

Usability of high porosity ceramics for the separation of oily impurities

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Organic impurities fallen to the ground water and to surface waters (rivers, lakes, seas and oceans) contribute to the degradation of the fauna and flora. Taking into account the public welfare, as the natural environment is, studies have been undertaken to develop a cheap and effective system for the purification of water from finely dispersed petroleum derivatives. The idea of the solution proposed consists in using a separator with high porosity ceramics of the pore size up to 100 μm , of high water permeability and ability to separate oily impurities of very tiny particle size. To improve the efficiency of the process the affinity of the filtering surface to organic particles was increased by the use of water-repellent media. The process of the separation of oily impurities was enhanced by means of ultrasounds of the 18 kHz frequency and various vibration energies.

Keywords: : porous ceramic materials, separation of oily impurities, silico-organic materials, ultrasounds.

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INTRODUCTION

The results of the investigations shown in this paper represent a small section of work carried out by our group and aiming at the determination of optimum filtration conditions and selection of filtration materials. For the determination it was necessary to characterize as many as possible partial processes occurring in the course of the separation of oily impurities from strongly dispersed water-organic systems. It was also important to have a reasonable interpretation of the phenomena observed, and of mutual correlations between the filtration surface of the discs and the organic particles, the effect of ultrasonic waves on the coagulation of oil particles inside the separator, as well as the effect of the internal structure of the filtering materials on the concentration of the oil phase and the possibility of the existence of a different mechanism of the action of vibrations inside the porous ceramic materials as compared with their effect on the separation in the bulk of the liquid. In the tests performed until now a number of filtration discs were prepared from quartz sand of particle size 63 – 1000 μm , alundum, silicon carbide, and iron oxide. Ceramic filtration materials were prepared with the use of expanding agents in order to increase the overall porosity of the filtration discs and to extend the path to be traveled by the water-organic emulsion from the lower surface of the filtration disc to the upper one in order to obtain the maximum concentration of the organic phase.

EXPERIMENTAL METHODS

Filtration discs were prepared from quartz sand fractions 0,4 – 0,8 mm and 0,8 – 1,0 mm and from aluminium oxide of mean particle size 0,5 μm .

Quartz sand discs were prepared in the following stages.

Preparation of a demi-sec mass from a necessary fraction of sand with 10% of ceramic binder including glass dust, cryolite, and boric acid. After careful mixing of the loose components a 7% by weight of technological binder was added in the form of a 40% aqueous solution of

dextrin. The discs were shaped in steel moulds by uniaxial, one side pressing at the 10 MPa pressure. At the following stage the plates were dried for 24 h at 60°C, then sintered at 900°C with the heating rate of 3°C/min, and were kept for 1 h at the final temperature.

The surface of the sintered plates was modified by the impregnation with silico-organic compounds in the form of 2,5%, 5% or 10% solution of methylsilicone resin in petroleum spirits and in similar concentration solutions of n-octyltriethoxysilane in the mixtures of alcohols. The wetting angle of the obtained plates was measured and the following parameters were determined: water absorption, open porosity, mean and maximum pore size, and compressive and tensile strengths.

Filtration discs from aluminium oxide were obtained by the *polymeric sponge method*, based on the use of polyurethane materials soaked in a casting slip. Ceramic slurry from Alcoa aluminium oxide of mean particle diameter 0,5 μm was prepared on the water basis with an addition of binders and liquefying agents. Two casting slips were prepared with different contents of aluminium oxide and different binders and liquefying agents. One of them consisted of Al₂O₃ 75% with an addition of citric acid (CA), diammonium hydrogen citrate (DAC), basic liquefying agents and a binder Rokryl 73B obtained from the Organic Works Rokita (Poland). The other casting slip contained 85% by weight of Al₂O₃, poly(vinyl alcohol) of degree of hydrolysis 88 – 89% and molecular mass 72 000 as a binder, and CA, DAC and Dispex A40 (ammonium acrylate of low polymerization degree). The viscosity of both casting slips was measured with the aid of the DV2 Brookfield viscometer.

The weighed amounts of the components were mixed together for 60 min in an excentric ball mill type PM 100, produced by Retsch, at a rate of 300 r.p.m. The plates cut from polyurethane foam of pore size 440 – 520 μm were soaked with the casting slip, and the excess of the slip was removed by compressing the plate down to 15% of its height. In the successive step the plates were dried at 25°C, then sintered at 1550°C using a heating rate of

1°C/min up to 800°C then 3°C/min at higher temperatures, and were kept for 1 h at the end temperature.

The sintered discs were subjected to measurement of open porosity, water absorption and compressive strength.

The discs prepared from quartz sand were impregnated with Konsil Z by immersing for 20 min in a solution of appropriate concentration, with subsequent drying on filter paper under a hood. The dried porous ceramic plates were kept for 24 h in a drier for the hardening of the methylsilicone resin and formation of a stable hydrophobic film on the surface of the plates.

Also the solutions of n-octyltriethoxysilane in a mixture of alcohols were used for the impregnation. The conditions of impregnation were different than those used with Konsil Z. The plates were kept for 1 h at 60°C in the impregnating solution, then the alcohols were distilled off and the temperature was raised to 120°C with a simultaneous reduction of pressure to 10 mbar. Such process parameters provided the possibility to obtain a good adhesion of organic particles to the surface of quartz sand plates.

Figure 2 shows the results of wetting angle measurements on the surface of ceramics prepared from quartz sand of particle size below 63 µm modified with Konsil Z and with n-octyltriethoxysilane.

The process of the separation of oily impurities was carried out in a setup consisting of a separator fitted with a number of inlet/outlet connector pipes, a differential manometer, an exchangeable ultrasound head, and the filtration modulus containing 7 filtration discs. The separator was supplied with a system for continuous reception of the oily phase with a container. Other fittings contained in the setup for the separation of oily impurities include: a container for water-oil emulsion of 100 l capacity with a condenser, circulating pump, manometer and a thermometer mounted on the connector pipe feeding the emulsion to the separator, and a thermostat.

The following parameters are being measured and recorded during the separation of oil particles on porous ceramic materials: emulsion temperature, pressure in the tube before the separator, and the differences of pressure between the upper and the lower surface of the filtration discs. The filtration process was carried out with the cruciform flow of media in the separator and two kinds of emulsion flow: straight-line and rotational motions. The difference between the emulsion flows through the sepa-

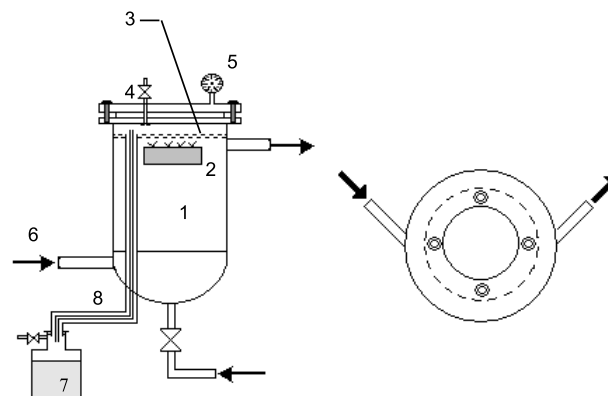


Figure 1. A diagram of the set-up for the separation of oily impurities from water-oil emulsions with a rotational flow of the emulsion: 1 – oil separator; 2 – ultrasound head; 3 – filtration module with CPM (porous ceramic materials) discs; 4 – deaeration valve; 5 – manometer; 6 – circulating stream of water-oil emulsion; 7 – container for oil phase separated; 8 – system for a continuous reception of the product

Table 1. The effect of the impregnating medium and its concentration on the properties of quartz sand plates

Plates of quartz sand 0,4-0,8 mm hydrophobized with n-octyltriethoxysilane)		
Silane wt %	Water absorption, %	Open porosity, %
0	16,0±0,5	29,5±0,7
2,5	15,5±0,6	28,4±0,8
5	14,5±0,5	27,2±0,7
10	15,5±0,3	28,4±0,4
Plates of quartz sand 0,4-0,8 mm hydrophobized with Konsil Z		
0	16,0±0,5	29,5±0,7
2,5	16,6±1,5	31,1±1,8
5	16,1±1,9	30,4±2,5
10	15,8±1,4	30,1±1,8
Plates of quartz sand 0,8-1,0 mm hydrophobized with n-octyltriethoxysilane		
Silane wt %	Water absorption, %	Open porosity, %
0	11,9±1,2	23,1±1,9
2,5	12,9±0,8	24,6±1,3
5	10,9±1,2	21,9±1,8
10	10,9±0,8	21,7±1,3
Plates of quartz sand 0,8-1,0- mm hydrophobized with Konsil Z		
	Water absorption, %	Open porosity, %
0	11,9±1,2	23,1±1,9
2,5	12,6±1,1	24,4±1,7
5	10,9±1,7	22,1±2,6
10	12,0±1,9	23,7±2,9

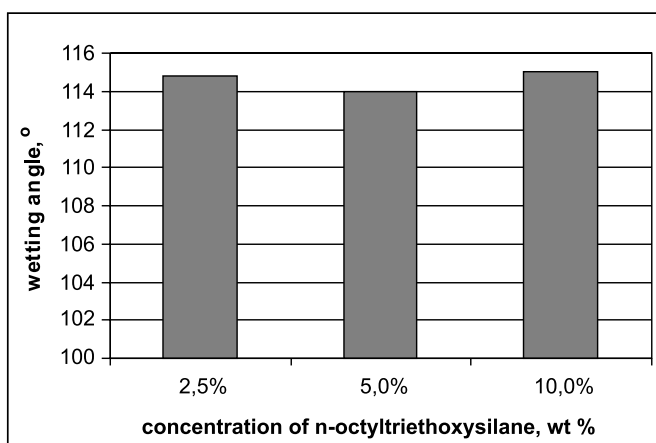
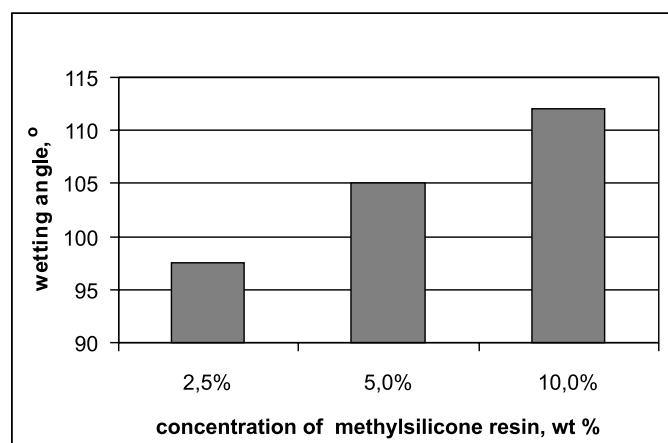


Figure 2. The influence of methylsilicone resin and n-octyltriethoxysilane on the wetting angle of the impregnated plates of quartz sand of particle size <63 µm

Table 2. The effect of methylsilicone resin and n-octyltriethoxysilane on the mechanic properties of the impregnated quartz sand plates

Concentration [wt %]	methylsilicone resin		n-octyltriethoxysilane	
	Quartz sand fraction 400-800 μm		Quartz sand fraction 400-800 μm	
	mean W_{ten} [MPa]	mean W_{com} [MPa]	mean W_{ten} [MPa]	mean W_{com} [MPa]
0	1,0 \pm 0,1	6,8 \pm 0,3	1,0 \pm 0,1	6,8 \pm 0,3
2,5	1,3 \pm 0,1	8,4 \pm 1,3	1,0 \pm 0,2	4,7 \pm 1,4
5	1,6 \pm 0,1	11,9 \pm 0,6	0,9 \pm 0,0	6,4 \pm 3,4
10	3,3 \pm 0,2	15,9 \pm 2,3	0,71 \pm 0,1	5,0 \pm 1,4

Table 3. The influence of the solid phase concentration in the cast slip on the properties of Al_2O_3 plates obtained by the polymeric sponge method

Plates from 420-540 μm Al_2O_3 obtained by polymeric sponge method			
Cast slip	Water adsorption %	Open porosity %	W_{com} [MPa]
75 wt % of Al_2O_3	173 \pm 11,2	87 \pm 0,8	0,9 \pm 0,4
85 wt % of Al_2O_3	150 \pm 8,9	85 \pm 0,7	1,2 \pm 0,3

rator was that the linear velocity in the former was smaller than that in the latter one. Higher emulsion flows with respect to the filtration discs cause the oil particles to be in turbulent motion which has a favorable effect of the coagulation process of organic particles. The results of the separation of organic impurities from water-oil emulsions presented in this paper were obtained for a rotational flow of the medium through the separator, Fig. 1.

RESULTS

Tables 1 – 3 and Figs. 2 – 5 show the results of the tests characterizing the properties of the obtained plates from porous ceramic materials and the effect of some process parameters on the degree of organic phase concentration in the permeate.

DISCUSSION OF RESULTS

The surface modification of porous ceramic materials by means of two silico-organic compounds of different molecular structure was a result of a different effect of these substances on the wetting angle of the filtering surface. The difference in the wetting angle should also influence the affinity of the organic particles to the surface of the filtering material. The hydrophobic properties of a silico-organic compound depend mostly on the length of the carbon chain, which is decisive for the surface energy of the film formed on the filter surface. Silico-organic compounds have the ability to bind with the impregnated surface by means of hydrophilic groups present in the molecule, with a simultaneous turning outside the hydrophobic part of the molecule, thus creating the so-called hydrophobic comb¹. The greater differences in the surface energy of silico-organic films with respect to water affect the value of the wetting angle measured. They are the higher, the greater are the differences in surface energy. The use of methylsilicone resin and n-octyltriethoxysilane for the hydrophobization of ceramic filter surface con-

firmed the former assumptions. The wetting angle of the porous ceramics modified with n-octyltriethoxysilane with a longer carbon chain increased with respect to that of the plates modified with the methylsilicone resin, see Fig. 2.

The wetting angle values measured for the plates modified with n-octyltriethoxysilane were, within the range under consideration, independent of the concentration of the silico-organic compound in the impregnating solution and they amounted roughly to 115°. In the case of the surface of porous ceramic materials modified with the methylsilicone resin, the wetting angle increased with increasing the concentration of the resin in the hydrophobizing solution, see Fig. 2. The different behaviour of silico-organic surfaces arises probably from a different structure of the films formed on the surface of quartz sand plates. The short-chain (one methyl group) silicone resin undergoes cross-linking during the impregnation and it gives continuous areas of film on porous ceramic materials, the wider the higher is the concentration of the hydrophobizing medium. In the case of the modification with n-octyltriethoxysilane, the silico-organic film formed is not continuous as the n-octyltriethoxysilane molecules are linked separately with the plate surface with no mutual bonds formed in the case of methylsilicone resin.

The effect of the hydrophobizing medium on the water absorption and open porosity is different than that on the wetting angle, since no changes in the properties of the modified quartz sand plates, relating to reduced water absorption or open porosity, are observed irrespective of the concentration or the kind of the silico-organic compound used. The changes are small enough to remain within the limits of an experimental error. It is probably a result of the enormous difference of dimensions between the thickness of the organic phase and the particle size. The only change observed in hydrophobization of CPM is the increase of mechanical strength of the plates observed on increasing the concentration of methylsilicone resin in the impregnating solution (see Table 2). This tendency seems to be evident as resulting from the increase of the amount of a cross-linking agent used for the initiation of the cross-linking process. As a result, a more stable, continuous silico-organic film is formed on the surface of quartz sand grains.

The Al_2O_3 discs obtained by the polymeric sponge method from the polyurethane foam of pore size 420 – 540 μm with the use of two different casting slips differ in their properties (see Table 3). The discs obtained from a casting slip with a smaller content of aluminium oxide have a higher water absorption and open porosity, but a smaller compressive strength as compared with the discs obtained from the casting slip containing 85% by weight of Al_2O_3 . The differences may be explained by means of viscosity diagrams of the two slips, see Fig. 4. The casting slip containing 75% by weight of aluminium oxide has the rheological parameters similar to those of the slip containing 85% by weight of alumina, but the increased content of the solid phase causes that the aluminium oxide layer deposited on the polyurethane material is thicker and more compact. The packing of aluminium oxide grains is more dense and this corresponds to a greater number of intergranular contacts. As a result, the sinter

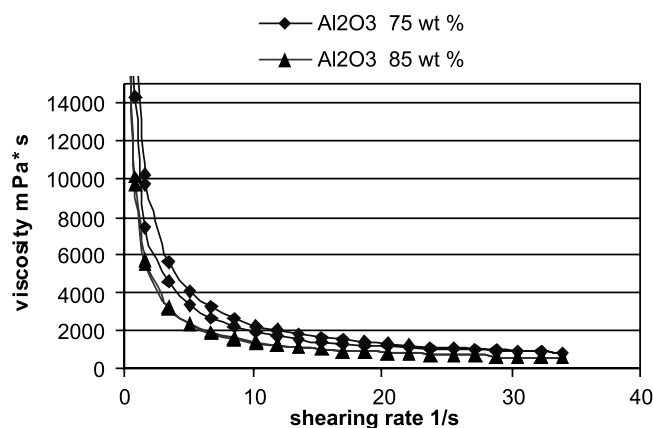


Figure 3. The rheological properties of Al_2O_3 casting slips used for the manufacture of filtration discs by the polymeric sponge method

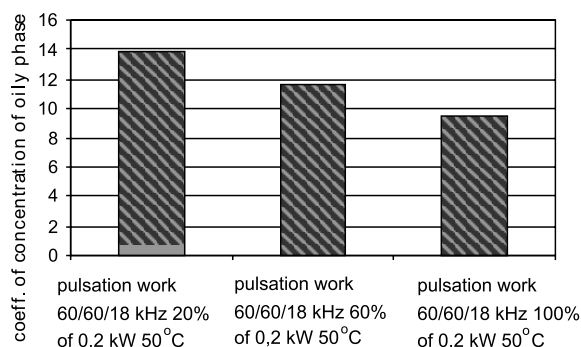


Figure 4. The influence of the power of ultrasounds of the 18 kHz frequency on the coefficient of the oily phase concentration for the plates of quartz sand fraction 0,4 – 0,8 mm

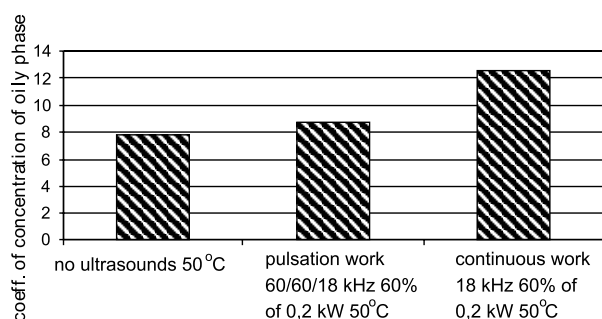


Figure 5. The coefficient of the oily phase concentration obtained for the plates of quartz sand fraction 0,8 – 1,0 mm without and with the ultrasound support

obtained in roasting has a higher density, hence a greater mechanical strength and lower water absorption.

The above-shown results of the separation of oily impurities obtained with the discs of quartz sand fractions 0,4 – 0,8 and 0,8 – 1,0 mm were obtained in the flow under the pressure of 0,17 MPa with the use of the ultrasounds of the 18 kHz frequency of different vibration energy. Two regimes of the ultrasound action were applied: the continuous and the pulsation work (60/60). In the latter case every 60 s period of work in the given medium was followed by a 60 s pause.

The concentration coefficients of the oily phase obtained by the separation of the oily phase from finely dispersed water-oil emulsions on quartz sand discs of mean pore size $72 \mu\text{m}$ for the fraction of 0,4 – 0,8 mm and

$99 \mu\text{m}$ for the fraction of 0,8 – 1,0 mm, shown in Figs. 4 and 5, allow for a positive evaluation of the work of filtration discs modified with Konsil Z (10% solution of methylsilicone resin in petroleum spirits). For the CPM of the fraction of 0,4 – 0,8 mm the organic phase concentration coefficient in the permeate obtained is observed to decrease with increasing the power of ultrasound waves, the other process parameter being constant (see Fig. 4). Such a situation may be due to an effect of the superposition of two phenomena of similar action: intense stirring caused by the rotational motion and medium discontinuity due to cavitation evoked by excessive energy of the ultrasonic waves. Such a superposed action may result in undesirable dispersion of oil particles instead of the expected coagulation².

For quartz sand plates of mean pore diameter $99 \mu\text{m}$ the obtained coefficients of the oily phase separation at 50°C under the conditions of pulsation work are only slightly smaller than those obtained for the filtration discs with smaller pore dimensions of $72 \mu\text{m}$ at the identical working regime. The use of ultrasounds improves the separation of oily impurities from water-oil emulsions³, as proved by the higher concentration coefficients, see Fig. 5

CONCLUSIONS

1. A favourable effect of the use of ultrasounds has been observed in the separation of oily impurities with the aid of filtration discs from quartz sand fraction 0,8-1,0 mm impregnated with methylsilicone resin.
2. The increase of the wave energy of ultrasounds in the filtration process decreases the concentration coefficient of the organic phase obtained, probably due to breaking of oil particles by stronger vibrations.
3. Further improvement of the technology of *polymeric sponge method* for manufacture of stronger filtration discs from aluminium oxide will give a possibility of using filters with increased contact surface and interaction with water-oil emulsion and, in consequence, a higher separation efficiency.

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LITERATURE CITED

- (1) Rościszewski P., Zielecka M.: „Silikony właściwości i zastosowanie” (Silicones, their properties and applications) WNT, Warszawa 2002.
- (2) Śliwiński A.: „Ultradźwięki i ich zastosowania” (Ultrasounds and their applications) WNT, Warszawa 2002.
- (3) Stack L. J., Carney P. A., Malone H. B., Wessels T. K. „Factors influencing the ultrasonic separation of oil in water emulsions” *Ultrasonics Sonochemistry* 12 (2005) 153 – 160.