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Efficiency of Extracting Bitumen from Bituminous Sand and Phase Boundary Phenomena in Sharable Heterogeneous System

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Abstract: An extreme nature of the dependence of bitumen output on concentration of alkaline reagents in a process solution at ultrasonic separation of bituminous sands has been identified. Facial and surface tensions on the borders of a process solution with air and oil product, which confirmed the formation of natural surfactant in the course of process, have been measured. It is established that the minimum yield of bitumen is observed in the lowest values of surface tension, facilitating the formation of stable emulsions. The influence of the concentration of sodium cations in solution on the position of the minimum surface tension has been shown.

Key words: Bitumen · Ultrasonic · Oil products

INTRODUCTION

With the increase of consumption, depletion of conventional oil reserves and growth of its value the extraction of viscous and residual oil from oil-producing rocks has become more and more important problem. A huge source of energy is stored in bituminous (oil-producing) sands.

The presently known resources of oil bituminous rocks (OBR) and high-viscosity oils (HVO) in the world are estimated at 630-1050 billion tonnes [1,2], which is in its turn exceeds the amount of proven reserves of conventional oil. Canada and Venezuela possess the largest potential resources of this raw materials. By some estimates, the total content of bitumen and heavy oil only in sands of the province of Alberta (Canada) and in Orinoco (Venezuela) exceeds 4 trillion barrels.

On the territory of Russia, the main possibilities for mining and processing petroleum bitumen are associated with the Permian rocks of the central regions of the Volga-Ural bituminous oil and gas producing province. More than 400 deposits and local bituminous sites have been identified here and probable reserves of bitumen in the Permian deposits exceed the resources of oil Devon Carboniferous strata. The initial total resources of bitumen of Russia are estimated at tens of billions of tons and are characterized by low exploration [3, 4].

Tatarstan natural bitumen is best explored, where more than 85 clusters have been revealed. 27 deposits among them with varying degrees of detail have been explored. Most part of the bitumen containing rocks of the Permian deposits of Tatarstan refers to the layers at a depth of 1 to 40 meters, with a density of from 0.95 to 1.1 g/cm3, viscosity of from hundreds to many thousands of centipoise, tar 19.4-48.0% and sulfur 1.7-8.0 %.

The issue on the study of OBR in Western Kazakhstan was first considered in the forties of the twentieth century. The layout of placing OBR in the Kazakh SSR was drawn by Kolpakov V.B., Meshcheryakov S.V. and a visual description of the basic fields is given [5]. As a result of the works by Nadirov N.K., Altaev S.A., Strelnikova V.Y. and others [6-10] the interest in exploration, production and use of the OBR has significantly increased from the 70s. In the Kazakh SSR in Aktobe, Guriev areas while outcrops on the surface of search, structural and exploration wells in the core, as well as the analysis of materials of geographical research more than one hundred deposits and emersions of the OBR and HVO have been identified and registered. And even according to the

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most approximate estimate only in twelve fields of Tyubkaraganskiy and Bekebashkudukskiy meganticlines of Mangyshlak at least 500 million tons of natural bitumen (5-6 million tons in terms of the NBP) is contained. The reserves comparable with them, apparently, are concentrated in the suprasalt sediments of numerous local structures of Caspian Sea oil and gas bituminous basin. This allows to suggest that in Western Kazakhstan more than 1 billion tons of natural bitumen or over 15-20 billion tons of OBR lies not in the depth of 120 m [8].

More than half of all bitumen deposits of the CIS are concentrated at the depth, which allows them to explore by career and mining method. The main part of the OBR in the Western Kazakhstan lies at a shallow depth and has an exit to the ground surface. Herein a grouped location of deposits with a relatively small distance from each other and a small power of capping near the location to consumers create favorable conditions for profitable operation. It is rather important to note that according to bitumen content OBR of the Western Kazakhstan are the most promising for extraction and processing, as the bitumen content in them reaches 15-20% (sometimes more) of the mass of rock.

Beginning with the classical works of Clarke in the 20-30 years of the last century [11] and up to these day investigations of the influence of the nature and composition of the bituminous sands, mode of conditioning and conditions of the separation process conduct on the yield of bitumen are being widely (especially in Canada) conducted [1, 2, 12, 13].

There are considerably less works devoted to the use of ultrasound at the separation of bituminous sand [14-17]. Possibilities and examples of use of powerful ultrasound for the rehabilitation of soil polluted by oil products are considered in Mason's review article [18]. However, small size and fragmented nature of the available data do not allow to reveal the nature of the dependencies of the kinetic parameters of an ultrasonic process and product yield from OBR components properties and the conditions of separation.

The aim of this work is the research of ultrasonic process efficiency of bituminous sands separation and its dependence on the composition of the process solution and interfacial properties in sharable heterogeneous system.

MATERIALS AND METHODS

Separation of oil producing sand using ultrasonic treatment was carried out on samples of rocks containing bitumen 12-15 wt.%. The experimental setup with an ultrasonic bath of volume of 1.5 is shown in Figure 1.

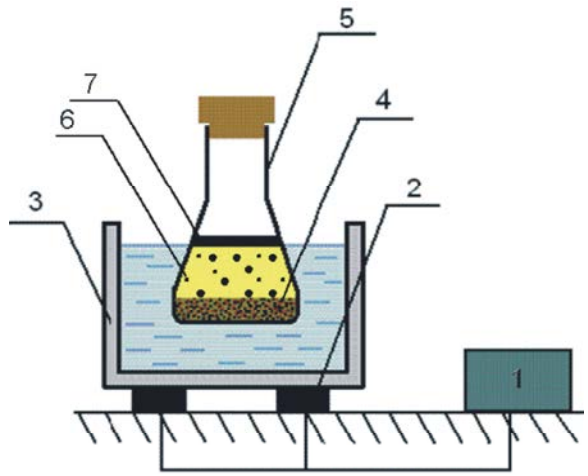

Fig. 1: Installation with an ultrasonic bath: 1 - generator; 2 - transformers 3 - ultrasonic bath, 4 - bituminous sand; 5 - a glass container with a process solution, 6.7 - popup drop and a continuous layer of oil product.

An electric generator 1 feeds the ultrasonic piezoelectric transducers 2 with recurrent pulses of high voltage with the required frequency. Transducers convert electrical energy into sound one. Ultrasound generated by the transducers passes through the water filling the bath 3 and reaches the walls of the reactor flask container 5. The process of cavitation develops in the water surrounding the reactor container. On the surface of the section "glass-water" a weakening of the acoustic field takes place, ultrasound intensity is reduced inside the bulb, but it is sufficient for active influence on the loaded rock.

A weighed sample of oil producing sand 4 weighing up to 15 g was placed in a flask 5 with volume of 0.3l with distilled water, where a particular mass of required reagent was dissolved. To prepare process solution of alkali type silicate, carbonate or sodium hydroxide additives were used. The flask was placed into an ultrasonic bath 3 (frequency is about 20 kHz, power is 60 Watt) filled with water, heated by electric heater to a predetermined temperature T = 50-70°C. After that timer was set and ultrasonic processing of the content of flask for a certain period of time was being spent at a constant temperature.

Under the influence of ultrasound large pieces of rock were being collapsed with formation of sufficiently homogeneous slurry, bitumen was gradually being separated from the sand particles and its drops 6 came to surface of the solution, where they coacervated into a solid black layer 7. At the bottom of the flask clear purified sand remained.

Pop-up portions of bitumen were periodically collected from the surface, placed on pre-weighed leaves of filter paper and weighed again after drying. Since the selected samples of bitumen may contain trapped solid particles of rocks, then for their selection the leaves with bitumen were placed in weighing bottles with dichloromethane solvent. After the dissolution of mineral oil the solution was poured out and the weighing bottle with the bottom of the settled particles and the leaves were located in a fume cupboard to remove traces of solvent. After that, weighing bottles were weighed and the mass of the trapped particles was determined. At the end of experiment sedimentation and decantation free of bituminous rock in the reaction container was also carried out. The solid residue was dried, weighed and then a complete material balance was drafted.

RESULTS AND DISCUSSION

The kinetics of bitumen release to the surface of the process solution in a wide range of concentrations of such alkaline additives as: C = 0.1-6 wt. % has been studied. All studied reagents ($NaSiO_3$, $NaCO_3$ and NaOH) increase separation efficiency and reduce the occupation of solid particles by pop-up bitumen droplets. At the temperature of the process solution of 60-65° C, the maximum yield of bitumen exceeds 90%. Comparison of the impact effectiveness of various alkaline reagents shows that the best result is given by sodium silicate additive. With its use it is possible to achieve nearly complete extraction of bitumen (up to 95%) with a minimum sand occupation for 30-60 minutes. Investigation of the effect of concentration of chemicals in the solution on the ultrasound separation process showed the complex nature of influence of additives such as alkali (Figure 2).

The obtained results from the figure showed that, at concentration lower than 0.01 mol / L (0.01 M), there is less yield of bitumen, on the other hand at concentration not more than 0.2 mole / l there is higher final yield of bitumen and significantly lower proportion of entrained solid particles. All the dependences of the bitumen yield on the concentration of the solution have a pronounced minimum in the sphere of middle concentrations. At the point of minimum the output fell in the 5-8 times. Moreover the position of the minimum when using the molar concentration of the solution changed little in case of transition from one additive to the other: all three minima in Figure 2 are in a narrow interval concentration from 0.001 to 1 mol./L. In this range, the color of process solution dramatically changed. It quickly acquired a dark brown color, while in the areas of lower and higher concentrations the solution was quite light in color to

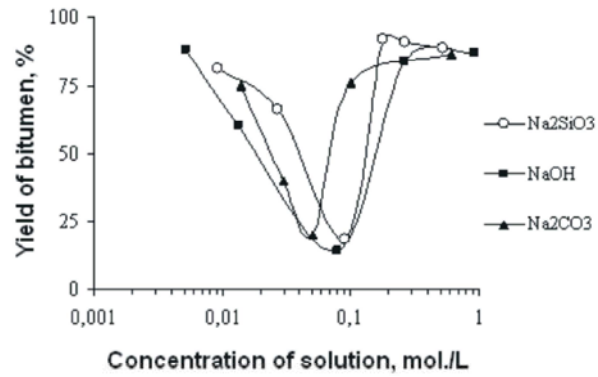

Fig. 2: Effect of concentrations of different alkaline additives in the process solution on the final yield of bitumen from bituminous sands.

the end of the ultrasonic treatment. Such metamorphoses are associated with chemical interaction of alkaline reagents with some components of petroleum products.

Bitumen is a material of complex composition, the components of which vary greatly in molecular weight, chemical structure and size of the hydrophilic-lipophilic balance [19]. A specific feature of the bitumen is that it is amphoteric in nature and contains many components with the surface-active properties (asphaltenes, resins, carboxylic acids). These polar compounds with ionizable groups determine phase boundary properties in the system of bituminous sand-process solution and stipulate non-linear nature of dependencies of some parameters (e.g. surface tension) on pH and concentration of electrolytes in aqueous solution. In the process of separation of heterogeneous systems bitumen (oil) / solids / water with large areas of separation surface, phase boundary properties play a crucial role. Surface tension, rheological and electrical properties of the phase boundary surfaces (oil / water and oil / solid) make a strong influence on the efficiency of separation carried out in an alkaline aqueous medium.

Possible factors of alkaline additives impact : the neutralization of organic acids with the formation of natural surfactant in the form of corresponding soluble salts, the shift of the hydrophilic-lipophilic balance towards hydrophilicity, increasing pH medium and the concentration of sodium cations, the ionization of the components of the solution and the change of electric charges at the boundary surface of the system. In moderate alkalinity positive impact of these factors will help to reduce the adhesion forces between bitumen and silica sand, an increase of electrostatic repulsion forces, the separation of bitumen from the sand particles and exit to the surface of an aqueous solution.

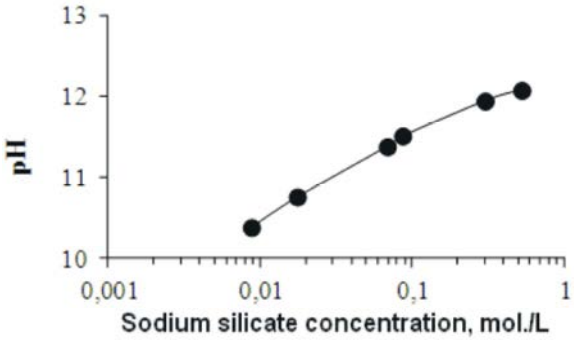

Fig. 3: The dependence of pH of the initial process solution on concentration of sodium silicate.

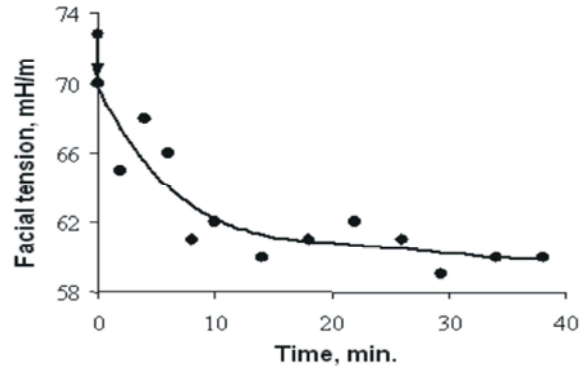

Fig. 4: Change of surface tension on the "process solution - air" during the ultrasonic treatment, C = 0.081 mol. / L, T = 25° C.

In processing of bituminous sands by alkaline solution in an ultrasonic field reduction in the bitumen yield to minimum values, accompanied by a sudden darkening of process solution confirm emulsification (and possibly partial dissolution) of bitumen. The minimum yield for the sodium silicate is observed at C = 0.08-0.1 M (about 1 wt.%), when the pH of initial process solution increases to 11.5 -11.7 (Figure 3).

These pH values can contribute to increase concentrations of new forms of natural surfactant in the process of solution, respectively, reduction of surface tension and strengthening of the repulsive forces between bitumen surfaces (these factors and ultrasound effects result in emulsification of bitumen, they help to reduce the size of the droplets and increase emulsion stability). Under these conditions, emulsification can take place even spontaneously and when it reaches the critical micelle concentration, the formation of microemulsions. is not the exception.

To test the hypothesis on the formation of soluble surfactants from bitumen during ultrasonic treatment in an alkaline medium the measurements of surface and surface tension on the borders of the process solution of sodium silicate with air and petroleum product.

Measurement of surface tension was performed by counting the drops (stalagmometer method). At regular intervals during the processing of bituminous sand ultrasonic bath was switched off, part of the process solution was poured out from the flask, filtered and then a sample was selected by a syringe. The numbers of drops at streaming samples from syringe with known radius of exit hole (1 mm) were being counted and their mass was determined using electronic scales. Based on these data surface tension at the "process solution-air" for each sample by the formula were being calculated:

$$\sigma_1 = mg/2\pi rn, \quad (1)$$

where: σ1 - surface tension, mN / m; m - total mass of the droplet, kg; g - acceleration of free fall, m/s2; r - radius of the syringe hole, m; n - the number of drops.

The measurement results are presented in Figure 4 shows that the surface tension falls during the ultrasonic treatment of a heterogeneous system. This testifies the formation of new surfactants. The arrow on the y-axis shows the drop in surface tension before the ultrasonic treatment - during heating of the process solution with bituminous sand.

It is noticed that the repeated use of the spent process solution to separate a new portion of the bituminous sand reduces the induction period before the first bitumen drops increases the initial rate of recovery and slightly increases the yield of the final product. This is additional evidence of the fact that the spent solution already contains natural surfactants which were formed earlier in the interaction of alkali additives with organic components of the bitumen.

More important role in the process of separation of oily mixtures is the surface tension on the line of liquid oil or bitumen with process solution. To estimate the extent of surface tension a method that allows to measure the diameter of a drop of petroleum product, extruded from the syringe into the process solution of given composition has been proposed. Thermostated container of small volume of 15 ml, with process solution selected during the process, was tightly closed by a tube through which the needle was injected gently of the syringe with petroleum product heated to 50-60°C (to reduce viscosity), one drop of which was slowly squeezed out into the process solution. Droplet diameter was measured using an optical device - a cathetometer at the time of its separation from filed end of the needle. According to the diameter of the drop and the density difference between

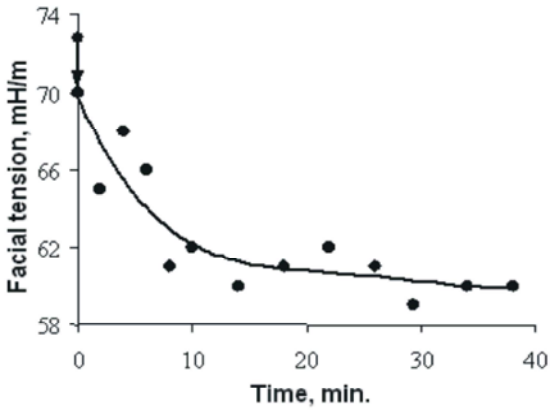

Fig. 5: The dependence of the surface tension on the line of "petroleum product - a process solution" on the concentration of sodium silicate in solution.

oil and process solution the extent of surface tension was calculated for each concentration of the solution on the basis of the ratio

$$\sigma_2 = 2\Delta\rho g R^3/3r, \quad (2)$$

where: σ2 - surface tension, mN / m; r - radius of the syringe needles outlet, m; Δρ - density difference of process solution and petroleum product, kg/m3; R - radius of a drop of petroleum product, m.

Measurements were made at three different concentrations of sodium silicate (0.0082, 0.081 and 0.48 M). The first and third concentration in correspondence with Figure 2 are in the range of the highest yields of bitumen and the second, on the contrary, in the very low yield area. The results of measurements of surface tension depending on the concentration of sodium silicate in the process solution are shown in Figure 5.

Comparison of Figure 2 and Figure 5 showed a good correlation between the concentration dependences of the output of petroleum products and the surface tension. From Figure 5 it is seen that the minimum surface tension corresponds to the concentration of sodium silicate, where the lowest yield and the formation of fine emulsions were observed. In the areas of low concentrations of alkaline agent emulsion is practically not formed and in the areas high ones it is destroyed. In a highly alkaline environment possibility of formation of soluble surfactant in an aqueous medium is already exhausted and only the content of insoluble carboxylates can go up. Full ionization of acidic functional groups is achieved and further increase of Na^+ ions concentration and ionic strength only increases the surface tension. Accordingly, consistency of the emulsion is reduced and coalescence

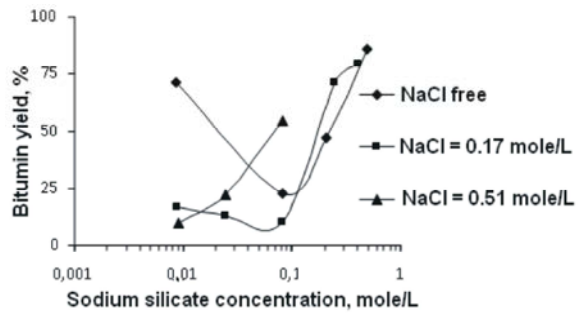

Fig. 6: Impact of sodium chloride additions into the process solution on the dependence of the bitumen yield on the concentration of alkaline agent - sodium silicate.

processes are enhanced. Eventually, the excess of sodium ions completely destabilize the emulsion.Since the increase of the concentration of sodium silicate in solution simultaneously with the growth of pH raises the amount of Na^+ ions and ionic strength, it was of interest to determine the influence of only one last factor on the separation efficiency.

For this purpose, the study of the kinetics of bitumen release from bituminous sands according to the method described above with the addition of NaCl into the process solution Na_2SiO_3 has been conducted. Results of experiments at concentrations of sodium chloride 0.17 and 0.51 M are shown in Figure 6 in comparison with the results of experiments without the addition of NaCl (conditions for this series of experiments differed somewhat from the experiments the results of which are shown in Figure 2).

It is clearly seen that increase of sodium ions content in the solution and correspondingly of ionic strength leads to a shift of the minimum on the dependence of the yield on the concentration of sodium silicate. It is strongly shifted towards lower values of concentration and the absolute values of the output at the point of minimum are reduced. A similar shift of the minimum when adding sodium chloride into the solution is noticed also on the dependencies of surface tension from the value of concentration. Moreover, for small values of concentration (to the left of minimum) the addition of sodium ions increases the surface tension and to the right it reduces. Thus, under conditions of pH ˜ const the ability of ionized carboxylic acid to reduce the surface tension is strongly dependent on the concentration of Na^+ ions.

The correlation between the output of petroleum products and the surface tension indicates the decisive role of phase boundary phenomena in the separation of oil-containing heterogeneous systems. By changing the

pH values of the process solution and ionic strength it is possible to affect the phase boundary properties and the kinetics of petroleum product output with the aim to achieve maximum separation efficiency.

CONCLUSIONS

The results of conducted measurements of facial and surface tension indirectly confirm the formation of new forms of natural surfactant in the process of combined chemical and ultrasonic treatment of oily heterogeneous mixtures and they are in keeping with experimental data on the kinetics of their separation. These data help to understand the mechanism of processes taking place in the sharable heterogeneous system and may be useful in developing recommendations on separation of specific oily mixtures.

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