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INFLUENCE OF EMULSION INNER PHASE CONCENTRATION ON PERMEABILITY OF DEPOSIT DURING FLOW THROUGH POROUS MEDIA

Abstract
The issue of emulsion flow through porous media plays an important role in the development of land purification methods from various oily substances, as well as during the oil extraction process. The concentration of the emulsion dispersed phase exerts a strong influence on the rheological properties. The oil in water emulsions (O/W), that have a concentration of less than 0.5 (or 50%), show Newtonian behavior, and those with higher concentrations non-Newtonian. The flow of such systems through the structure of the porous medium is, therefore, also dependent on the variable rheological properties of the liquid. When the emulsion flows through the porous medium, a reduction of the relative permeability occurs. Due to that the transport may be very effectively limited, as the pores of deposit are being blocked by oil droplets. The paper presents studies on emulsion flow, with various concentrations, through a granular bed. It allowed to track changes in the permeability of the deposit over time. The results of experimental studies of transport and elution of highly concentrated emulsions from granular structures are also presented. This enabled tracking of changes in flow resistance of the emulsion through the porous bed in time. Moreover, the development of the mathematical model, which allows us to define the relationship between the bed blockage degree and the concentration of the emulsion internal phase could be the result of the experimental works. The results of such studies are very widely used in practice, among other things, in the issues of migration of pollutants, such as petroleum substances, in the soil layers. The development of knowledge in this field may contribute to the optimization of existing oil recovery techniques and methods of remediation of soil from organic substances.

Key words
Emulsion, porous media, multiphase flow

Introduction

Industrial development led to increased consumption of oil products, used as a source of energy or materials for industry. These substances are highly toxic and mutagenic and pose a serious threat for ground and water environments. They can enter the soil and groundwater as a result of various leaks and disasters, and have the ability to penetrate all living organisms inhabiting the affected area, causing irreversible changes. Furthermore, the reduction of crop production can occur due to the presence of oil products in the structure of the soil. Therefore, knowledge about the flow of oil substances through porous media is of great importance, as it can be useful during estimation of the contamination scale and for operations of the removal of such contaminants from the soil. During the spillage of a petroleum substance, taking of appropriate decisions for dealing with the contamination is important. In such cases the most important thing is to properly estimate the risks caused by the spread of the pollution, both in the structure of the soil and in the groundwater. The contamination of these waters can have far-reaching consequences and lead to the poisoning of a much larger ecosystem. Therefore, the correct prediction of the movement speed of contaminants through granular layers and when and at what concentrations they will reach the groundwater is of great importance. Quickly taking the appropriate steps and selecting the best remediation methods will prevent the further spread of contaminations and will also significantly reduce any costs related to the removal of their effects.

When the multiphase fluid flows through the porous medium, the individual phases can mix together, which results in the formation of emulsion systems. Emulsion flow in porous media is different from the independent movement of the individual phases [1], and therefore must be considered separately. The mechanisms, that appear here, need to be taken into account to describe the complex nature of such flows. This can be helpful in understanding and predicting the way in which emulsion systems behave during movement through a porous medium. This knowledge can be useful in obtaining of a comprehensive picture of multiphase flow through porous media. Although, the issues of the flow of various fluids through porous media can be found in the literature [2, 3, 4], they do not refer to the flow of the emulsions. Knowledge on the emulsion flow through porous media can be used in many practical applications. Understanding the phenomena of the flow of the emulsion is immensely important in developing methods for remediation of soils from the organic liquids, which entered into them as a result of various leaks, failures and accidents [5, 6].

The flow of emulsion through the granular medium depends on the properties of medium and emulsion. Emulsions, as two-phase systems, behave differently than one-phase fluids. Parameters such as emulsion stability, concentration, droplet size and interfacial interactions are important. The concentration of the dispersed phase exerts a strong influence on the rheological properties. O/W emulsions with a concentration less than 50% exhibit Newtonian characteristics, and those with higher concentrations have non-Newtonian ones [1, 7]. When the concentration of emulsion is up to 50%, there is a linear dependence of the pressure drop from the flow rate, which means that Darcy's law can be used for the description of the flow. In the case of concentrations greater than 50% there is no linear relationship of the pressure drop and the flow rate, which suggests non-Newtonian behavior of emulsion. The phenomenon can be explained as the result of the forces of attraction and repulsion present between the droplets. For emulsions with low concentrations, repulsive forces acting between the droplets are sufficiently large compared to the attractive forces, which means that there is minimal aggregation. However, in the case of highly concentrated emulsions, distances between the drops are small and the repulsive forces are reduced, hence the attraction will lead to the formation of aggregates and the coalescence and flocculation will occur [8]. The aggregates rotate as single particles at low shear rates, which results in high fluid viscosity. When the shear increases (the higher flow velocity), the aggregates break up, causing a decrease in the viscosity of the system. This explains the observed non-Newtonian behavior of highly concentrated emulsions [9].

To describe the process of the flow of oil in water emulsions in the porous medium it is important to specify if they can be treated as homogeneous liquids. The assumption that the fluid is a continuous medium can be stated when the emulsion droplets are very small compared to the size of the flow channels. In such cases the influence of microscopic droplets of the emulsion on the flow can be totally ignored [10]. However, in most practical cases, the presence of droplets in the bed cannot be omitted, due to the fact that their sizes are not much smaller than the pore sizes, but even larger than the pores [7]. The reduction of the bed's relative permeability occurs when the O/W emulsion flows through the porous medium. This phenomenon is connected with the size of oil drops. When the droplets of the internal phase are larger than the pores, they can become an effective blocking agent. In actual cases, the oil droplets and pores have a wide range of sizes. Thus, a small amount of emulsified oil may block the flow very effectively [11]. Blocking of the flow channel by emulsion droplets is called the "straining" mechanism [1] and researchers [10, 11] have found that it is mostly caused by permeability reduction. They also observed that in the gaps or pockets the droplets with diameters smaller than the pore size are also captured [12, 13]. It was concluded that the reduction of permeability can also be caused by a different mechanism, called "interception" [1, 9]. The emulsion droplets can be trapped in a porous medium due to the attachment to the pore walls under the action of van der Waals forces and hydrodynamic forces. However, this mechanism has only a small impact on the overall reduction of permeability [14]. In conclusion, there are two capture mechanisms: straining and interception. Straining occurs when the emulsion droplet is trapped in a pore with a smaller size than the drop diameter. Interception is when droplets attach themselves onto the solid surface and pore walls. Capture of emulsion droplets effectively reduces permeability and diverts flow to large pores, through the reduction of pore diameter.

The issues of emulsion flow through porous media can be used to describe methods of remediation of soils contaminated with petroleum substances [15]. In such cases, the techniques used are based on gravitational or pressure elution processes. Gravitational elution often fails to give satisfactory results, so pressure elution is applied to enhance the process. It is based on injecting a lower viscosity fluid into a bed using a pump, which allows the fluid to flow through the bed and wash out the oily substances that residue upon deposit. For both in situ and ex situ cases, the eluting liquid is forced into the contaminated soil. Soil remediation methods based on liquid flow are relatively simple technologically and characterized by high values of coefficient of elution, and thus high efficiency. This is a widely used practice also in the oil extraction industry and it refers to the concept of EOR (Enhanced Oil Recovery). Secondary and tertiary extraction methods are based on the pumping of elution liquid through a bed, which is often a solution of water, salt and various surfactants. The flowing liquid can carry off a significant amount of oily substance trapped in the reservoir, whose production, with the use of other methods, causes many difficulties [16]. There are several scientific works concerning the important role of emulsions in improvement of microscopic displacement efficiency in chemical EOR methods. Investigations on this essential issue have been exactly and thoroughly described by the researchers [17, 18]. It can be found that the main mechanism of EOR efficiency improvement is the reduction of surface tension of the displacing fluid or reduction of interfacial tension between the displacing and displaced fluid.

Experimental studies on the emulsion flow through the porous bed, which can be found in literature, relate largely to a low concentration of emulsions (up to 20% of the internal phase). There is a lack of experimental data for emulsion systems with inner phase concentrations greater than 50%. The behavior of highly concentrated emulsions in the porous media is different from the transport of low concentrated systems, as they exhibit characteristics of shear thinning fluids. Changes of the flow rate through the bed will also cause a change in viscosity of the examined emulsions, which in turn will affect the flow resistance [19]. This paper presents studies on emulsion flow, with various concentrations, through a granular bed. It allowed us to track changes in the permeability of the deposit over time and to determine changes in the structure of the emulsion flowing out from the reservoir during the process. The results of the experimental studies of transport and elution of highly concentrated emulsions from granular structures are also presented. This enabled tracking of changes in flow resistance of the emulsion through the porous bed over time. Also there is a lack of universal mathematical models that account for the parameters of fluids and deposits, enabling a reliable way to predict the rate of change of the relative permeability and the concentration of the oily substance during flow through the porous medium. Therefore, the development of the mathematical model, which allows the definition of the relationship between the degree of bed blockage and the concentration of emulsion internal phase could be the result of the experimental works. In this paper, studies of the flow of emulsions through granular deposits, at different flow rates of liquids, are presented. The analysis covered emulsions, whose share of the internal phase exceeds 50% and, for comparison, less than 50%.

Experimental apparatus

To perform studies on the flow of emulsions through granular media, the experimental apparatus was designed, whose picture and scheme are presented in Fig. 1 and Fig. 2, respectively. It consisted of the following elements: high-speed stirrer with a stainless steel tank (1), dosing membrane pump (3) with a pulsation damper (4) and horizontal cylindrical measuring column (7) filled with granular material. The test stand has a measuring system included: two flowmeters (5), two temperature sensors (2) and a pressure transducer (6). The system was connected to a computer and with special software, which allowed the continuous monitoring and acquisition of parameters such as the pressure at the inlet to the bed, the temperature of examined fluid and the inflow and the outflow rate of liquid from the bed.

Fig. 1. Picture of research equipment

Source: Author's

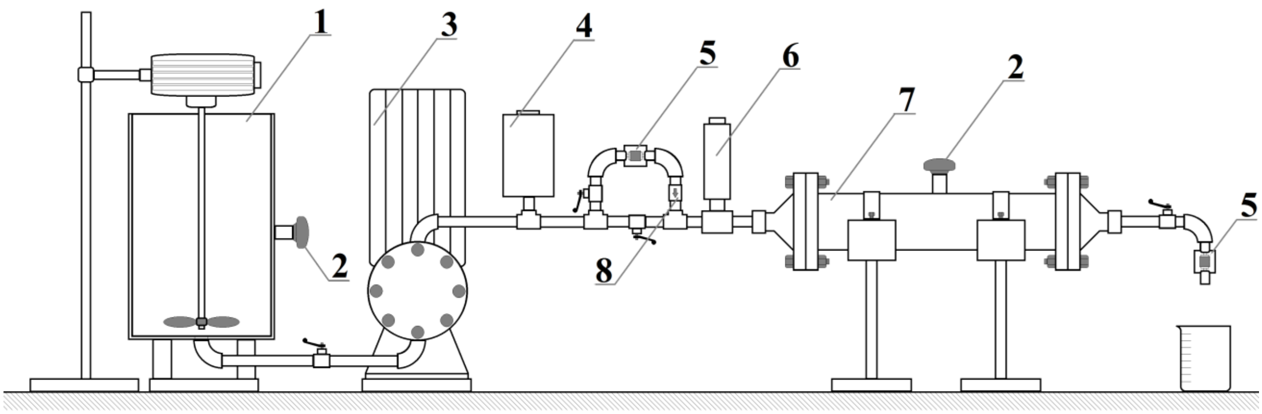

Fig. 2. Scheme of research equipment: 1- high-speed stirrer, 2 - temperature sensor, 3 - pump 4 - pulsation dampener, 5 - flowmeter, 6 - pressure sensor, 7 - column with the bed granular 8 – non-return valve

Source: Author's

Experimental media

During the studies, glass microspheres were used as model deposits, with particle size fractions in the range of 200 - 300 µm with a porosity of 0.34, in the range of 100 - 200 µm with a porosity of 0.34, and in the range of 90 - 150 µm with a porosity of 0.33. Alumetal - Technik in Lodz (Poland) was the manufacturer of used glass beads. To examine the flow and elution of emulsions from porous deposits oil-in-water emulsions were prepared as a model fluids, where the continuous phase was tap water (η = 0.001 Pa·s, ρ = 996 kg/m^3 at 22°C) while the inner phase was a vegetable oil (η = 0.06 Pa·s, ρ = 887 kg/m^3 at 22°C). The emulsions systems had different volume concentrations in the inner phase, which equaled 20, 40, 60 and 70% (see Tab. 1). An emulsifier Rokacet 07 (Exol PCC) of 2% volume was used. The precisely measured volumes of emulsion components (water, oil and surfactant) were thoroughly mixed. Emulsification was performed using a high-speed homogenizer (10000 rpm), and the mixing time was 500 s. For the purposes of a single measurement, 2.5 l of emulsion was prepared. To determine the rheological properties and the structure of formed emulsions, a rotational rheometer Rheotec RC20, Nikon microscope Alphaphot 2 YS2 and Turbiscan Lab Expert were used.

Table 1. Emulsion composition

Emulsion concentration [%]	Continuous phase amount [ml]	Inner phase amount [ml]	Emulsifier concentration [%]
20	2000	500	2
40	1500	1000	2
60	1000	1500	2
70	750	1750	2

Source: Author's

Rheological measurements

Based on rheological studies of the emulsions with different volume concentrations of the oil phase, it was possible to present flow curves in the form of a dependence of viscosity on shear rate in Fig.3. It can be seen that the emulsions with lower concentrations (50%) exhibit the properties of Newtonian liquids, and emulsions with greater participation of the internal phase display characteristics of shear thinning fluids.

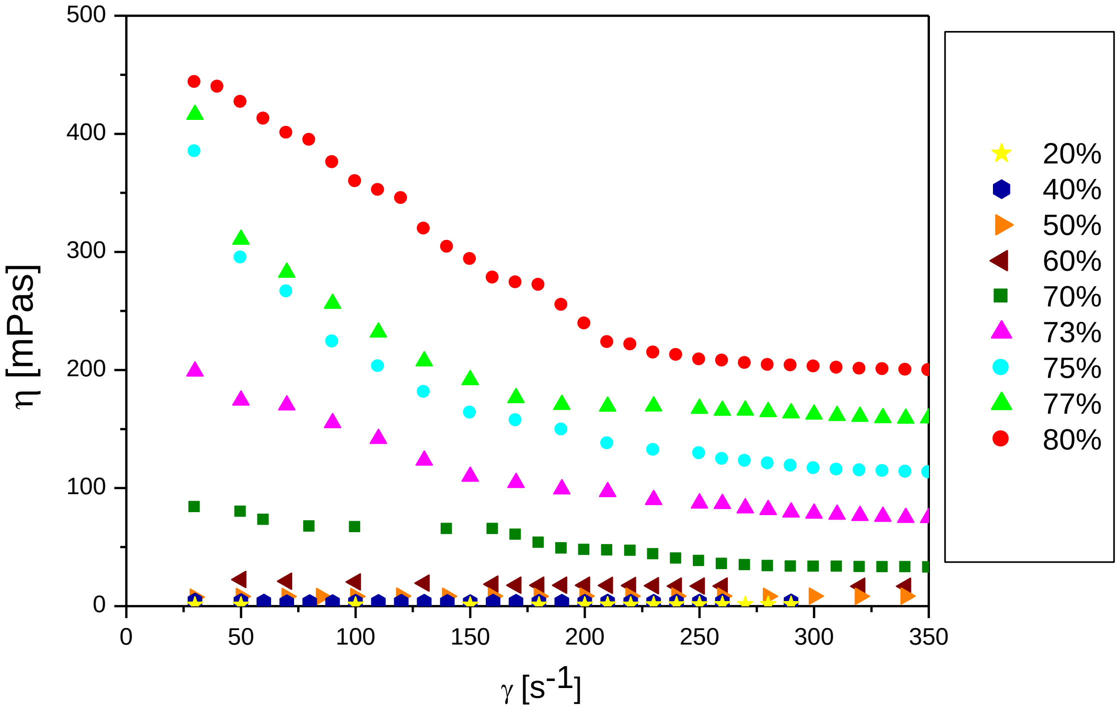

Fig.3. The dependence of viscosity on shear rate for various concentrations of the emulsion oil phase
Source: Author's

Experimental procedure

The research methodology was developed to ensure optimal conditions and the repeatability of tests. At the beginning, a strictly defined amount of glass microspheres was weighed and placed in a measurement column (7). During the tests, only water was pumped at first through the granular bed in the column, until the pressure at the inlet to the bed reached a constant value, i.e. when steady state was obtained. After that, emulsion was pumped through the bed until the steady state was obtained. Then, again the flow of pure water took place. With this methodology, the simultaneous examination of flow and elution processes and observation of the flow resistance changes was possible using a single measurement. By comparing permeability measured for water flow through the reservoir before and after the passing of emulsion through the deposit, it was possible to determine the degree of blockage.

Results and discussion

As a result of the experimental work, it was possible to track changes in flow resistance of the bed during the process. This made it possible to create a graph of the pressure drop dependence Δp at the inlet to the bed from time t. Fig. 4 presents exemplary test results for emulsions of different concentrations, flowing through the bed with a particle size in the range of 90-150 µm. According to the test procedure, clear water flowed first through the bed, followed by a flow of emulsion and water again. The moments, in which successive flows began, were marked with the vertical lines on chart.

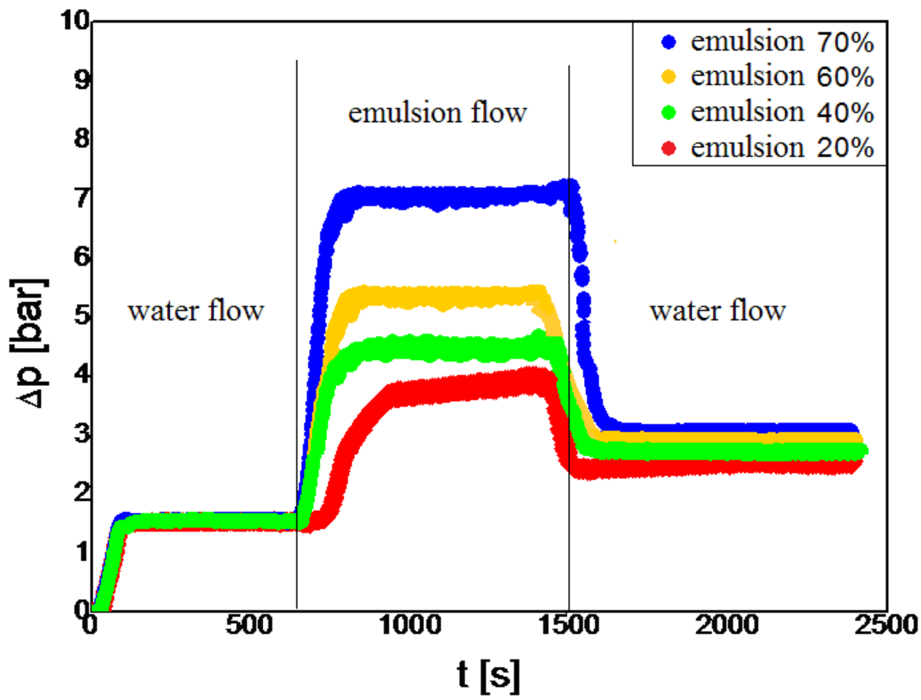

Fig. 4. Dependence of pressure at the inlet to the bed from the time for the emulsion with different internal phase fractions - bed 90 - 150 µm, length 50 cm
Source: Author's

In the first phase of the process, when the water was flowing through the bed, inlet pressure values were repetitive for each flow, which means that the same water permeability was obtained in each case. From the moment when the emulsion began to flow, the inlet pressure started to increase until the steady state was reached. The increase in pressure was due not only to the increase in the viscosity of the flowing liquid, but also to the fact that the oil droplets blocked the flow channels, as was explained in the literature [20]. The phenomenon of stopping of the emulsion inner phase droplets inside the bed structure and the consequent blocking of flow paths is called "straining" and was described in detail in work of Soo and Radke [12]. The increase in inlet pressure was, however, greater with higher concentrations of the emulsion. For a 20% emulsion, a gradual increase in Δp can be observed before the steady state is reached, while for an emulsion with an internal phase of 70% there was a rapid increase in pressure and steady state was achieved faster. This phenomenon can be explained by the fact that for emulsions with a low concentration, the amount of oil droplets is smaller and the time at which all the places in the bed (that can blocked) are filled is longer. In the case of emulsions with higher concentrations, the amount of oil droplets is large, so they quickly settle in the bed paths and block the flow causing the increase in pressure. The pressure value achieved in steady-state during the emulsion flow, at 20% concentration, was about 3.5 bar, while for the emulsion with 70% internal phase was more than 50% grater. This means that flow resistances are not directly proportional to the concentration of the flowing emulsion.

Once the steady state has been reached, the water was pumped again through the bed. There was a sudden drop in pressure and a rapid achievement of a new steady state. However, the new steady state was not reached at the level before the flow of emulsion, but the pressure drop values were higher. This means that a part of the oil phase was trapped in the bed and blocked the flow paths. The pressure drop values during the repeated water flow through the bed were dependent on the concentration of the emulsion, which previously passed through the bed. In the case of processes where an emulsion with a higher concentration was flowing through the bed, the pressure drop values during the washout were higher than those for the lower concentrated emulsions.

During flow and elution of the emulsion from the bed, the outflow rate of liquid from the bed was also measured in time. Exemplary results of these tests, corresponding to the cases discussed above, are shown in Fig. 5. There is a direct relationship between the pressure drop at the inlet and the outflow rate from the bed. This is due to the operation of the apparatus, i.e. the characteristics of the pump, where defined flow resistances cause specific efficiency.

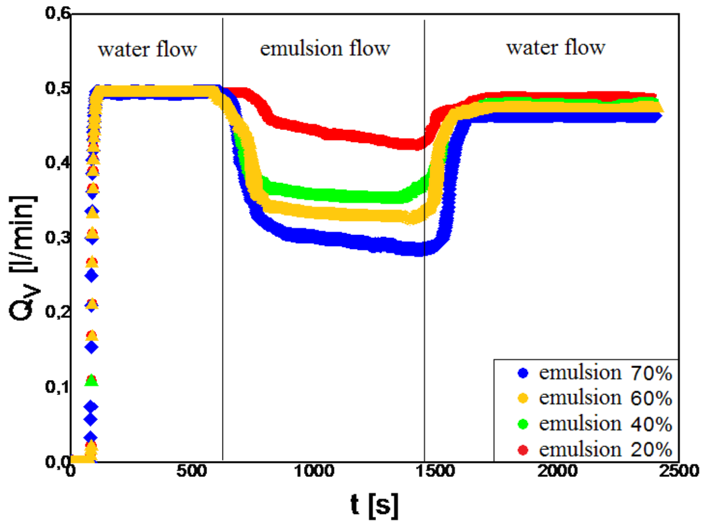

Fig. 5. Dependence of the outflow rate from time for the emulsions of various concentrations - bed 90-150 μm, length 50 cm

Source: Author's

The assessment of bed permeability reduction

This work was further focused on the issue of the pressure drop values at the flow of water through the clean bed are different from values obtained for the bed through which the previous emulsion flowed. Results for the steady states determined before and after the flow of the emulsion through the bed were analyzed. To compare these two states, the relative permeability of the bed and the degree of blockage of the bed were calculated. For this purpose, the classical theory of Darcy was used, whereby bed permeability k can be determined by the following relationship:

$$k = \frac{\eta Q_v L}{A \Delta p} \tag{1}$$

where: k – bed permeability, L – bed length, Δp – pressure drop at inlet to the bed, η – liquid viscosity, A – bed cross section, Q_v - flow rate

For comparative purposes, the concept of relative permeability was introduced. Relative permeability is expressed by the ratio of bed permeability k_p, determined for the flow of water through the clean deposit, permeability k_k, defined for the flow of water through the bed after the flow of the emulsion:

$$k_r = \frac{k_k}{k_p} \tag{2}$$

If the relative permeability determines what fraction of the bed pores is available for the flow (where the flow actually takes place), it can be stated that the bed blockage will determine the pore fraction that is not available for flow. Considering the above relationships, one can write that the degree of blockage of the deposit S_r can be determined according to the formula:

$$S_r = 1 - k_r \tag{3}$$

In Fig. 6 and Fig. 7 the relative permeability dependences from the degree of bed blockage and from the concentration of the emulsion flowing through the bed are shown respectively. The graphs present the results for deposits with grain fractions of 90-150, 100-200 and 200-300 μm. In the case of larger grains, it was possible to carry out experiments for higher concentration emulsions using the test apparatus, so the results also include emulsions with an internal phase content of up to 80%. Above this concentration the phase inversion occurs, so studies were limited to this value. At high concentrations in the range of 80% and greater (Fig. 3), slight changes in the emulsion inner phase content cause a significant increase in the viscosity of the fluids and thus an increase in flow resistance through the bed. This results in changes in the course of the trend lines describing variations in the permeability and in the bed blockage, as can be observed in Fig. 6 and Fig. 7, respectively.

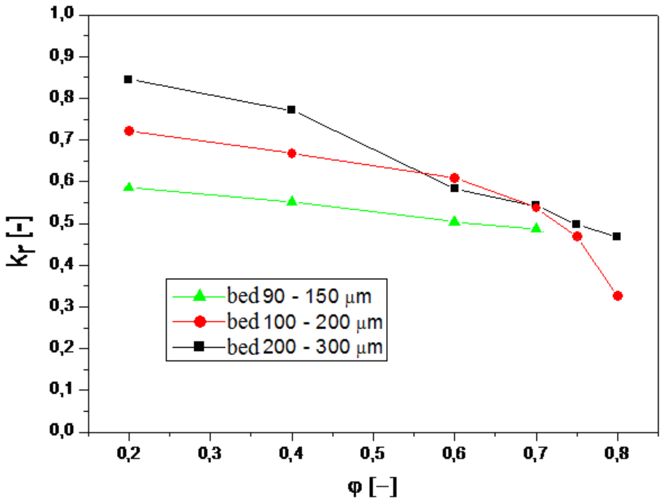

Fig. 6. Changes of relative permeability with emulsion concentration (L – 0.5m, vegetable oil)
Source: Author's

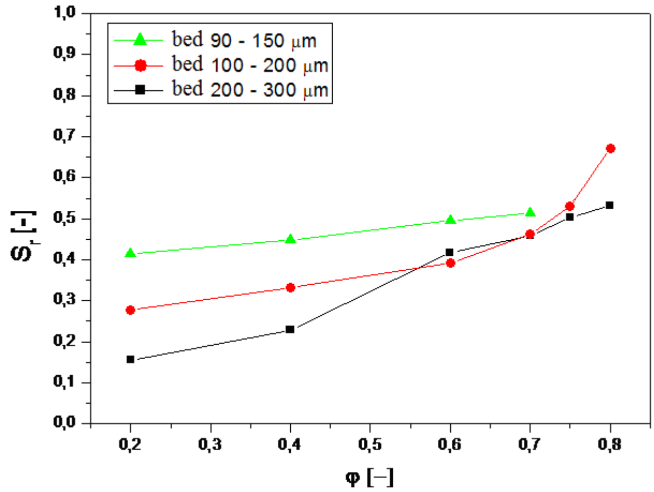

Fig. 7. Changes of the bed blockage with the concentration of the emulsion (L - 0.5m, vegetable oil)
Source: Author's

The flow behavior has been discussed through the analyzes of changes in the degree of blockage (see Fig. 7), with respect to the content of internal phase of the emulsion. It can be stated that S_r values increase as the concentration increases for each analyzed bed. For a bed with a particle size within 90-150 µm, it can be seen that for a 20% emulsion the degree of blocking was about 0.42, while for an emulsion with an internal phase of 70% it was up to about 50%, which means that half of the pores were blocked by the oil phase droplets. Considering a bed with larger grains, i.e. a 200-300 µm, for a 20% emulsion only 15% of the flow pathways were blocked, and for 70% emulsion this value reached about 40%. It is also noteworthy that differences in the degree of bed blockage for the analyzed fractions are decreasing as the concentration of the oil phase of the emulsion increases. In the case of highly concentrated emulsions, the difference between the degree of blockage is within a few percentage points, while for the emulsion with lower concentration it is up to 40%. This means that for the emulsions with a high content of internal phase, the size of the bed granules is not as significant for the degree of deposit blockage as for emulsions with a low concentration.

Conclusions

The paper presents the results of experiments relating to the flow and elution of emulsions with different concentrations of internal phase in a porous bed. During the transport of the emulsion, a gradual increase in flow resistance was observed, the intensity of which depended on the proportion of the inner phase of the emulsion. The steady state was achieved fastest for deposits with the highest grain fractions. The value of the pressure drop achieved in the steady state was also greatest for the highly concentrated emulsions, but it resulted not only from the same emulsion viscosity but also from the effect of blockage of the bed by oil drops.

Using a test procedure involving the pumping of water, emulsion and water again through the bed, it was possible to determine the degree of blockage of the bed by oil droplets. This was done by comparing the bed permeability at the flow of water through a clean bed with permeability at the flow of water through the bed, through which the emulsion previously flowed. Based on this work, it was found that the degree of bed blockage increases with increasing concentration and this dependence has been quantified. It has also been stated that the size of the bed grains has a greater effect on the degree of blockage in the case of low concentrated emulsions.

The results of the research and the presented analysis gives the opportunity to estimate the value of such an important factor as the degree of blockage of the deposit. This will make it possible to predict how the flow of a particular emulsion affects the bed through which it flows. These issues can be very useful in processes of soil cleaning from a variety of organic compounds and for various methods in the course of the recovery of crude oil, wherein the flow of emulsion through the bed is important.

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References
[1] F. A. L. Dullien, Porous Media Fluid Transport and Pore Structure, Acad. Press Inc, San Diego, California, 1992

[2] M. Ahmadlouydarab, Z. S. Liub, J. J. Fenga, Relative permeability for two-phase flow through corrugated tubes as model porous media, Int. J. Multi. Flow, 47, (2012), 85–93

[3] E. Idorenyin, E. Shirif, A new simulation model for two-phase flow in porous media, Braz. J. of Pet. and Gas, 6, 1, (2012), 001-018

[4] T.F. Tadros, Emulsion Formation, Stability, and Rheology, Wiley-VCH Verlag GmbH & Co. KGaA, 1–75, 2013

[5] J. Parker, U. Kim, P. Kitanidis, M. Cardiff, X. Liu, G. Beyke, Stochastic cost optimization of DNAPL remediation – Method description and sensitivity study, Environ. Model. Softw., 38, (2012), 74-88

[6] A.N. Piscopo, J.R. Kasprzyk, R.M. Neupauer, An iterative approach to multi-objective engineering design: Optimization of engineered injection and extraction for enhanced groundwater remediation, Environ. Model. Softw., 69, (2015), 253-261

[7] Z. E. Heinemann, Fluid flow in Porous media, Texbook Series, 1, Leoben, 2005

[8] T. F. Tadros, Rheology of Dispersions: Principles and Applications, ISBN-13: 978-3527320035, 2011

[9] J. Török, J. Tóth, G. Gesztesi, Polydispersed O/W emulsions in porous media: Segregation at low-tension conditions, J. Coll. Int. Sci., 295, (2006), 569–577

[10] W.K. Vidrine, C.S. Willson, K.T. Valsaraj, Emulsions in porous media I. Transport and stability of polyaphrons in sand packs, Coll. Surf. A, Physicochem. Eng. Asp., 175, (2000), 277–289

[11] A. Cortis, T. A. Ghezzehei, On the transport of emulsions in porous media, J. of Coll. and Int. Sci., 313, (2007), 1–4

[12] H. Soo, C.J. Radke, The flow mechanism of dilute, stable emulsions in porous media, Ind. Eng. Chem. Fund. 23, (1984), 342–347

[13] S. Cobos, M.S. Carvalho, V. Alvarado, Flow of oil–water emulsions through a constricted capillary, Int. J. Multi. Flow, 35, (2009), 507–515

[14] J. Li, Y. Gu, Coalescence of oil-in-water emulsions in fibrous and granular beds, Sep. Pur. Tech., 42, (2005), 1–13

[15] S. Crawford, J. Clifford, K. David, W. John,. Effects of emulsion viscosity during surfactant enhanced soil flushing in porous media. J. Soil Cont., 64 (1997), 355-370

[16] X. Fu, R. H. Lane, D. D. Mamora, Water-in-Oil emulsions: flow in porous media and EOR potential, SPE Canadian Unconventional Resources Conference, 2012

[17] A. Bera, A. Mandal, T. Kumar, Physicochemical Characterization of Anionic and Cationic Microemulsions: Water Solubilization, Particle Size Distribution, Surface Tension, and Structural Parameters, J. Chem. Eng. Data 59, 8 (2014), 2490-2498

[18] A. Mandal, A. Bera, Modeling of flow of oil-in-water emulsions through porous media, Pet. Sci. 12, 2 (2015), 273-281

[19] J. Cai, C. Li, X. Tang, F. Ayello, S. Richter, S. Nesic, Experimental study of water wetting in oil – water two phase flow—Horizontal flow of model oil, Chem. Eng. Sci., 73, (2012), 334–344

[20] V. A. Tabrizy, Relative Permeability Relationship with Environments of Deposition, Pet. Univ. Techn., Fac. Pet. Eng., Dep. of Pet. Eng., Iran, Ahwaz, 2006