A Technological Nanofluid for Washing Off Oil Deposits and Increasing Oil Recovery

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Received: 3 April 2023 | Revised: 30 April 2023 | Accepted: 2 May 2023

 DOI: https://doi.org/10.48084/etasr.5904

ABSTRACT

The productivity of wells in the late stage of oil production is directly related to oil deposits, which gradually form blockages, fill the pipeline, and interfere with the free movement of the flow of produced oil. Based on chemical composition, oil deposits are difficult to remove and require the selection of process fluids. An extractive method is proposed for the removal of oil deposits with the participation of process fluids, including nanofluids. The proposed nanofluid was prepared on the basis of low-viscosity petroleum oil with the addition of an organic solvent, a mixture of various classes of surface-active substances (surfactants), and alkali metal salts. The nanofluid contains a nanosolution based on alkali metal salts, with concentrations of Na_3PO_4=13700ppm, KCl=950ppm, and $CaCl_2$=241ppm, which were determined by the readings of an ICPE-9820 spectrometer. It was found that the tested process fluid reduces the viscosity of deposits and interfacial tension and leads to an increase in fluid movement in the pipeline. The experiments were carried out in the direction of reducing the interfacial tension at the interface with the solvent. It was shown that the process of sediment reduction depends on the composition of the ARPD, the surfactant, the composition of the solvent, and the salinity of the nanosolution. It is advisable to flush oil deposits from the surface of the tubing using the process fluid when creating a circular circulation in a closed annular space - tubing – annulus circuit.

Keywords-nanofluid; oil deposits; solvent; surface tension; surfactant; tubing

I. INTRODUCTION

In many countries, including Georgia, at old mines (Supsa, Shromysubany, Telety) most of the production wells work in a reduced format of their potential. which is connected with the deterioration of the filtration properties of rock collectors and the formation of heavy components of the final oil (asphalts, resins, and paraffins). Productivity and rates of oil production are decreasing. Increasing the output of such wells is possible with the help of innovative methods and effective technological fluids. Inexpensive and non-toxic nanofluids can be used for the effective extraction of even heavy, highly viscous oil from formations. with the help of nanofluids. Metallic sodium was used as a nanomaterial for effective oil extraction from heavy oil and oil sand layers. Preliminary tests of the batch showed that when mixing 1g of heavy oil (2000 cP at 25 °C, density 12.5 °API) and 40 mg of sodium nanoparticles dispersed in 0.2 ml of silicone oil, and 1ml of physiological solution containing 5.66 wt.% NaCl, as a result of the reaction of sodium with water, a sufficient amount of heat is released, preventing the formation of oil deposits [1-2].

Authors in [7, 8] recognized the potential of low salinity waterflooding when they discovered that additional recovery of residual oil could be achieved using LSW flooding. The efficiency of LSW in oil recovery can be related to the presence of potential ions (Mg^{2+} and SO_4^{2-}) in LSW. However, brine salinity is a major factor in oil recovery. Additional oil recovery from LSW flooding is only possible if the salinity is in the range of 2000–5000 ppm [3]. Recently, nanoparticles have been used for boosting oil recovery. Nanoparticles can improve the performance of the injected water in the Enhanced Oil Recovery (EOR) process. A nanofluid consists of a liquid and nanoparticles dispersed in it. The properties and efficiency of nanofluids in EOR depend on various parameters, such as the size and type of the dispersed nanoparticles. The behavior of the pressure drop in nanofluids differs from that in conventional fluids. Nanoparticles dispersed in nanosuspensions usually have a size of 1 to 100nm. The small size of the nanomaterials increases their effective surface area, which will change some of the properties of fluids containing these particles, such as heat transfer, viscosity, and particle surface activity [4]. The main methods for removing deposits from tanks are mechanical cleaning or hot washing with the use of solvent removers. As removers, individual organic substances and their mixtures with the addition of surfactants, oil and its fractions, products of the petrochemical industry, and surfactant solutions are used. Despite the widespread use of this method, there is the problem of the selecting effect [5].

The use of natural SAS and bio additives in petroleum oils and fuels improves their performance. Bio fuel for jet engines has been obtained with the addition of nettle seed oil. As a result, the operational properties of fuels are stabilized [9, 21]. Authors in [19] propose the use of a combined method for cleaning small-diameter oil pipelines utilizing, as a flush solution, used engine oil with toluene added to dissolve ARPD followed by the displacement of softened deposits by devices of various designs. A composition for the removal of paraffin deposits containing a mixture of hydrocarbons, in wt.%, is proposed: the spent cyclohexanefraction - 70-80 and the spent tall oil or rapeseed oil -20-30 (RF Patent 2185412, C 09 K 3/00, E 21 B 37/06, publ.20.07.02) [20].

II. MATERIALS AND METHODS

The main goal of the current work is the development of new effective process fluids, the use of which will ensure the washing out of salt and paraffin deposits in the tubing of the well and intensify the flow of residual oil of the productive formation. The objects of study were asphalt-resin-paraffin deposits taken from different sites. Their compositions are shown in Table I.

TABLE I. COMPOSITION OF THE STUDIED ARPD

No	Compound	1	2	3	TEST
1	Asphaltenes, % mass	4.7–7.74	6.5-25	10-15	GOST 11851-85
2	Resin, % mass	9.8-20.3	7-21.5	20-25	GOST 11851-85
3	Paraffin, % mass	3.2–3.9	3-4.5	45-60	GOST 11851-85
4	Mechanical ipurities, % mass	12-17	15-18	15-30	GOST 6370-83
5	Water, % mass	0.3-0.8	5-8	5-18	GOST 2477-65
6	Density, g/cm^3	0.9–1.0	0.93-1.3	1.2–1.5	GOST 3900-85

The chemical composition of petroleum residues of ASPO is different: 1-reservoir oil, 2-transit oil from the tank, 3-from the main oil pipeline. The compositions are presented in Table I. At this stage, the composition of the liquid was developed to remove petroleum deposits formed on the tubing (pumping equipment) of well No. 15 of the Supsinsky field. The following instruments and reagents were used in the laboratory study:

- Plazma Atomic Emission Spectrometer ICPE-9820 Japan, 2017, Shimadzu [22].
- BioBaseBK-R2SABBEDigital Refractometer, China [23].
- Stalagmometer, viscometer, density meter.
- Aromatic alcohols and their derivatives: Isopropyl and isobutyl alcohol.
- Industrial solvent -646 (RF) [15], composition: 15% ethanol, 10% butanol, 50% toluene, 7% acetone, 10% butyl acetate and 8% cetate, industrial solvent, GENC, Turkey
- Used petroleum oil.
- Diluted solutions of surfactants.
- Nano-solutions alkali metal salts.

The parameter calculation follows [12-14]:

The solubility of the deposits is derived by:

$$E = [(M_1 - M_2)/M_1] \times 100\% \quad (1)$$

where M_1 is the mass of the taken for the experiment (g) and M_2 the mass of the residues in the basket after the experiment.

- Solvent liquid that prevents the rapid evaporation of the light fraction of solvents.

It was revealed that the use of a mixture of solutions of an anionic and non-ionic surfactant composition regulates the uniform washing off of deposits of paraffin deposits and ensures the free movement of oil in the tubing and formation reservoirs. The kinematic viscosity (mm^2/s) is:

$$V = \tau K \quad (2)$$

where τ is the expiration time (s) and K= 0.1006, viscometer capillary d= 0.99.

Interfacial tension at 20^{0}C:

$$\sigma = \frac{mg}{\pi D n} \quad (3)$$

Liquid density:

$$d_{20}=d_t+\alpha(t\text{-}20) \quad (4)$$

where t is the temperature.

III. RESULTS AND DISCUSSION

The ASPO dissolution process comprised the controlled gravimetric method and refractometry. The experiments were carried out in the educational laboratory of the Batumi Shota Rustaveli State University.

A. Testing of Solvents

The following reagents were selected as ARPD deposit removers:

- Waste and refined petroleum oil (OM)
- Solvents 646 or 647 (RF) [15]
- GENC solvent
- Aromatic alcohols, isopropyl alcohol
- Ethyl acetate

Figure 1 shows the dynamics of the dissolution of the ARPD sample depending on time with the reagents under study, in the ratio of ARPD / solvent (1/30) at t = const.

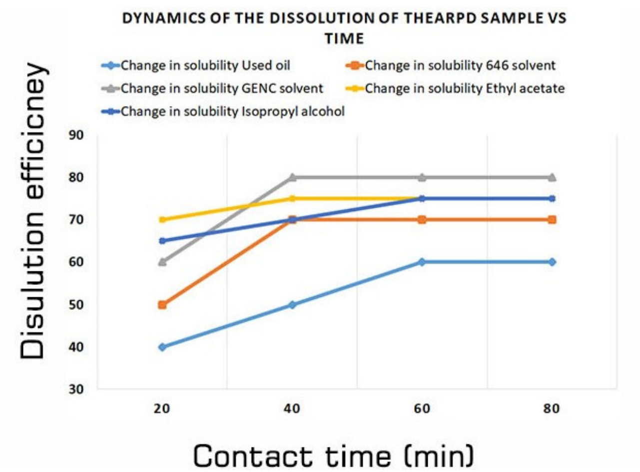

Fig. 1. Dynamics of the dissolution of theARPD sample vs time.

TABLE II. CHANGE IN SOLUBILITY IN TIME FOR DIFFERENT SOLVENTS

Contact time	Change in solubility				
	Used oil	646 solvent	GENC solvent	Ethyl acetate	Isopropyl alcohol
20	40	50	60	70	65
40	50	70	80	75	70
60	60	70	80	75	75
80	60	70	80	75	75

The obtained result shows that ARPD deposits dissolve well in aromatic solvents, especially at the initial stage of dissolution within 60 min. Asphaltenes dissolve well in aromatic hydrocarbons, paraffins in light hydrocarbons, and resins in both [14].

B. Testing of Used and Enriched Petroleum Oil

Waste petroleum oils are concentrates of complex component compositions, fatty acids, heterocyclic compounds, additives, etc., forming a liquid with a density of 0.8862–0.920 g/cm^3 at 20°C. It should be noted that the waste oil, based on the degree of contamination, was purified with the use of extractive and adsorption methods. The results of technological research on the purification and regeneration of used engine oil are presented in [16] by the grant - GNSF project 496-7-201 (Georgia).

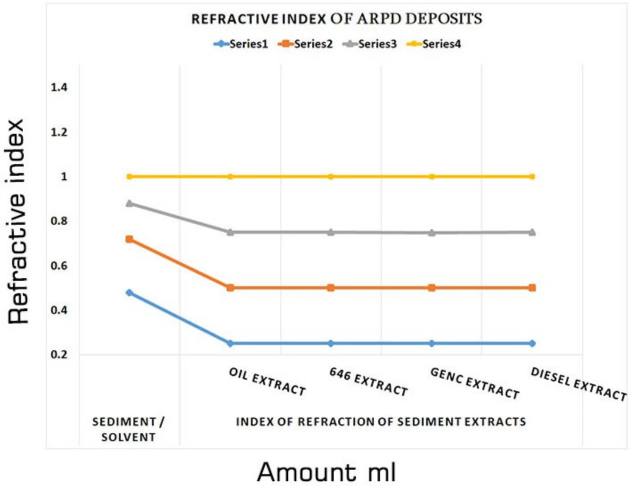

Fig. 2. Refractive index of ARPD deposits: 1. Oil extract, 2. GENC extract, 3. diesel extract.

The obtained results confirm that the deposits are most dissolved in the EGNK solvent. Waste (and refined) petroleum oil contains an insufficient amount of fatty acids, so it was enriched with vegetable oils with a high content of fatty acids: ricinoleic, oleic, and linolenic [21]. When natural surfactants are added to used oil, its physicochemical parameters, such as CMC, pH, etc., improve. Enriched oil was used to obtain oil extracts, which are oil-soluble surfactants and are actively involved in the process of dissolving deposits. All oil extracts and organic solvent extracts were tested on a BioBase BK-R2 ABBE digital refractometer to determine their refractive index. The test results are presented in Table III.

TABLE III. INDEX OF REFRACTION OF SEDIMENT EXTRACTS

Sediment / solvent	Index of refraction of sediment extracts			
	Oil extract	646 extract	GENC extract	Diesel extract
1/10	1.4752	1.4355	1.3763	1.4578
1/20	1.4752	1.4323	1.3538	1.4528
1/30	1.4750	1.4323	1.3536	1.4528
1/40	1.4752	1.4355	1.3763	1.4578

C. Testing of Surfactants and Nano Fluid

The main ability of surfactants is that their activity reduces surface tension at the interface. However, the surfactant has a CMC solubility limit - (critical Micelle concentration), with the achievement of which, with the further addition of a surfactant to the solution, its concentration at the interface remains constant. For this study, the decrease in interfacial tension and then the decrease in the viscosity of deposits of ARPD is the most significant phenomenon. Therefore, work was carried out in the direction of reducing the viscosity of ARPD deposits [17] (Table IV). The object of study was surfactants in concentrations ranging from 0.01% to 2.0 wt%. Solutions of surfactants of various classes, such as washing, working reagents, anionic, and non-ionic surfactants and their mixtures, were chosen. The physical parameters, such as the coefficient of surface tension, of the reagents were determined. The sulfanol solution had the lowest coefficient of surface tension, so it was preferred as an additive to washing liquids [17-18].

TABLE IV. SURFACTANT TEST RESULTS

Surfactant concentration	Surface tension 10^{-3} N/m	
	Sulfanol	**Alkane DE 202**
1.0	0.93	3.74
0.5	1.83	5.26
0.25	2.40	7.00
0.125	3.61	8.90
Oil without SAS	44	

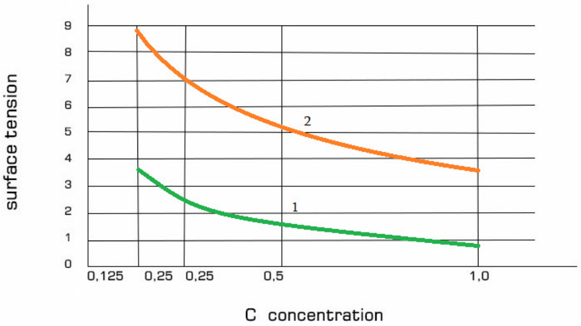

Fig. 3. Dependence of surface tension coefficient on the concentration of the investigated reagent: 1. Sulfanol, 2. alkane DE 2 02.

Authors in [6-8] propose the use of nanofluids containing nano-solutions for the effective flushing of oil deposits. Researchers of the Gubkina Institute of Oil and Gas [10] offer process fluids, without nano-solutions, which include a solution of mineral salts and various surfactants (Naphthols), which reduce interfacial tension at the interface with the solvent. We propose a composite composition of nano-liquid which contains waste petroleum oil, solvent, sulfanol surfactant, and nano-solution, which was prepared on the basis of alkali metal salts with the following composition:

- Na_3PO_4 nanosolution with concentration of 13700 ppm
- KCl nanosolution with concentration of 950 ppm
- $CaCl_2$ nanosolution with concentration of 241 ppm

In order to reveal the effect of nano solutions on the interfacial tension of a liquid, experiments were carried out at different salts and concentrations of nano solutions and at different surfactant concentrations. The results are shown in Table V. The study was carried out at a temperature of 20 °C, and the best solvent (GENC) was used as the hydrocarbon medium in all experiments. Studies have shown that the interfacial tension reduction can be maximized when using a nano-solution of sodium salt, whereas in the case of calcium salt, the nano-solution did not work. The concentration spectra of nano-solutions obtained on the device Plazma Atomic Emission Spectrometers ICPE-9820 are shown in Figures 4-6.

TABLE V. NANOSOLUTION INTERFACIAL TENSION AT THE INTERFACE WITH THE GENC SOLVENT AT DIFFERENT SURFACTANT CONCENTRATIONS

#	Nanofluid composition	Interfacial Tension(IFT) 10^{-3}N/m, 20°C				
1	Nanosolution Na_3PO_4 13700ppm	3.62	0.52	0.46	0.42	0.46
2	Nanosolution KCl 950ppm	2.28	0.56	0.56	0.56	0.58
3	Nanosolution $CaCl_2$ 241ppm	1.98	1.98	1.94	1.94	1.94
4	Surfactant, SAS concentration %	0.01	0.25	0.5	1.0	1.5

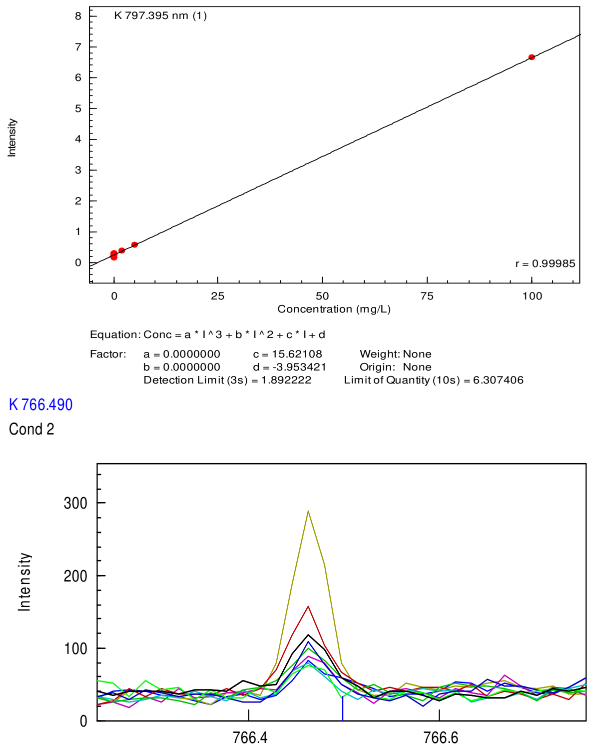

Fig. 4. Nano solution # 1. Wavelength 589nm.

The field work that is planned to be carried out on wells, in relation to equipment and technology, is reduced to the existing methods of well treatment. Of the existing technological schemes for well treatment, tubing and annular space are recognized as the best (Figure 7). Removal of deposits from the surface of tubing using process fluids is carried out on the basis of creating a circular circulation along a closed circuit: annular space - tubing - annulus [12-14].

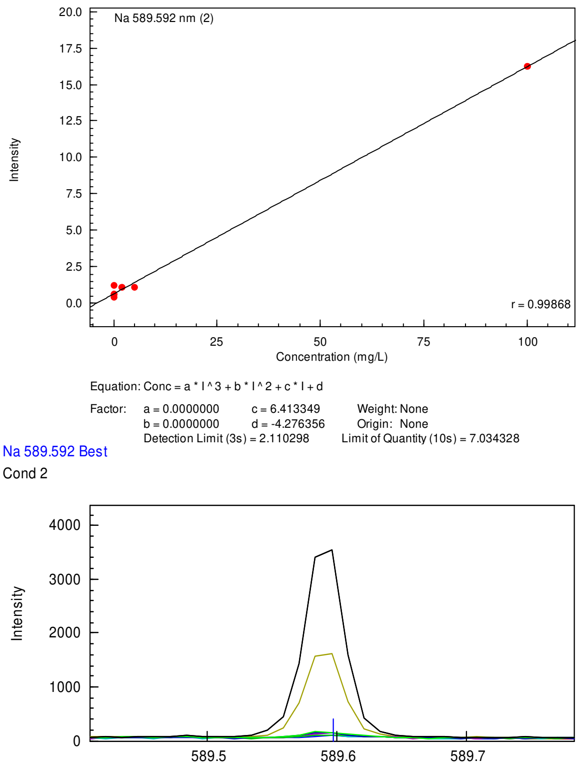

Fig. 5. Nano solution #2. Wavelength 787nm.

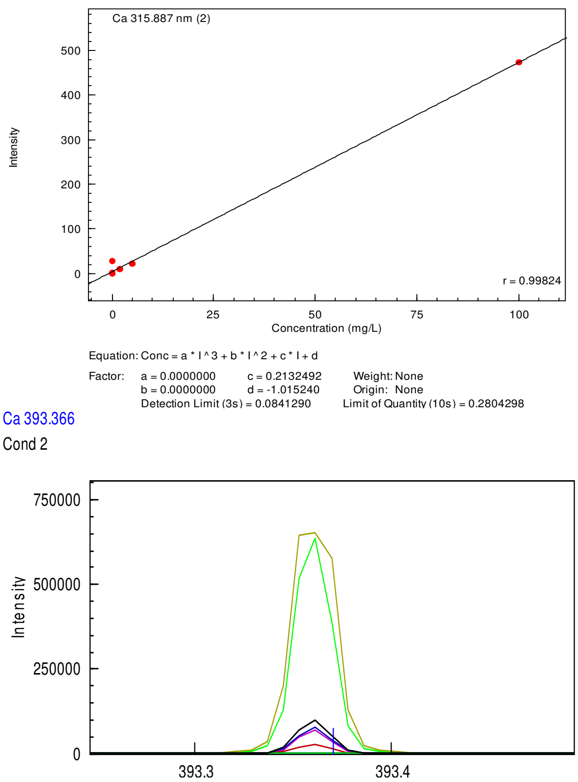

Fig. 6. Nano solution #3. Wavelength 315nm.

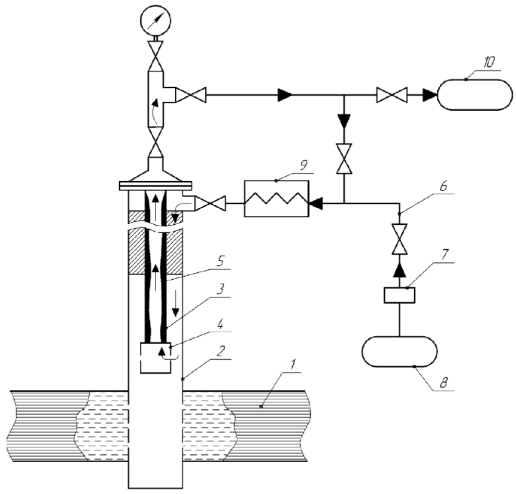

Fig. 7. Tubing flushing. 1. Well 1 oilreservoir, 2. colons, 3. tubing, 4. pump, 5. oil deposits, 6. injection zone, 7. pumping unit, 8. volume for solvent, 9-10. volume for waste.

IV. CONCLUSIONS

The effectiveness of the use of nanofluids for washing off oil deposits was revealed as a result of the current research. It is shown that when sodium phosphate, potassium chloride, and calcium chloride, in a combination of aqueous solutions of surfactants and a hydrocarbon medium, are introduced into the composition of the nanofluid, the ARPD washing improves by 45%. This ensures the free movement of oil flow through the tubing and increases the productivity of the well. The dynamics of dissolution of ARPD samples by individual reagents under statistical conditions was studied.

The proposed nanofluid has a number of advantages. It is shown that ARPD deposits are effectively dissolved at the initial stage of dissolution within 60 minutes. It was revealed that nano-solutions based on alkali metal salts using a mixture of solutions of anionic and non-ionic surfactant compositions are effectively involved in reducing interfacial tension, regulating uniform flushing of deposits in tubing, and ensuring free movement of oil flow through the well.

In [13], the authors propose the elimination of the AFS of the Zhanaozen (Ozen) oil field with a solvent mixture consisting of 50% gasoline and 50% kerosene. This paper shows that ARPD deposits dissolve well in industrial solvents, especially at the initial stage of dissolution within 60 minutes.

In [10], surfactants (naphthols) for dissolving ARPD were proposed, which are much more expensive than sulfanol. Petroleum oil in the composition of the nanofluid increases the density of the cleaning solution and prevents the rapid evaporation of the light fraction of solvents. It also ensures the safety of their storage in the conditions of downhole equipment.

ACKNOWLEDGEMENT

We would like to thank the Rectoral and Research Service of Batumi State University for their support and the funding of this publication.

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