation of oil which was tested at the OTU is considered in the direction of the Varandey oil terminal. Distance to coastal tank battery is more than 160 km, time of oil transportation is 14 days.

One of the most important tasks of pipeline transportation of paraffin oil with high pour point temperature is implementation of technological activities to improve the hydraulic characteristics of pipelines. That is caused by the fact that pumping of such oil under non-isothermal conditions leads to deposition of paraffin on the inner surface of pipes. Decrease in oil transportation temperature down to paraffin saturation temperature a solid phase begins to appear in the pumped liquid. That phase is paraffin crystals organized as conglomerates that adhere to the surface of the pipeline.

Studies of rheological properties of oil of South-Khylchuiu field were carried out on forward and reverse moves of a viscometer with cylinder-cylinder measuring instrument. The direct move was reduced to successive discrete formation of shear velocities that started from lowest and ended with the greatest. The direct stroke corresponds to start operating conditions of a pipeline, when there is a gradual destruction of internal bonds (structural forms) in oil with an increase in movement speed.

The reverse move is related to cases of existence of destroyed internal bonds and corresponds to stationary operating modes of a pipeline. It comes down to sequential discrete formation of motion velocities from the largest to the smallest.

If the considered liquid has a tendency to structure itself at any temperature, then rheograms of straight and reverse move do not coincide.

Fig. 3 shows rheograms for oil of South-Khylchuiu field at various temperatures. Since the rheograms of straight and reverse move do not coincide it is clear that oil of this field tends to structure itself, especially at temperatures close to the pour point of oil.

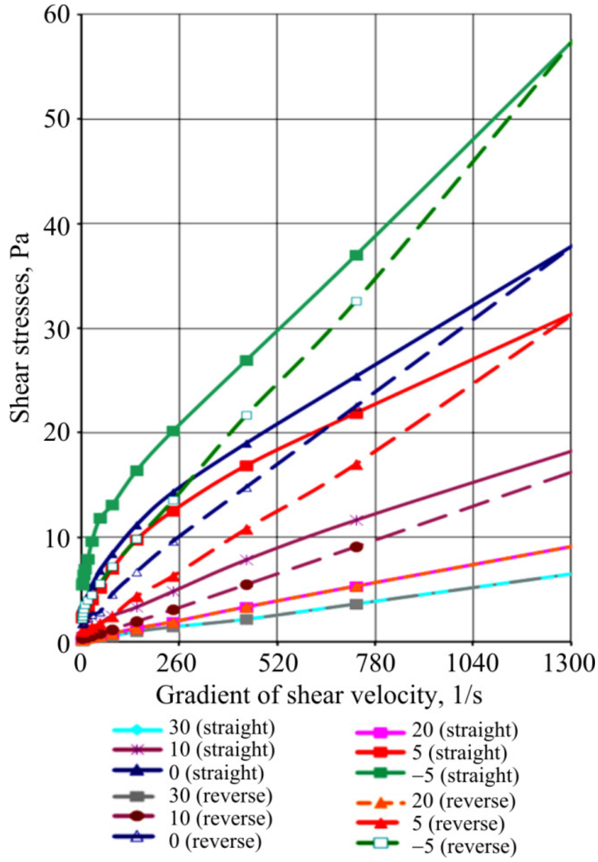

Fig. 3. Rheograms of South Khylchuiu oil field

Rheograms of straight and reverse move practically coincide at temperatures of 20 and 30 °C. Values of viscosity and shear stresses for start and stationary modes are close.

As it was mentioned above, one of the ways to pump oil of high pour point is its transportation with input of depressant additives.

Additives were input into the oil heated up to 60 °C (temperature of oil after completion of treatment processes). Consumption of depressors was 50 g/tonne. Samples were thoroughly mixed because that is one of the conditions for use of depressant additives. Rate of oil temperature decrease did not exceed 20 °C/h. Pour point of oil then was determined.

Results of studies given in Table 3 show that the best indicators obtained with use of agents Servo CW-288 and DN-1 are depression of pour point exceeds 25 °C and this decrease persists for at least 16 days. In addition, additives also have high ability to inhibit wax (at least 86 % in efficiency), which was determined according to the generally accepted "cold finger" technique [30, 31], which allows to estimate the efficiency of agents as paraffin inhibitors for specific operational conditions with high reliability.

Table 3 describes depressant additives Sepaflux-3120 and CF-2145 produced by Baker Petrolite, depressant additive DN-1 produced by VNIISPTneft, depressant additive Servo CW-288 produced by Nalko; depressant additives FLEK-IP-103 and FLEK-DP-009 produced by OOO FLEK (Perm) and depressant additive PROCHINOR AP-174 produced by ATOFINA/SEKA.

Table 3

Results of laboratory studies dedicated to reduce pour point of oil using depressant additives at South-Khylchuiu field

Additive's name	Consumption, g/tonne	The effect of inhibition, %	Pour point after 24 hours, °C						
			1	2	3	4	8	10	16
No additive	–	–	+5	–	–	–	–	–	–
Sepaflux-3120	50	73.5	–8	–12	–20	–20	–20	–20	–2
DN-1	50	86.8	–36	–38	–38	–38	–32	–32	–20
Servo CW-288	50	87.9	–38	–40	–40	–40	–40	–40	–22
CF-2145	50	69.7	–14	–20	–20	–20	–15	–12	–4
FLEK-IP-103	50	–	–8	+4	–	–	–	–	–
FLEK-DP-009	50	–	–11	–12	–12	–12	–6	–4	0
PROCHINOR AP-174	50	64.8	–13	+4	–	–	–	–	–

Thus, depressant additives DN-1 or Servo CW-288 will prevent paraffin crystals to grow and weaken their ability to aggregate. Consequently, they can be recommended for transportation of oil of South Khylchuiu field.

Conclusion

1. The agent RP-6522 produced by Baker Petrolite showed the greatest efficiency in transportation and treatment of oil of South Khylchuiu field.

2. The inhibitor CRW-82275 used for protection against corrosion is compatible with the demulsifier RP-6522 and has no negative effect on oil treatment process.

3. Depressant additives Servo CW-288 and DN-1 showed good results in reducing the pour point of the oil. Temperature depression exceeds 25 °C and persists for at least 16 days. In addition, additives have also a strong ability to inhibit wax (at least 86 % in efficiency).

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