

## **THE STUDY OF RESIDUAL WATER SATURATION FORMATION IN HYDROPHILIC AND HYDROPHOBIC RESERVOIRS BY NMR METHOD**

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### **ABSTRACT**

The issue of reliability of residual water saturation estimation by logging methods in hydrophobic reservoirs is often an intricate one due to high values of producing formation resistivity. The authors carried out an experimental study of residual water saturation formation in such reservoirs by NMR method.

Samples of reservoir rocks with different wettability were selected. The authors varied water content in rock by capillary displacement via a semipermeable membrane, changing displacement pressure. NMR spectra of transverse relaxation time  $T_2$  were obtained at every displacement stage.

Analysis of the obtained results reveals significant differences of drainage process in hydrophilic and hydrophobic rocks. Disappearance of the longest components of relaxation time as the water content decreases is typical of hydrophilic rocks. The above suggests that water is always displaced out of the largest pores. In contrary in hydrophobic rocks water displacement out of large pores is accompanied by its transfer from the smallest pores to relatively bigger ones. It is demonstrated by the fact that with the decrease of water content in rock in the spectrum of relaxation time there is observed simultaneous gradual disappearance of the longest components as well as the shortest ones. In the result with residual water saturation the character of water distribution in the pore space differs considerably in hydrophilic and hydrophobic rocks.

The conclusion is: an ordinary method of cutoff in the spectrum of relaxation time cannot be used for determination of residual water saturation in hydrophobic reservoirs in contrast to hydrophilic ones.

Additionally, electric measurements showed that these effects can lead to the understatement of Archie's parameter  $n$  value in resistivity index versus water saturation relation. In laboratory conditions true resistivity values of actual deposits might not be obtained due to inadequacy of processes of residual water saturation formation.

## INTRODUCTION

Wettability of rock grains surface greatly affects the value and distribution of capillary pressure in producing formations, permeability for water and oil, residual oil saturation. It causes the necessity to study the character of water and hydrocarbons distribution in pores of rocks with different wettability. In this respect NMR is the most effective method [1-4].

On the other hand, while defining the character of fluid distribution in producing deposits, wettability greatly affects well logging results and electric measurements in particular. It means that correct interpretation of logging data is impossible without regard for rock wettability.

Laboratory core examination often yields erroneous results due to incorrect selection of a procedure of hydrophobic samples preparation for measurements that can result in disagreement between the character of fluid saturation and actual formation conditions.

To find out the factors causing the above effects the authors have performed experimental NMR studies of the process of residual water saturation formation in rocks with different wettability. Wettability index ( $WI$ ) of samples under study was determined by Amott method.

For that, the following classification was used:

- hydrophobic rocks -  $WI = 0.0 - 0.4$ ;
- rocks with intermediate wettability -  $WI = 0.4 - 0.6$ ;
- hydrophilic rocks -  $WI = 0.6 - 1.0$ .

## RESULTS AND DISCUSSION

### Electric Measurements

When validating the calculated parameters of the oil pool in the carbonate part of the section represented by hydrophobic reservoirs of Verkhnevozeisky field the authors obtained resistivity index ( $I$ ) versus saturation ( $S_w$ ) petrophysical relations that did not agree with electric logging data. In the terrigenous part of the section, represented by totally hydrophilic Middle Devonian quartz sandstone, classical  $I=1/(S_w)^{1.7}$  relations were obtained.

The carbonate part of the section is timed to Lower Silurian and is represented by pure non-argillaceous secondary dolomites with up to 22 % porosity and permeability up to hundreds mDarcy. Resistivity in the producing part of the section is within the range from 100 to 2000 Ohm\*m.

Capillary pressure  $P_c$  versus saturation  $S_w$  relations were obtained with the use of a semipermeable membrane. Resistivity was measured at every stage of displacement.

For a hydrophilic reservoir, the core samples were cleaned with an alcoholic-benzol mixture. For a hydrophobic reservoir, experiments were performed with cleaned core (after extraction) as well as with preserved core that retained its initial wettability. The samples were extracted with alcoholic-benzol mixture (25 % alcohol – 75 % benzol) in a Soxhlet apparatus until residual oil was completely removed. Cleaning process termination was defined by the color of the solvent-oil mixture. When the mixture became fully transparent, the cleaning process was considered to be finished. Oil in preserved samples from S-D<sub>2</sub> deposits, occurring in the interval of 3-4.1 km, is characterized by relatively high density (0.85-0.89 g/cm<sup>3</sup>), average viscosity, low gasoline content (18-26 %), and low initial boiling point of gasoline (43-63 °C).

Figures 1a-c show resistivity index  $I$  versus water saturation  $S_w$  results for 6 rock samples of different wettability. For the terrigenous quartz reservoir (Fig. 1a),  $I=f(S_w)$  relation is of a typical classical character  $I=1/(S_w)^{-1.7}$  with Archie's parameter  $n = 1.7$ . The same relation for the cleaned hydrophobic reservoir (Fig. 1b) is of non-linear character and with  $S_w = S_{wir}$  has very low resistivity values that contradict electric logging data. For the relation obtained at the core with natural wettability (Fig. 1c) parameter  $n=2$ , that fairly well agrees with electric logging data.

Fig. 2 shows the  $S_{wir}$  - porosity  $\phi$  relation, that was obtained for this section at the core with water displacement via a semipermeable membrane and the same relation calculated from logging data with the use of  $I=f(S_w)$  petrophysical relation for rocks with natural wettability (Fig. 1c). The presented data reveals that the results obtained with the core fit the results calculated from logging data. It suggests the agreement of  $I=f(S_w)$  relation for rocks with natural wettability to reservoir conditions in contrast to clean (extracted) hydrophobic rocks.

Thus the given results of electric measurements suggest a major dependence of undersaturated rock resistivity on their wettability.

### **NMR Measurements**

To understand the reasons for the observed resistivity dependence on wettability, NMR studies were performed at residual water saturation conditions. Results of NMR that are given below were obtained with the same six core samples that correspond to electric measurements in Fig. 1a-c.

The studies were performed with a CoreSpec-1000 magnetic resonance core analyzer. Water content in rocks was varied by capillary displacement via a semipermeable

membrane by changing the displacement pressure  $P_c$ . NMR spectra of transverse relaxation time  $T_2$  were obtained at every stage of displacement.

### Hydrophilic Rocks

Disappearance of the longest components of relaxation time as the water content decreases is general for hydrophilic rocks, showing that water is always displaced out of largest pores (Fig.3). In this case, the signal in the spectrum of short relaxation time can increase. It is caused by the fact that, at 100 % saturation, part of small pores are in contact with large pores (Fig.4a). In the result the corresponding short relaxation times are not clearly seen. In particular it can be the case with rough surface of rock grains. However after displacement of water out of large pores small pores that contact large pores are separated (Fig.4b) and the signal from them starts to manifest itself in the spectrum of short relaxation times in accord with their small sizes. Besides this effect can be additionally enhanced by the signal from the water films that remain on the surface of hydrophilic grains after displacement of water out of pore volume. Thus NMR data support the well-known fact that water saturation decrease in hydrophilic rocks is due to the gradual displacement of water out of the largest pores.

### Hydrophobic Rocks

With hydrophobic reservoirs the process of residual water saturation forming greatly depends on the uniformity of wettability of pore surface. With this two most important cases can be emphasized.

1. In the first case hydrophobic core samples were **extracted** prior to measurements, in the result residual oil was removed and pore surface became more or less uniform in its wetting properties.

According to the obtained data water starts to be displaced out of the largest pores. It is shown by the fact that the longest components were the first to disappear in the spectrum of relaxation times. Still with saturation decrease water displacement out of large pores started to be accompanied by its transfer from small pores to fairly larger ones. It is demonstrated by the fact that with the decrease of water content in the spectrum of relaxation times a simultaneous gradual disappearance of the longest as well as the shortest components is observed. In the result the spectra become narrower (Fig.5). Correspondingly the range of pore sizes filled with water becomes narrower. Here, according to data in Fig.1b we observe the lowest resistivity values at  $S_w = S_{wir}$  exactly for these samples. It can be considered as a proof that there's no water discontinuity with water redistribution in pores i.e. all pores filled with water are interconnected. So under such conditions both electric current and filtration are possible.

We are to note that in hydrophobic rocks besides narrowing of relaxation time spectrum an increase of the portion of components with medium relaxation times can be observed.

It can be explained if we assume that not all water is displaced out of some large pores – as it is shown in Fig.4c. In the result the signal from the water left in such a pore is shifted to the region of shorter times  $T_2$ , thus increasing the portion of components with medium times of relaxation.

The obtained results yielded an important conclusion: an ordinary method of cutoff in the spectrum of relaxation times has no application with determination of residual water saturation in this type of hydrophobic reservoirs in contrast to hydrophilic reservoirs. It relates to the fact that the cutoff method is based upon the assumption that with residual water saturation the smallest pores only are filled with water and the water can't move to larger pores.

2. In the second case hydrophobic samples with residual oil were saturated with aqueous solution **without preliminary oil extraction**. Taking into consideration the fact that residual oil is localized mainly in large pores we can assume that surfaces of small and large pores differ in their wettability. By data given in Fig.6 the character of drainage process in this case changed considerably if compared with pure hydrophobic samples. By their character the changes in  $T_2$  distribution with saturation decrease were similar to the changes that were observed with hydrophilic samples (Fig.3). In the spectrum there was observed a gradual disappearance of the components that corresponded to the largest pores. In this case it was apparently related to the fact that the surface of large pores with residual oil was more hydrophobic than the surface of small pores without oil. In the result the process of drainage was similar to that in hydrophilic rocks.

Nevertheless despite the similarity of changes in  $T_2$  spectra the character of solution distribution in pores for hydrophilic and non-extracted hydrophobic rocks can differ considerably. It relates to the fact that non-uniformity of the pore surface wetting properties can result in fractures in the system of pores filled with solution. In the result individual pores or pore groups can be isolated from the main system of pores that specify rock conductivity. It will cause resistivity increase. This mechanism of residual water saturation formation can be corroborated by the fact that non-extracted core samples (according to Fig.1c) have higher resistivity if compared with hydrophilic (Fig.1a) and extracted hydrophobic samples (Fig.1b).

The study of thin sections revealed that in most cases the presence of small as well as large pores (caves) was typical for the carbonate rocks studied. With saturated non-extracted samples relaxation times in large pores could be as high as several seconds (Fig.6). Still after extraction of residual oil from the samples the long relaxation times started to get shorter – down to 1 second and less and the second (“long”) mode started to better manifest itself. In the result the spectra became bimodal similar to the spectra shown in Fig.5.

## SIMULATION

To explain the observed peculiarities of rock resistivity depending on the character of residual water distribution in pores a lattice model of porous medium suggested by one of the authors [5] was used. This model is based on the assumption that porous medium consists of a great number of cubic cells of the same size and with the same structure of porous medium (Fig.7 and Fig.8). The cells differ from each other by the size of pores  $\delta$  only. Random distribution of pore sizes by cells is described by a  $f(\delta)$  function. In ref. [5] there were obtained formulae to calculate the main petrophysical characteristics of the model. For porosity factor

$$\phi = \frac{1}{a^3} \cdot \int_0^a \delta^2 (3a - 2\delta) f(\delta) d\delta \quad (1)$$

For formation resistivity factor

$$F = \frac{a^2}{2} \cdot \left( \int_0^a d\delta_2 \int_0^a \frac{(\delta_1 \delta_2)^2}{\delta_1^2 + \delta_2^2} f(\delta_1) f(\delta_2) d\delta_1 \right)^{-1} \quad (2)$$

Here  $a$  is the size of cubic cells,  $f(\delta)$  function specifies the distribution of probability density that the size of pores of an arbitrarily chosen cell keeps within the range from  $\delta$  to  $\delta+d\delta$ .

The objective of the simulation was to prove that the porous medium resistivity in the case when residual saturation is formed by the simultaneous displacement of solution out of large and small pores can be less than that in the case when the saturation is formed by the displacement of solution out of the largest pores only. The first case corresponds to extracted hydrophobic rocks (Fig.5), the second one – to hydrophilic and non-extracted hydrophobic rocks ( Fig.3 and Fig.6).

The calculation procedure consisted in the following. Gamma-distribution was taken as  $f(\delta)$  function

$$f(\delta) = \frac{p^p}{G(p)} \cdot \frac{\delta^{p-1}}{\delta_0^p} \cdot e^{-p \frac{\delta}{\delta_0}} \quad (3)$$

Here  $G(p)$  is a gamma-function;  $\delta_0$  is a mean size of pores, and  $p$  parameter specifies dispersion, i.e. spread of pores in sizes with respect to  $\delta_0$  mean value. The higher  $p$ , the narrower  $f(\delta)$  distribution is. Three simulative distribution of saturation by pore sizes were used for calculations (Fig.9). Distribution # 1 was taken as initial distribution that corresponded to 100%-saturation of hydrophilic as well as hydrophobic rocks. Distributions ## 2 and 3 simulate distribution of the same residual saturation ( $S_{wir}=28\%$ ), in cases of hydrophilic and pure hydrophobic rocks respectively.

Parameters of corresponding lattice models used in calculations of each of the above distributions are given in Table 1. According to the obtained data the value of the resistivity index  $I$  for distribution 2, when solution was being displaced mainly out of large pores, really exceeds the corresponding  $I$  value, when solution was being simultaneously displaced out of large and small pores. Their ratio shows that rock resistivity in the second case is smaller by a factor of nearly 1.5 than in the first case.

Thus according to the model calculations water transfer from the smallest pores to medium-size pores (Fig.9, distribution 3) results in resistivity decrease. On the other hand the same redistribution of residual water is observed in extracted hydrophobic samples (Fig. 5). This simulation result can explain the fact that it is for these rock samples that we observe the lowest resistivity values in residual water saturation formation.

## CONCLUSIONS

- Analysis of NMR results reveals substantial differences in drainage processes and formation of residual water saturation in hydrophilic and hydrophobic rocks.
- Data of electric measurements together with NMR data show that the very wettability of pore surface as well as its surface non-uniformity affect the character of residual saturation distribution in rock pores that is displayed by the resistivity value.
- In pure hydrophobic reservoirs similar effects can cause the decrease of Archie's parameters  $n$  value in resistivity index vs water saturation relation. In laboratory conditions true resistivity values of actual deposits could not be obtained due to inadequacy of the processes of residual water saturation formation.
- Rock wettability is to be considered when choosing cutoffs in  $T_2$  distribution for residual saturation determination from NMR data.

## NOMENCLATURE

- $WI$  wettability index  
 $T_2$  transverse relaxation time  
 $I$  resistivity index

$F$	formation resistivity factor
$S_w$	water saturation
$S_{wir}$	irreducible water saturation
$n$	Archie's parameter
$P_c$	capillary pressure
$\delta$	pore size
$\delta_0$	mean size of pores
$a$	size of cubic cells
$p$	dispersion parameter

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Table 1. Parameters of the model.

	$\phi$ , %	$F$	$S_w$ , %	$I$	$\delta_0$ , $\mu\text{m}$	$p$	$a$ , $\mu\text{m}$
Distribution 1	18	25.5	100	-	15	1.1	60.4
Distribution.2	-	-	28	5.22	7.44	1	72.5
Distribution.3	-	-	28	3.63	15.6	2.3	134



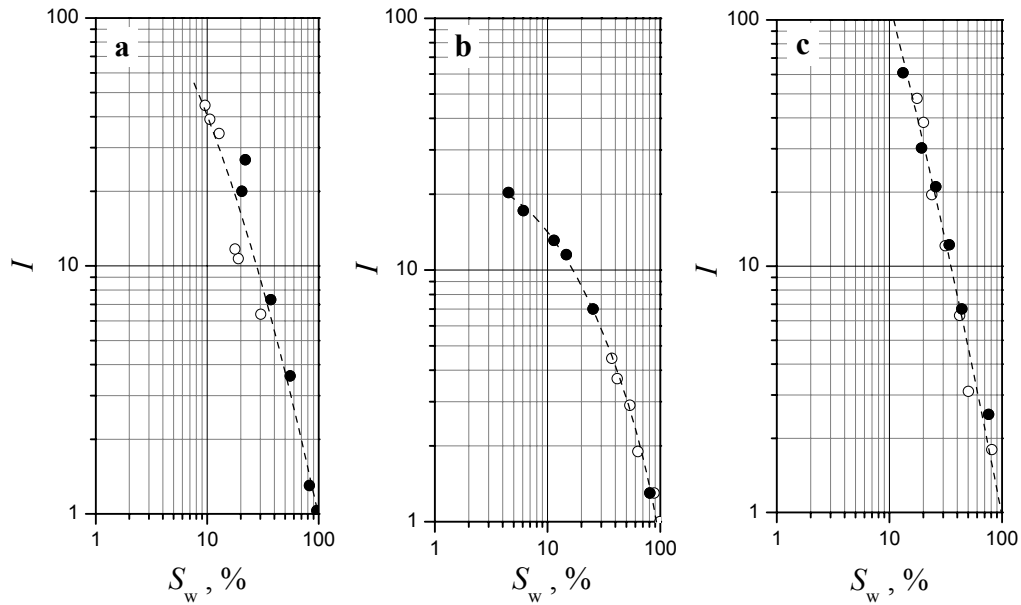


Fig.1. The resistivity index  $I$  - water saturation  $S_w$  relation for core samples with different wettability:  
 (a) 2 samples of hydrophilic rocks;  $WI = 1$ .  
 (b) 2 samples of hydrophobic rocks after cleaning with a solvent;  $WI = 0.38$  and  $WI = 0.11$ .  
 (c) 2 samples of hydrophobic rocks with natural wettability and residual oil saturation;  $WI = 0.08$  and  $WI = 0.3$ .

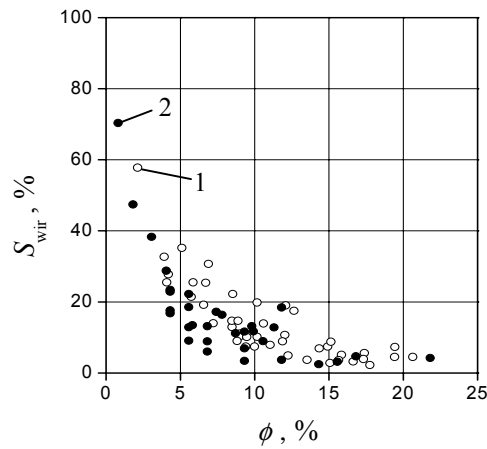


Fig. 2. Residual water saturation  $S_{wir}$  versus porosity  $\phi$  relation by the results of core measurements (1) and logging data (2).

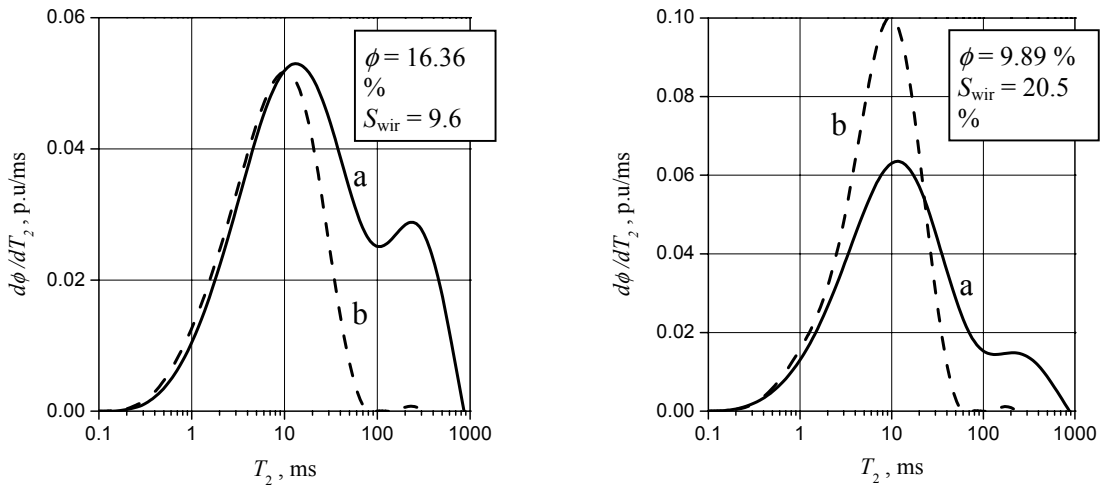


Fig. 3.  $T_2$  distributions for 2 samples of hydrophilic rocks.  
 (a)  $S_w = 100\%$  ; (b)  $S_w = S_{wir}$  (with  $P_c = 0.4$  MPa)

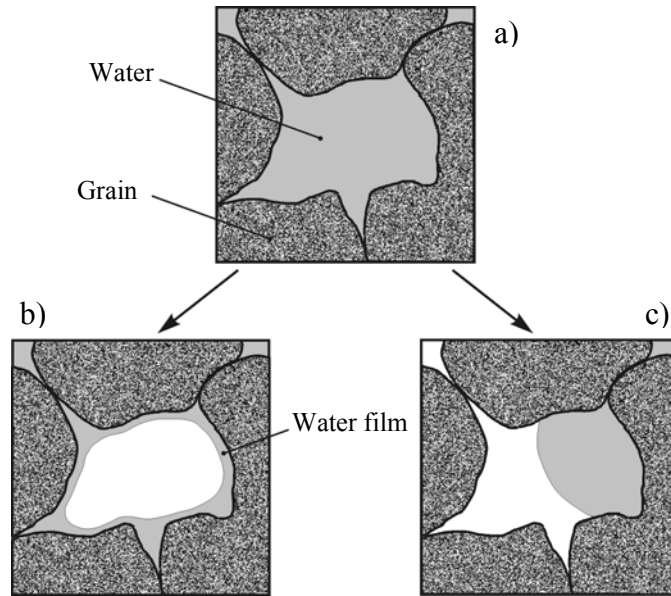


Fig. 4. Formation of residual water saturation  $S_{wir}$  with hydrophilic (b) and hydrophobic (c) rocks.

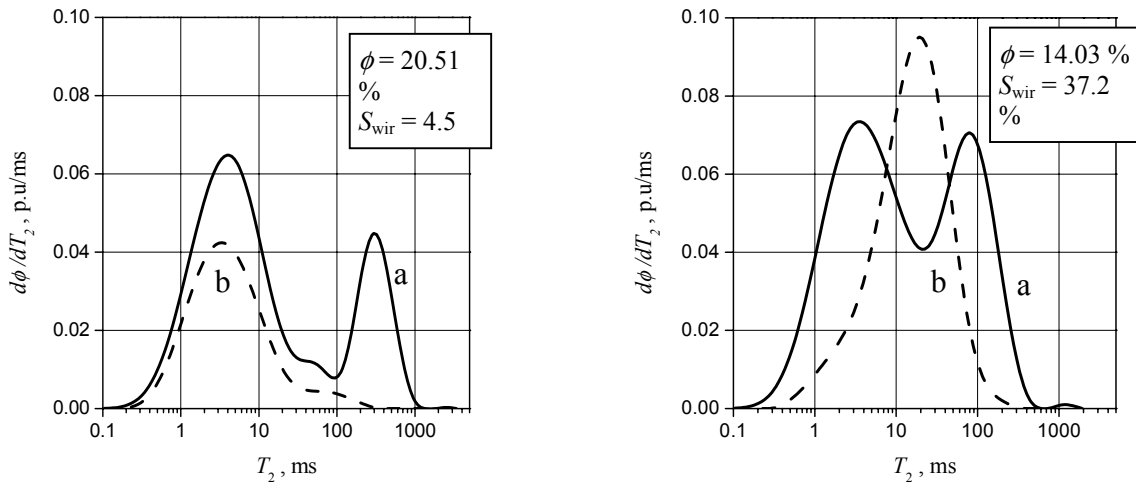


Fig. 5.  $T_2$  distributions for 2 samples of extracted hydrophobic rocks. (a)  $S_w = 100\%$  ; (b)  $S_w = S_{wir}$  (with  $P_c = 0.4 \text{ MPa}$ )

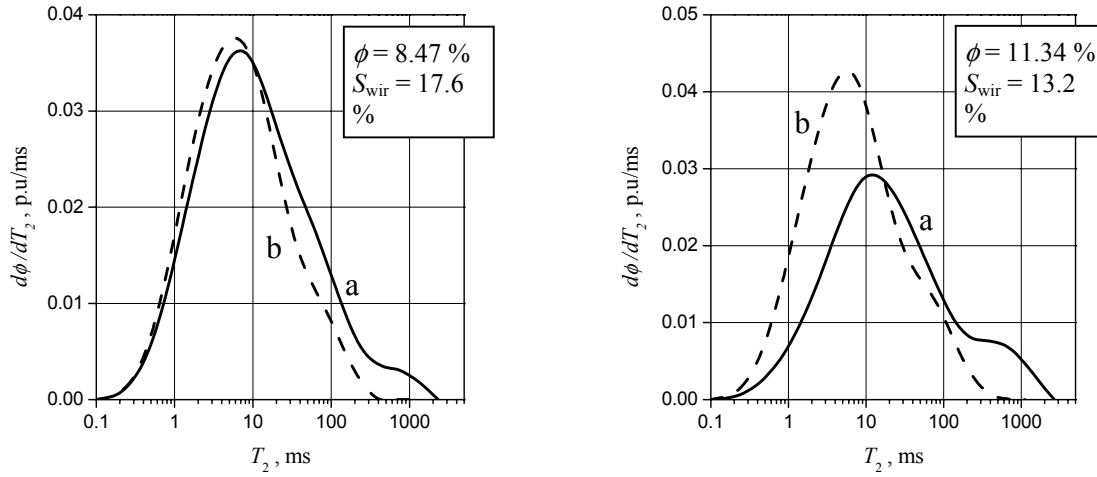


Fig. 6.  $T_2$  distributions for 2 samples of hydrophobic rocks with residual oil. (a)  $S_w = 100\%$  ; (b)  $S_w = S_{wir}$  (with  $P_c = 0.4 \text{ MPa}$ )

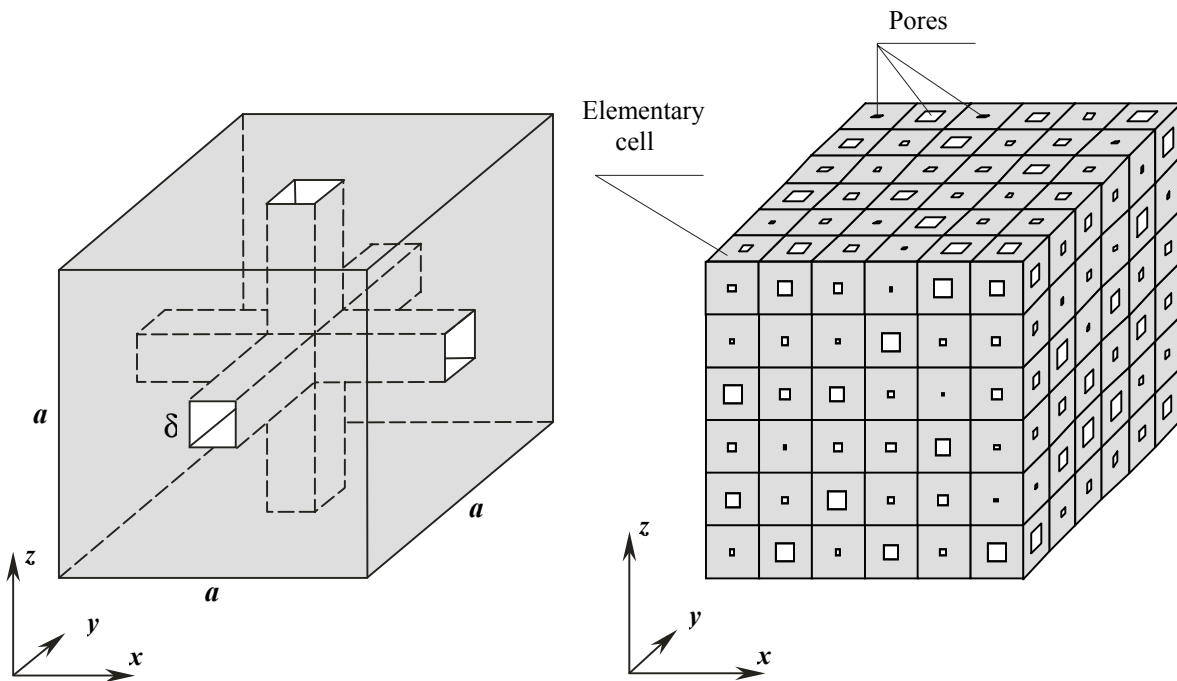


Fig. 7. Pore structure in an elementary cell.

Fig. 8. Model of rock.

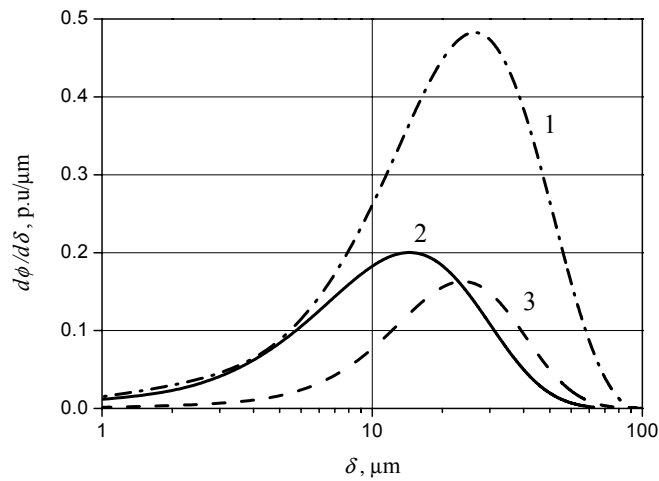


Fig. 9. Simulative distributions of saturated porosity vs pore sizes for hydrophilic (2) and extracted hydrophobic (3) rocks.

(1)  $S_w = 100\%$  ; (2)  $S_w = 28\%$  ; (3)  $S_w = 28\%$  .