



NEW METHODS OF STRUGGLE WITH ASPHALT-RESIN-PARAFFIN DEPOSITS IN THE PROCESSES OF OIL TRANSPORTATION

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Keywords:

ABSTRACT

Asphalt; Factors; Chemical; Mechanism; Control; Processes.



Modern views on the state of the problem considered asphalt-resin-paraffin deposits (ARPD) in oilfield equipment and possible methods for its solution. The main factors of the ARPD formation listed in this paper. Special focus given to the group chemical composition of the crude and mutual influence of separate high-molecular crude oil components on the structurization in the oil system at low temperatures. The chemical methods concerning with application of various additives, reagents and removers are considered in more detail. The mechanism of action of reagents on ARPD was clarified and was it determined that the reagents of BAF-1 and BAF-2 in interaction with sediments, grind associates and ensure there uniform distribution in oil.

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1. INTRODUCTION

The development of the Azerbaijan oil industry at the present stage characterized by a decrease in the quality of the raw materials base. In the overall balance from the developed oilfields, the oilfield, which entered into the late stage of development, is dominated and as a result there is a significant deterioration of their structure, increasing of share of hard-to-recover oil reserves, flooding reservoirs and production wells.

Thus, in the production of paraffinic oils, the formation of asphaltene-tar-paraffin deposits (ARPD) causing complications in the operation of oil wells, oilfield equipment and pipeline communications, formation of which leads to a decrease in system productivity and efficiency of pump installations (Persiyantsev, 2000, Kusi-Sarpong et al., 2018). The formation of emulsions

at the exit from the well with the associated formation water increases sedimentation.

As is known, the struggle with ARPD in the oil production processes conducted in two directions: prophylaxis (or prevention) of deposits; removal of already formed deposits. The choice of the optimal methods of control mode of asphalt, resin and paraffin deposits and the effectiveness of various methods depends on many factors, in particular, on the method of oil production, pressure-and-temperature conditions, the composition and properties of the extracted products. In the bottomhole formation zone (BFZ), the overexposed factors change continuously from the periphery to the central region of the well, and in the well from the bottom to the well, so the amount and nature of the deposits are not constant. The site of ARPD can be located at different depths and depends on the operating mode of the well.

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Among the conditions contributing to the formation of deposits, we can name the reduction of pressure and temperature and degassing oil. It is known that the solvent ability of oil relative to paraffins decreases with a reduction of temperature and degassing of oil. At the same time, the temperature factor prevails (Goroshko, 2003).

2. LITERATURE REVIEW

The intensity of heat transfer depends on the difference temperature between the fluid and the surrounding rocks at a certain depth and the thermal conductivity of the annular space between the rising pipe and the production column (Sorokin et al. 2007). The practice of oil production in the oil fields shows, that the main accumulation zones of the ARPD are downhole pumps, lifting columns in wells, flow lines from wells, gathering tank (Mineev et al. 2004). ARPD is most intensive deposited on the inner surface of the lifting pipe wells. In flow lines their formation increases in winter, when the air temperature becomes significantly lower than the gas-oil flow temperature (Persiyantsev, 2000).

The intensity of ARPD formation in the transport system, collection and preparation of oil is affected by a number of factors, the main of which are pressure decrease in the bottom area and associated disturbance of the hydrodynamic equilibrium of the gas-liquid system; intensive gas emission; decreasing of temperature in the formation and wellbore; changing a speed of the gas-liquid mixture and its separate components; composition of hydrocarbons in each phase of the mixture; the ratio of the volumes of each phases (oil-water) (Tronov, 1970; Kayumov et al. 2006). With increasing speed of oil, intensity of the deposits first increases, which explain the increase in flow turbulence and, consequently, an increase frequency of formation and detachment of bubbles from the surface of the tube, floating the suspended particles of paraffin and asphaltic substances (ARS) (Sorokin et al. 2009). In addition to these main factors, the intensity of the paraffinization of pipelines during the transportation of flooded wells production may be affected flooded production (Nebogina et al. 2008) and the pH of the formation water (Goroshko, 2003).

ARPD, formed in different wells differ from each other in chemical composition depending on the hydrocarbon composition group of the oils produced at these wells. But with all the possible variety of compositions for all deposits is established that the content of asphaltic and paraffinic components will be the inverse: the more paraffin, the proportion of asphaltic substances, the less paraffin will be contained, which in turn, are determined by their ratio in the oil. This feature is due to the nature of the mutual influence of paraffins, resins and asphaltenes in oil until the moment of their allocation to deposits (Sharifullin 2006).

As experimental and practical studies have shown, before the paraffin is released on the surface of the downhole equipment, its crystals transform their structures so that, by joining together, they organize a continuous lattice like a wide band. In this form, the adhesive properties of paraffin increased many times, and its ability to adhere to solid surfaces is significantly intensified. However, if oil contains a sufficiently large amount of asphaltenes (4-5% and higher), their depressor effect is affected. The formation of a continuous lattice does not occur, since asphaltenes themselves act as germinal centers and as a result of this, the release of paraffins on the surface significantly weakened.

Resin, because of its structure, on the contrary, create conditions for forming banded aggregates of paraffin crystals and their adhesion to surfaces and by its presence prevent the effects of asphaltenes on the paraffin, neutralizing them. Like asphaltenes, the resin affects the paraffin oil saturation temperature, but the nature of this influence is the opposite: with the growth of their mass content in the oil saturation temperature increases (if, for example, the presence of resins increase from 12% to 32%, the saturation temperature will increase from 22 °C to 43 °C) (Baimukhametov, 2005). Saturation temperature of paraffin oil is directly dependent on the mass concentration of the resin and in the reverse concentration of asphaltenes. Consequently, the process of paraffin formation depends on the ratio of asphalt (A) and resin (R) compounds in the composition of oil. As the parameter A/R increases, the saturation temperature will decrease - associates of asphaltenes in oil are less stabilized due to a lack of stabilizing components (resins), which leads to a decrease in the saturation temperature, the crystallization of paraffins of such oils is suppressed by associates, and paraffin deposition does not occur; at small values of A/C on the contrary, the saturation temperature increases - asphaltenes have no effect on paraffin formation, paraffin is freely released from oil (Goroshko, 2003).

The mechanism of "paraffinization" understood as the set of processes leading to the accumulation of a solid organic phase on the surface of the equipment. In this case, the formation of deposits can occur either due to the adhesion to the surface of already prepared, solid particles formed in the flow of particles, or due to the appearance and growth of crystals directly on the surface of the equipment (Zevakin et al. 2008). The probability of fixation paraffin particles on the surface of equipment under the conditions of an operating well is practically negligible- paraffin particle can be fixed on the equipment wall, but on the condition that, initially, it will get stuck on it mechanically (Sharifullin et al. 2006). During transportation of oil by pipeline, the following processes occur. Oil enters the pipeline and contacts the cooled metal surface. This gives rise to a temperature gradient directed perpendicularly to the cooled surface toward the center of the flow. Due to

flow turbulence, the oil temperature in the volume reduced. In this case, two processes proceed in parallel; the isolation of n-alkane crystals on a cold surface; crystallization of n-alkanes in the volume of oil.

Practically important is not the release of paraffins, but their deposition on the surface of pipes and equipment in the direction of heat transfer (Sergienko, 1959). Such deposits formed under a number of conditions: the presence of high-molecular hydrocarbons in the oil, primarily the methane series; reduce the flow temperature to values at which there is a loss of the solid phase; the presence of a substrate with a lower temperature, on which hydrocarbons crystallize and with which they are so firmly entangled that the possibility of stripping deposits by flow at a given technological regime is virtually eliminated. Studies of recent years have reliably established that there is no direct relationship between the content of paraffin and the intensity of its deposition (Ibragimov et al. 1986). The absence of such a connection is due, first of all, to a significant difference in the composition of solid paraffin hydrocarbons, the difference in the proportions of aromatic, naphthenic and methane compounds in the high-molecular part of hydrocarbons, which is not determined by standard methods of studying the oils. Meanwhile, it is proved that the differences in the composition of solid hydrocarbons that mainly predetermine the features of formation of paraffin deposits. The higher the content of hydrocarbons with branched aromatic, naphthenic and iso-alkane structures, the less strong are the paraffin deposits, because this type of connection has an increased ability to retain crystalline formations of a liquid mass. Hydrocarbons of the methane series - especially high-molecular paraffins, on the contrary, are easily released from the solution with the formation of dense structures. It is clear that the loose and semi-liquid crystalline deposits can relatively easily be removed by the natural flow of liquid during the operation of the wells without causing any complications, and conversely, dense and strong deposits formed mainly from n-alkanes create serious complications in liquidation of which consumes a lot of resources and labor (Petrova et al. 2005).

Oil dispersed systems are classified as a class of colloids in which asphalt-resinous substances is dispersed in the maltten environment. It is obvious that the physico-chemical and technological properties of oils are largely due to intermolecular interaction in the systems "asphaltene-resin" and "maltenes-resin-asphaltenes."

As a rule, the structure of resins and asphaltenes considered in the form of "sandwich" structures, which are parallel naphthoaromatic layers, connected together by the formation of complexes with charge transfer. It is generally accepted that resins and asphaltenes are paramagnetic liquids, and oil and oil products thermodynamically stable paramagnetic solutions.

Asphaltenes are a combination of many associates, depending on the degree of homolytic dissociation of diamagnetic particles. The change in the concentration of paramagnetic resins and asphaltenes in oil is associated with a change in the structure of combinations of associates.

Asphaltenes and resins have the following characteristics (Ibragimov, 2003):

1. Chemical and physico-chemical processes involving ARS has a collective nature. Asphaltenes are not individual components, but form associative combinations in the center of which stable free radicals are located.
2. The appearance of a solvate shell from diamagnets is an indispensable condition for the existence of paramagnetic particles in solutions. The formation of solvate shells weakens the attraction forces of paramagnetic molecules and prevents their recombination as a result of thermal movement.
3. Resins consist of diamagnetic molecules, some of which are capable of transition into an excited triplet state or undergo homolysis. Therefore, resins are a potential source of asphaltenes.
4. The properties of ARS are not determined by elemental composition, but the degree of intermolecular interaction of the components. The intensity of ARPD formation depends on the prevalence of one or several factors that can vary over time and depth, so the amount and nature of the deposits are not constant.

Thus the knowledge of the composition of ARTD is of practical importance for determining the optimal methods of controlling them, in particular, for the selection of chemical reagents. This selection is often carried out on the basis of the type of ARTD (Sharifullin, 2006).

3. RESEARCH METHODOLOGY

In the case where the bottomhole pressure is less than the gas saturation pressure of the gas, the equilibrium state of the system disrupted, thereby increasing the volume of the gas phase and the liquid phase becoming unstable. This leads to the precipitation of paraffins from it.

Under the pumping method of operation, the pressure at the pump intake may be less than the gas saturation pressure of the gas. This can lead to the loss of paraffin in the receiving part of the pump and on the walls of the production column.

Analysis of the composition of ARPD, taken at different depths of the wells showed that at a depth of more than 1000 m contains more ARS than paraffins (Sharifullin et al. 2006). Mechanical impurities at these depths do not participate in the formation of deposits (their content does not exceed 4-5% wt.).

The struggle with the ARPD involves works to prevent the formation of deposits and their removal. There are several methods that are most known and actively used in the oil industry to combat ARTD. But the variety of mining conditions and the differences in the characteristics of the extracted products often require an individual approach and even the development of new technologies. Chemical methods are based on dosing in the production of chemical compounds that reduce, and sometimes completely prevent the formation of deposits. The action of paraffin deposition inhibitors is based on adsorption processes occurring at the interface between the liquid phase and the surface of the pipe metal. Chemical reagents are divided into wetting, modifiers, depressants and dispersants (Ismayilov et al. 2016).

Wetting reagents form a hydrophilic film on the surface of the metal, which prevents adhesion of paraffin crystals to the pipes, which creates conditions for their removal by the flow of liquid. These include polyacrylamide (PAA), IP-1, 2, 3, acidic organic phosphates, alkali metal silicates, aqueous solutions of synthetic polymeric surfactants. Modifiers interact with paraffin molecules, preventing the process of crystal coarsening. This helps to keep the crystals in a suspended state during their movement. Such properties are possessed by atactic propylene with a molecular weight of 2000-3000, low molecular weight polyisobutylene with a molecular weight of 8000-12000, aliphatic copolymers, ethylene / ester copolymers with a double bond, a triple copolymer of ethylene with vinyl acetate and vinyl pyrrolidone, a polymer with a molecular weight of 2500-3000.

The mechanism of action of depressors is the adsorption of molecules on paraffin crystals, which makes it difficult for them to aggregate and accumulate. The known depressors include ParaflowAzNII, alkylphenol IPX-9, Dorad-1A, VEO-504 Tyumen, Azolat-7 (Usubaliev et al. 2015). Dispersants are chemical reagents that provide the formation of a fine dispersion system that carried away by the flow of oil, which prevents the deposition of paraffin crystals on the pipe wall. These include metal salts, salts of higher synthetic fatty acids, silicate-sulfonate solutions, sulfated alkaline lignin (Nurullayev, 2016). The use of chemicals to prevent the formation of ARTD in many cases is combined with: the destruction of stable oil emulsions, the protection of oilfield equipment from corrosion, protection from sedimentation, the process of formation of optimal structures of gas-liquid flow.

Developed a wide range of chemical reagents for struggling with ARPD. Currently, the following reagent grades used: butylbenzene fraction (butylene benzene, isopropylbenzene, polyalkylbenzenes). A toluene fraction (toluene, isopentane, n-pentane, isoprene), SNPCH-7p-1 is a mixture of paraffinic hydrocarbons of normal and isostructural, as well as aromatic

hydrocarbons (OJSC "NIIneftechem", Kazan), SNPCH-7r -2-hydrocarbon composition consisting of their light pyrolysis resin and hexane fraction (JSC "NIIneftechem", Kazan), HPP-003, 004, 007 (ZAO Kogalym Chemicals Plant, Kogalym), ML-72 - mixture synthetic reagents, SNPCH-7200, SNPCH-7400 reagents - complex mixtures of oxyalkylated surfactants and aromatic hydrocarbons ode (OJSC NIIneftechem, Kazan), ICB-4 reagent, which has a complex effect on ARPD and corrosion of metal pipes (INPP, Ufa), INPAR (Neftechem Experimental Plant, Ufa), SEVA-28 - copolymer of ethylene with vinyl acetate (VNIINP and VNIIneft, Moscow) (Nurullayev et al. 2016). In addition to the listed reagents of oil and gas production, Ural-04/88, DM-51; 513; 655; 650, DV-02; 03, SD-1; 2, O-1, B-1, XT-48, ML-80, Proqalit GM20 / 40 and HM20 / 40. Along with the high cost, a significant shortcoming of the chemical method is the difficulty in selecting an effective reagent, due to the constant change in operating conditions during the development of the deposit.

Despite the wide variety of methods of struggle with ARPD, the problem is still far from being resolved and remains one of the most important in the domestic oil industry.

3. RESEARCH RESULTS AND DISCUSSION

The aim of this work is to study the mechanism of action of oil multifunctional reagent, first obtained by us with of the coordination of nanostructured polymer. The results of experimental investigations have shown that reagents BAF-1 and BAF-2 (technical conventional name reagents) reduce the viscosity of petroleum such as heavy and crude oil, to facilitate transportation of the subterranean formation from the production site to the refinery or oil storage tanks, increased production, purified oil and oil from the sludge in the tanks (Usubaliev et al. 2015; Nurullayev, 2016).

As is known all these properties of oils (high viscosity, difficulty of transportation, the decline in production, the sludge formation in tanks, etc.) directly related to forming AFS.

X-ray diffraction and electron microscopic studies conducted to elucidate the mechanism of action of reagents us. To conduct the study, two samples of oil (for 300ml) from the same wells taken (№1573). To one sample of the oil added 40ml composite reactant solution, and another - left unchanged and distilled to their obtaining the fraction of tar.

As is known, tar is a dry distillate oil at 450-600 0C temperature (depending on the nature of oil) in vacuum condition and atmospheric pressure. The yield of tars depending on the oils composition is 10-45% (wt.). Resin- is a black viscous liquid and formed during the fragmentation of small glittering particles. The

composition of the sludge includes paraffin, the naphthenates aromatic hydrocarbons (45-95%), asphaltenes (3-17%), petroleum resin (2-38 %) and the atoms of metals. Depending on the nature of the oil and from the entrance of the transparent fraction of the density of the sludge varies from 0.95 to 1.03 g/cm³, coking 8-26% (weight) and the melting point of the 12-55 °C.

As is known at atmospheric and vacuum distillation the chemical composition of the oils not change. Therefore, test results obtained for dry and oil products relates directly to oils themselves.

Given the above, the dry product of oil samples subjected to X-ray diffraction and electron microscopy studies. The results are shown in Figures 1, 2, 3 and 4, respectively.

X-ray analysis and electron microscopic images obtained respectively From X-ray diffraction (Figure 1) shows that the dried product sample without reagent pronounced bright consists of three phases between planar distances 4.44, 4.22 and 3.64.

On the radiograph (Figure 2) are removed from the dry product oil sample with the reagent, the third phase completely disappears in the first two phases of the maxima are shifted to the low-angle side, i.e. between planar distances increase. This suggests that after the disappearance of the third phase, the structure of 1-st and 2-nd phase changes and their crystallinity increases.

The results of electron microscopic studies reagentless sample (Figure 3) showed that in the dry rest there is the associate consisting of asphaltenes, resins and waxes that worsen the rheological properties of oils.

The results of electron-microscopic investigations of the sample with the reagent (Figure 4) indicate that in this associate is fragmented and are distributed evenly in oil, which is in a dissolved state.

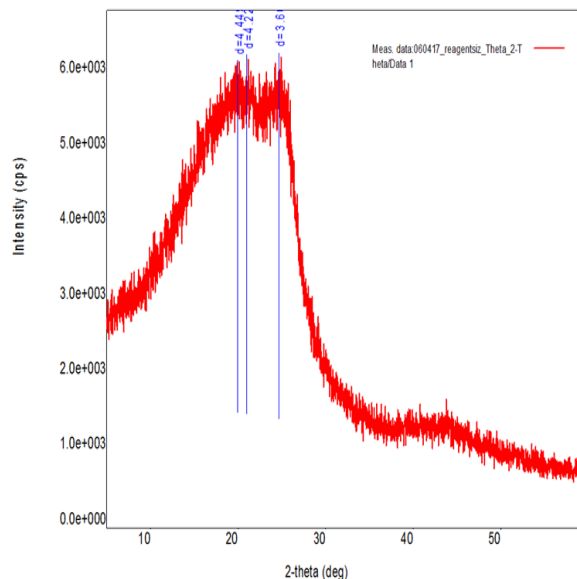


Figure 1. Radiograph of a dry oil sample without reagent

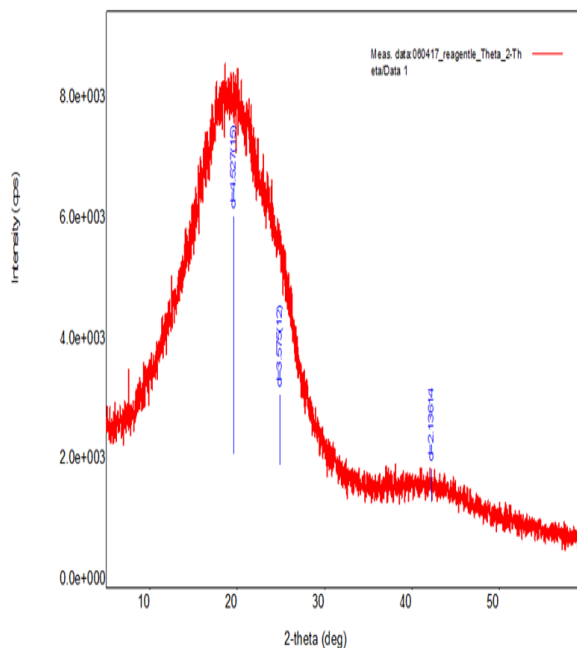


Figure 2. Radiograph of a dry sample oil with reagent

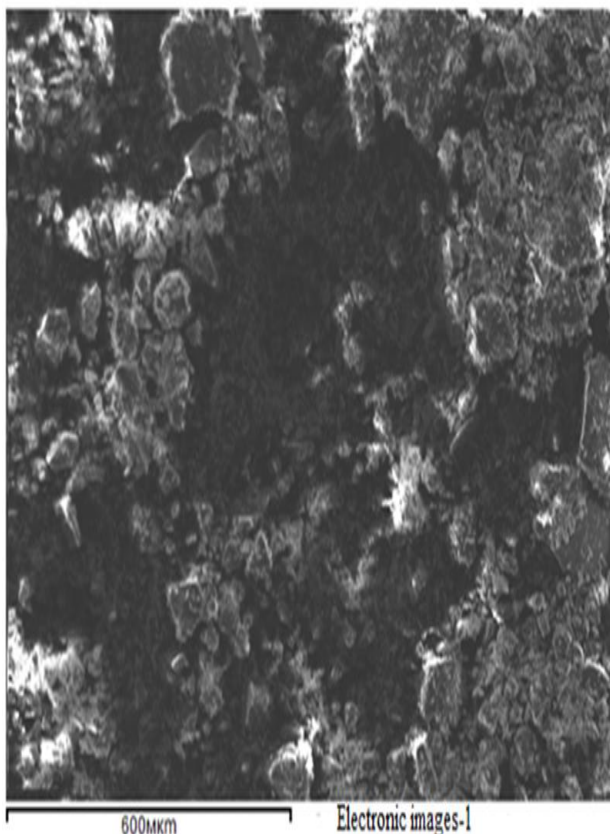


Figure 3. Electron- microscopic image of a dry oil sample without reagent

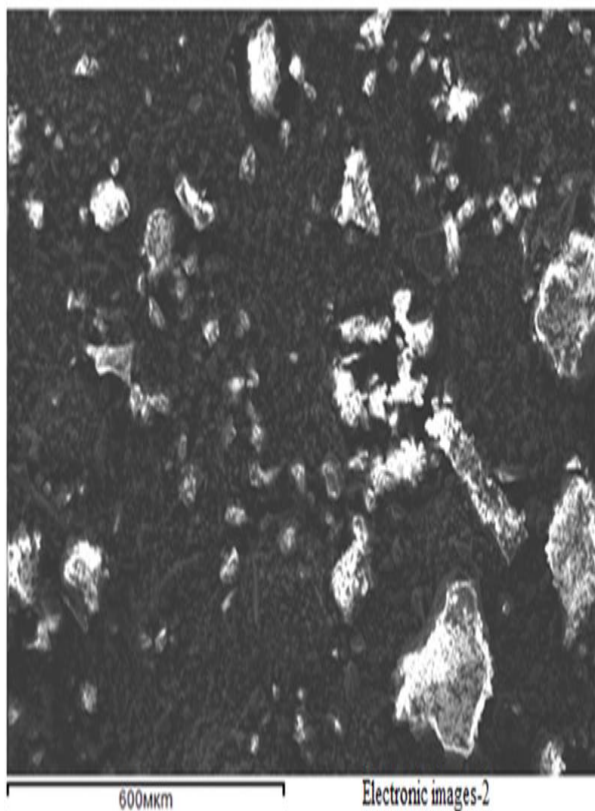


Figure 4. Electron microscopic image of a dry sample reagent free oil with reagent

The disappearance of the third phase (Figure 1) with between planar distance ($d = 3,60$) reveals that the reactants porous (pore size is 20Å ° BAF BAF-1 and-2 with the third phase non-valence form compounds with self-organization and self-construction , i.e. by reacting a reagent with oil arise non-valence skeking interaction between porous polymers and chromatic focal and heteroatom makroassociates third phase. liberated from the third phase of the first and second associates (AFS) turn into small particles and dissolve in the oil. In this regard, and improved rheological properties of oil.

An increase in the between planar spacing of the first and second phases shows that their structure changes. Comparative radiographs petroleum products without dry reagent with a reagent and are shown in Figure 5.

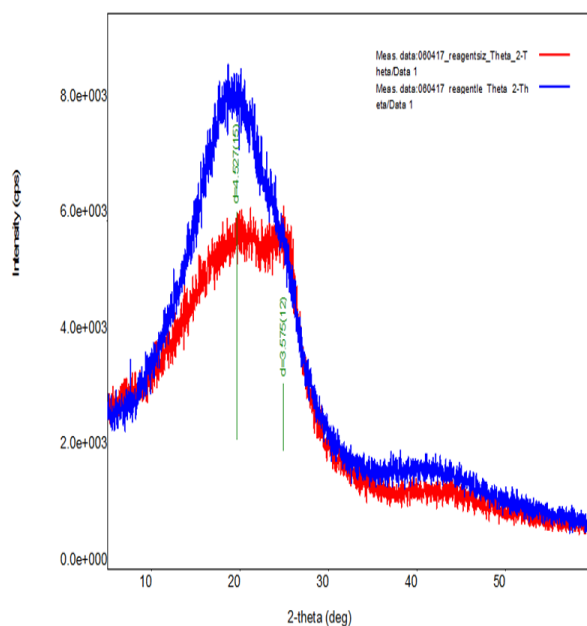


Figure 5. Comparative radiographs of a dry oil products without reagent (red) and with reagent (black)

5. CONCLUSION

According to the results of electron microscopic analysis also clear that in the dry product without reagent paraffin oil associates are in a solid mass, which deteriorate its properties. A dry product oil with a reagent AFS associates fragmented into small particles, i.e. they uniformly distributed in the oil and therefore improves the rheological properties of oil. This again proves that the reactants form a hetero chromatic non valence compound.

Thus, the research results show that the reagents can solve all the problems arising from paraffin formation, particularly, improve the recovery of oil wells, reducing the viscosity of heavy oils, improve the efficiency of transportation of such crudes and perform effective cleaning oil tanks of oil and petroleum deposits, then is

based on the technology of said reactant is multifunctional.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the research council of State Oil Company of the Azerbaijan Republic (SOCAR) and Azerbaijan State University of Oil and Industry.

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