Capacitive and migration parameters of the rocks of the upper part of the section in the east of the Russian platform

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Abstract. This paper deals with values of the filtration coefficients of reservoir rocks that contain fresh groundwater, and changes in these values in space in the oil region of Tatarstan Republic. The article also considers the filtration coefficients and diffusion coefficients of Quaternary clay loams and the absorption capacity of low permeable formations in the Nizhnekamskaya petrochemical industrial zone; this zone is one of the largest in Europe. The main result of our research is that five key factors control the significant variability of rock permeability. These factors are the depth of the rocks, the geomorphological and structural location, facies formation conditions and location of the Neogene palaeovalleys. Low permeable rocks in the upper section of the Nizhnekamskaya industrial zone are widespread and have a high absorption capacity, which is almost similar to the capacity of montmorillonite; these factors determine the high protection of groundwater from surface pollution. The results obtained by the authors are necessary for rational hydrogeological and geocological studies, as well as for the creation of computer geofiltration and geomigration models.

1. Introduction

Platforms are at least 50% of the continental area. Their sedimentary cover includes deposits of various ore and non-metallic minerals. Deposits of drinking underground water are one of the most important. They usually occur in the upper part of the section, therefore they are often under significant anthropogenic pressure.

Data of capacitive and migration parameters of rocks and data of their changes patterns in space are necessary for rational hydrogeological studies and the optimal location of water wells. These data are also important when geocological studies focused on the identification and prevention of underground water pollution are conducted. The creation of geofiltration and geomigration models is impossible without knowledge of the nature and degree of variability of capacitive and migration parameters in space. This determines the relevance of this work.

2. Objects and methods of research

This paper deals with features of changing the filtration coefficients of sandstones and carbonate rocks, the filtration and diffusion coefficients of clay loams, as well as the absorption capacity of various low permeable rocks.
The filtration anisotropy of sandstones and carbonate rocks is analyzed according to the results of study of the Lower Kazanian aquifer (Middle Permian) in the oil region of Tatarstan Republic. This aquifer is the most productive element of the section in relation to drinking underground water. The oil region has an area of more than 20,000 km². It is located within the South Tatar Arch (STA) of the Volga-Ural Anteclise on the Russian platform [1]. Large oil fields such as Romashkinskoye, Novo-Elkhovskoye and Bavlinskoye have been developed here for over 60 years. This led to significant pollution of fresh underground water [2]. In this regard, the organization of high-quality drinking water supply in settlements is very important. Since the 1990s, exploration for drinking underground water has been periodically carried out in the region. This determines the relevance of knowledge of the nature and main factors of rocks filtration anisotropy.

Filtration and diffusion coefficients and absorption capacity of low permeable rocks are studied on the area of the Nizhnekamskaya industrial zone located 6-8 km east of the city Nizhnekamsk (figure 1).

Large enterprises are located in this zone. They are PAO Nizhnekamskneftekhim (Nizhnekamskneftekhim, PJSC) (the largest petrochemical enterprise in Europe, the first products were launched in 1967), PAO Nizhnekamskshina (Nizhnekamskshina, PJSC) (the largest enterprise in Russia that produces automobile tires), AO TANECO (TANECO, JSC) (a complex of the latest refineries and petrochemical plants with design capacity 14 million tons of oil per year), OAO TAIF-NK (TAIF-NK, PJSC) (oil refining complex with an oil refining level of 8 million tons per year). Nizhnekamsk industrial zone is located on a high and wide forested watershed on the left bank of the Kama River. Its total area is at least 20 km², the height above the main erosion base level (drainage) is 150-160 m. Small settlements are located outside the sanitary protection zone of the industrial complex, there are also active agricultural activity and oil fields development. The upper part of the section in the industrial zone is composed of Quaternary eluvial-deluvial clay loams, which occur on Permian deposits. Clays
have a predominant development in the section. This causes significant buffer (protective) properties of the geological environment. Therefore, negative changes in the condition of the hydrosphere of the region are not observed in the last 40 years [3]. So the study of capacitive and migration parameters of these low permeable rocks is relevant.

The upper part of the section in the east of the Russian platform, where the studied objects are located, is represented by complexes of Permian deposits of different facies and mainly continental terrigenous Pliocene-Quaternary sediments [4]. Their thickness reaches 300–400 m. They determine the geoecological conditions and potential resources of a large territory. Fresh groundwater resources are very important. The Lower Kazanian aquifer is the most water-bearing in the oil region of Tatarstan Republic [5]. This aquifer is opened in the lower part of river valleys and consists of rhythmic succession formed by carbonate and terrigenous rocks (these rocks form interlayers with thickness 2-6 m). The total thickness of the Lower Kazanian aquifer is 50–100 m with the effective thickness about 40 m. The depth of occurrence of the Lower Kazanian top surface varies from 0 to 180 m. Sandstones and carbonate rocks (limestones and dolomites) are aquiferous. Filtration parameters of deposits were determined using results of experimental filtration testing of 552 wells and 122 laboratory determinations of water permeability of all major rock types. The results showed that filtration coefficients do not change much. So filtration coefficients of sandstones are 0.003-150 m/day (prevailing values are usually below 10 m/day) and filtration coefficients of limestones are 0.006-610 m/day (prevailing values are usually below 15 m/day). The data of laboratory determinations show that porous type of porosity determines filtration coefficients up to 6–10 m/day. The fracture of rocks causes additional porosity, so the permeability values increase.

Rock fracturing depends on the processes of diagenesis, tectonic stresses, exogenous processes. Geomorphological and structural features of the territories depend on the last two factors. Therefore, we can determine the degree of fracturing of rocks and their water permeability, based on orographic and geological-structural parameters. The authors analyze the following parameters to identify the main factors affecting the filtration capacity of rocks:

1) **hypsometric parameter** is represented by four levels of depth of water-bearing rocks occurrence;

2) **geomorphological parameter** considers seven elements: from the largest river valleys to the axial zones of the main watersheds;

3) **structural parameter** is represented by four types of position within the local geological structures at the base of the Lower Kazanian deposits;

4) **geological parameter** allows to take into account the Neogene palaeovalleys. It is represented by three well location;

5) **facial parameter** is represented by three types of facial conditions of rocks formation;

6) **morphometrical parameter** takes into account four forms of surface slopes;

7) **technogenic parameter** takes into account three methods of oil field development.

The mentioned parameters are digitized and presented in the research materials [6, 7].

The filtration and diffusion coefficients are determined for Quaternary clay loams of the Nizhnekamskaya industrial zone. They are widespread over the area. Top soil layer with thickness 0.2-0.6 m occurs on these deposits. The loam thickness is 1-4 meters in the axial parts of watersheds, and it can reach 20 meters on their slopes. Quaternary clay loams occur on the Urzhumian and the Kazanian
deposits. Clay loams are pulverescent, have different plastic properties. They are predominantly light brown, have quartz-feldspar composition with 26-33% of montmorillonite (X-ray diffraction analysis show this data). The composition of clay loams according to X-ray fluorescence analysis is similar to the average composition of clays [8].

Infiltration tests in wells were performed in 2017 at one of industrial sites. As the result of this experiment, clay loam filtration coefficients were obtained. Rocks diffusive saturation with NaCl made it possible to obtain diffusion coefficients of loams [9]. This process was carried out in plastic tubes 500 mm long and 32 mm in diameter. These tubes were filled with soil previously wetted with distilled water. A dry salt NaCl was at one end of the tube. After tubes were filled, authors waxed them with paraffin and placed them in the thermostat for 20 days with temperature 25°C. Next, experts took loam samples every 2 cm along the length of the tube through special slots, then they made water extracts from them. The content of rock and distilled water in water extracts was 1:5 and 1:10. Water extracts were analyzed after 1 day using ion chromatographs Dionex ICS-1600. The diffusion coefficients were calculated according to Fick's second law, which describes the concentration distribution (C) along the length (l):

$$\frac{dC}{dt} = D \times \left(\frac{d^2 C}{dl^2}\right), \quad (1)$$

A private decision of this law by A.A. Chernov [9]:

$$C = A \cdot e^{-\frac{l^2}{4Dt}}, \quad (2)$$

where $A$ – the constant.

So the diffusion coefficient can be determined as:

$$D = \frac{0.4343}{(4 \cdot t \cdot tga)}, \quad (3)$$

where $D$ – the diffusion coefficient, $sm^2/day$; $t$ – the time, day; $tga$ – the angular coefficient of a straight line approximating the analytical data of the concentration of chloride in water extracts ($lgC$) depending on the square of the distance ($l^2$) (figure 2).

![Figure 2. Graphoanalytical method that describes diffusion coefficients.](image)

Absorption capacity (base exchange capacity) was determined for soils, Quaternary clay loams and Permian clays. This parameter is also defined for clays of montmorillonite, kaolinite and hydromicaceous composition, as well as medical activated carbon. The determination of this parameter was carried out according to L.I. Kulchitsky’s method based on comparison of absorbency of a blank methylene blue solution (0.3%) and a solution of this dye, which reacted with 1 gram of a mineral substance [9]. The mineral substance was abraded, sieved through a sieve with holes 0.1 mm, dried at
105°С, and filled with 50 ml of blank methylene blue solution. After that, the solution was intensively stirred for 20 minutes and then it was filtered through a paper filter. Five milliliters of the filtrate was diluted 100 times with distilled water. Absorbency was determined in the blue region of the visible spectrum. The authors use the equation to calculate the absorption capacity:

$$E = \frac{308 \times (D_1 - D_2)}{g}, \quad (4)$$

where $E$ – base exchange capacity, m.eq./100 g; $(D_1-D_2)$ – difference between absorbency of the methylene blue solution and absorbency of the filtrate; $g$ – quantity of mineral substance, gram (g).

L.I. Kulchitsky’s method helps to determine the mineral surface area ($S$, m$^2$/g):

$$S = E \times 5.72, \quad (5)$$

3. Results and discussions

Filtration parameters of the Lower Kazanian aquifer in the oil region of Tatarstan Republic is variable (table 1).

A correlation analysis of filtration coefficients values of sandstones, limestones and specified digitized parameters was carried out to determine the main factors that determine the filtration capacity of rocks. This analysis was performed both for the entire data set and each tectonic unit of the South Tatar Arch (STA) [6, 7].

| Lithologic types     | Laboratory: NMR (mD) | Laboratory: using the filtering device (tube) for measuring the filtration coefficient (m/day) | Experimental filtration tests (single and cluster pumping, m/day) |
|----------------------|----------------------|------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| Clay                 | 10–71 (23)           | –                                                                                               | up to 0.5 (3)                                                     |
| Siltstone            | 103–395 (28)         | –                                                                                               | 0.09–3.7 (12)                                                    |
| Sandstone            | 13–1007 (32)         | 0.5–6.0 (30)                                                                                   | 0.003–150 (483)                                                 |
| Marl                 | 20–48 (3)            | –                                                                                               | 0.34–8.8 (15)                                                   |
| Limestone and dolomite | 1–182 (6)           | –                                                                                               | 0.006–610 (343)                                                 |

Note. The number of water permeability determinations is given in parentheses.

Water permeability of rocks is significantly associated with hypsometric, geomorphological, structural, geological and facial parameters (table 2). These parameters are the main factors of the filtration field changes and they are the filtration anisotropy factors of the hydrogeological section. The role of each of them, in respect that the values of other factors do not change, is shown in table 3.
Table 2. Correlation of the filtration capacity of deposits and individual parameters of the aquifer.

| Parameters          | Structural elements, lithology | | | |
|---------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|                     | The western slope of the South Tatar Arch | The western slope of the South Tatar Arch | Sand-stones | Lime-stones | Sand-stones | Lime-stones | Sand-stones | Lime-stones |
|---------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Hypsometric         | -0.21 | -0.40* | -0.36* | -0.25 |
| Geomorphological    | -0.37* | -0.20 | -0.30* | -0.39* |
| Structural          | 0.23 | 0.20 | 0.21* | 0.14 |
| Geological          | 0.56* | 0.51* | 0.52* | 0.58* |
| Facial              | -0.38* | -0.33 | -0.36* | -0.26 |
| Morphometrical      | -0.0 | -0.17 | 0.07 | 0.07 |
| Technogenic         | -0.15 | -0.02 | -0.05 | 0.03 |
| Number of data (pumping out) | 45 | 33 | 95 | 48 |

Note. * Significant coefficients of pair correlation.

Table 3. The role of the main factors causing the filtration heterogeneity of the Lower Kazanian aquifer.

| Factor       | Manifestation of these factors | Difference coefficient for extreme values |
|--------------|--------------------------------|------------------------------------------|
| Hypsometric  | The filtration coefficient decreases with increasing depth (especially if the depth is more than 80-100 m) | More than 10 |
| Geomorphological | The filtration coefficient has lower values on the axes of the watershed than on large valleys | Less than 5 |
| Structural   | The filtration coefficient has maximum values in the arches of positive structures and on their steep branches. | Less than 3 |
| Geological   | The filtration coefficient has maximum values in the nearest zone at a distance of 2-3 km from the contours of Neogene paleovalleys | Less than 5 |
| Facial       | Gray-colored marine deposits have greater water permeability than permeability of red-colored continental lithologic analogs | Less than1.5 |

First four factors’s influence on the water permeability parameter is easily explained. They are depends on the degree of rocks fracturing. The porosity and fissuring of rocks decrease while depth increases. Rivers are formed along the weakened zones with high fracture and porosity values. In addition, cracks occur within river valleys due to the lack of a geostatic load. Neogene formations often show ancient rivers. According to geophysical data, the connection of rivers with faults of the platform foundation is fixed. The data indicate tensile stresses in the central parts of anticline structures, and more intense stretching is noted on the steep branches of these structures. The facial factor determines the amount of porosity. Sandstones of continental facies, in contrast to marine facies, are granulometrically more heterogeneous and clay, which causes a decrease in their effective porosity and, accordingly, water permeability.
The role of these factors in the filtration heterogeneity of the geological section is clearly manifested at depths of up to 100 m. Water permeability gradually does not change much with increasing depth of occurrence of rocks. Their filtration coefficients below 150 m practically do not exceed 0.13 m/day, and they do not depend on the examined geological-geomorphological conditions. Maximum values of the filtration capacity of rocks (including anomalous ones) are manifested with a certain combination of all the above mentioned factors. Zones of this combination under optimal hydrogeochemical conditions are deposits (already explored or predicted) of drinking groundwater.

The calculation of the most probable values of the sandstone and limestone filtration coefficients for various conditions of their hypsometric, geomorphological, geological and structural position is carried out on the basis of the filtration anisotropy factors of the aquifer. The 252 values of filtering capacity of each lithological difference in reservoir rocks within the limits of each structural unit of the STA was determined [6, 7]. These data make it possible to determine the resource potential of the Lower Kazanian aquifer and the scale of the geological activity of underground water in the oil region of Tatarstan Republic [10].

Clay loams’ filtration coefficients in the Nizhnekamskaya industrial zone are determined from the data of 7 infiltration tests in wells; these values vary from 0.005 to 0.28 m/day with an average value of 0.11 m/day. Capacitive and diffusion parameters of low permeable rocks and soils are shown in table 4.

| Table 4. Filtration and diffusion parameters of rocks in the Nizhnekamskaya petrochemical industrial zone |
|---------------------------------|----------------|----------------|----------------|----------------|
| Mineral substance               | Number of samples | Base exchange capacity, m.eq. /100 g | Surface area, m²/g | Diffusion coefficient, 10⁻⁵ m²/day |
|---------------------------------|----------------|----------------|----------------|----------------|
| Soil                            | 8              | 9.39-13.86     | 53.7-79.3      | 3.59-5.95      |
| Clay loam                       | 7              | 9.7-16.79      | 55.5-96.0      | 4.47±0.99      |
| Mottled clay                    | 5              | 6.93-14.01     | 39.6-80.2      |                |
| Gray clays                      | 3              | 7.08-10.32     | 40.5-59.0      |                |
| Montmorillonite                 | 2              | 12.32-19.1     | 70.5-109.2     |                |
| Kaolinite                       | 2              | 2.16-3.39      | 12.3-19.4      |                |
| Hydromica                       | 1              | 8.32           | 47.6           |                |
| Medical activated carbon        | 1              | 18.17          | 103.9          |                |

Note. The numerator shows the limit values (minimum-maximum), the denominator shows the mean and standard deviation; the last 4 lines show comparative material.

Clay loams’ diffusion coefficients in the upper part of the section do not change much; this type of rock has precisely these values [11]. The values of absorption capacity are significantly lower than their possible real level. So according to the data obtained by the author, this value for montmorillonite is 12.3-19.1 m.eq./100g, while its real absorption capacity can reach 150 m.eq./100 g [12]. Despite this, the obtained data can be used at a comparative qualitative level. Within the Nizhnekamskaya industrial zone Quaternary clay loams have a maximum absorption capacity, soils and red-colored clays have...
slightly lower values of this parameter. The sorption capacity of these mineral formations approaches the capacity of montmorillonite clays.

4. Conclusions

Filtration coefficients vary greatly in reservoir rocks in the oil region of Tatarstan Republic in that part of the section that is the most productive in relation to drinking underground water. There are patterns in these changes. Filtration coefficients depend on five main factors (at a depth of less than 150 meters); these factors are the depth of the underground water reservoir rocks, their geomorphological and structural location, facial conditions of rocks formation, as well as the location of relatively Neogene paleovalleys. Geological and geomorphological conditions mentioned above no longer affect the filtration coefficients at a depth of more than 150 m (they usually do not exceed 0.13 m/day).

The Nizhnekamskaya industrial zone with large enterprises of the petrochemical and oil refining industries is characterized by low permeable rocks in the upper part of the section. These rocks have rather high values of absorption capacity. It can be confidently said that these factors play a decisive role in the local pollution of fresh underground water within the Nizhnekamskaya industrial zone, where enterprises have been operating for more than 50 years.

The results can be widely used in rational exploratory work to find fresh groundwater, in the optimal placement of water wells and landfills for storage of different types of waste. They can also be used in assessing fresh groundwater resources, in correct hydrodynamic calculations of the spread of real or potential pollution, and in identifying sanitary protection zones for water sources. In addition, they are extremely important for the creation of computer geofiltration and geomigration models.

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