The Main Regularities of Changes in the Composition and Properties of Saline and Non-Saline Clayey Sediments with Diffuse Leaching

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Abstract. The paper contains the results of their own research on the problem of diffusion leaching of unsalted sarmatian clays and analysis of data from other authors who study this problem on samples of saline clay rocks. Changes in the physical and mechanical characteristics of clay rocks, which may be the bases of buildings and structures, during their diffuse leaching are considered. It is concluded that unsalted sarmatian clays that do not have fine pyrite in their composition and saline quaternary clay rocks of various genesis are less resistant to flooding than saline marine clays.

1. Introduction
The research of saline clay rocks of various ages and origin in conditions of long-term interaction with water according to the PNIIS method was carried out in different years by: N. p. Zatenatskaya, N. S. Reutova, N. A. Okchina [1, 2], S.I. Pakhomov, A.M. Monyushko [3, 4, 5] and others. In these works, changes in the material composition and physical and mechanical properties during diffusion leaching were studied for: sarmatian clays of the Central pre-Caucasus, maikop clays of the Northern Caspian, the thickness of clays of the upper and lower Neogene of the Central pre-Caucasus, syrtic clays of the East Volga region, quaternary clays of the Central pre-Caucasus. Also, the following works are devoted to the problem of leaching of unsalted clay soils: Olyansky Yu.L., Shekochikhina E.V., Kalinovsky S.A., Alekseev A.F., and others [3, 6, 7, 8, 9, 10, 11]. We studied unsalted sarmatian clays located in the Northern black sea region. Their formation was due to the accumulation of terrigenous material in an isolated marine basin, whose water was diluted by surface runoff from the Russian platform.

Saline clays contain more than 0.3% of easily and medium-soluble salts. Clay rocks may have a primary (marine) salinity character - the clays were deposited in saline marine basins (maikop, sarmatian, khvalyn clays) or a secondary (continental) one - due to weathering and continental salinity accumulation (quaternary clays, syrtic clays). Salts in clays accumulate both in solid form (carbonates, gypsum, yarosite, iron oxides, amorphous silica) and in pore waters. In the latter, salted clays
concentrate easily soluble salts of chlorides and sulfates of sodium, magnesium and soda. A characteristic feature of saline clay rocks is their brown and red-brown color, due to the accumulation of iron oxides in the rock (Fe₂O₃).

2. Changes in the composition and properties of saline clay rocks during leaching

Absorption capacity and composition of exchange cations. Pore solution cations are in a mobile physical and chemical equilibrium with exchange cations adsorbed by colloid rock particles. The absorption capacity of maikop clays is 24.7 mg-EQ/100g of rock. The composition of the exchange complex includes: magnesium-48%; Na⁺ - 32%; calcium-17%. This arrangement of ions indicates the marine origin of clay [1]. In quaternary eluvial-deluvial and aluvial-deluvial clays, the absorption capacity varies from 21 to 33 mg-eq/100g of rock. The largest absorption capacity is observed in weakly aggregated differences of eluvial quaternary clays, whose exchange cations are arranged in a row: Mg⁺² > Na⁺ > Ca⁺² > K⁺.

When leaching saline clays containing gypsum, calcium and magnesium carbonates in the solid phase, the structure of exchange cations is rearranged. In leached clays (in comparison with saline clays), the content of exchange sodium sharply increases-exchange reactions occur between pore water cations and exchange cations – Ca⁺² is absorbed from pore water, and exchange Na⁺ passes into pore water. The content of exchangeable sodium in most samples increases and only in strongly leached differences its content decreases. Exchange cations are arranged in a row: Ca⁺² > Mg⁺² > Na⁺ > K⁺ - in highly leached clays, and at intermediate stages they are arranged in a row: Mg⁺² > Ca⁺² > Na⁺ > K⁺ and Mg⁺² > Na⁺ > Ca⁺² > K⁺.

The absorption capacity during leaching of highly aggregated delusive clays decreases from 24-25 mg-EQ/100g pore to 19-21 mg-EQ/100g pore. when leaching weakly aggregated eluvial saline Quaternary clays, the absorption capacity increases by 2-3 mg-eq/100g of rock.

Degree of salinity. The results of numerous analyses of saline clay water flows along the route of the Bolshoy Stavropol canal were analyzed by N.P. Zatenatskaya [1]. Quaternary clays have mainly a sulphate-sodium salinity of 1.2-2.8%. When interacting with water, clays are leached, which leads to a decrease in their mineralization to 0.4-1.2%. The degree of leaching is 0.25-0.60. When leaching maikop, syrtov and khvalynsk clays, the degree of salinity of which is less than 0.4-1.1%, the degree of leaching is slightly higher and is 0.36-0.75, and the content of water-soluble salts is reduced to 0.3-0.6% (table 1).

Dispersion. In experiments on long-term leaching of saline clays, large aggregates of the sand fraction are destroyed during the simultaneous coagulation of clay fractions into a fine-grained one. Aggregation of the clay fraction of the maikop clays during leaching is the result of a deeper manifestation of the processes of clay weathering - its desalination up to brining [1]. During the leaching of maikop and eluvial weakly aggregated quaternary clays, there is a slight increase in the content of clay fraction, as well as a slight increase in the dusty fraction due to a decrease in the content of sand fraction. The aggregation coefficient of such clays is slightly lower (table 1). In highly aggregated plastered deluvial clays with an aggregation coefficient of 14-16, long-term diffusion leaching results in peptization of clays mainly due to the destruction of sandy and coarse-grained fractions with an increase in the content of fine dust fraction. At the same time, the content of the clay fraction <0.005 mm changes slightly in the direction of increasing (by 2-3%). The aggregation coefficient either does not change, or increases or decreases slightly.

According to research [1], a high content of gypsum in the rock contributes to a stronger aggregation of the clay reaction. And only complete removal of gypsum from the rock during leaching and its strong desalination lead to peptization of the clay fraction.

Physical property. When leaching saline clays, their moisture content increases and their density decreases. At the same time, moisture is more important for weakly aggregated rocks than for strongly aggregated ones.

When leaching weakly aggregated saline clays, a stronger peptization of fractions occurs: interaggregate and intraaggregate bonds are destroyed. The rock is more strongly watered due to the
thickening of diffuse layers of clay particles in weakly mineralized pore water, which is also facilitated by the high content of sodium in the exchange complex.

Plasticity and yield strength. The roll-out limit increases in some cases, but does not change in others. Due to this, as well as an increase in the yield strength, the number of plasticity also changes: for montmorillonite clays, it increases by 0.01-0.09, for illite-chlorite clays, it does not change (table 1). According to the index, the leached clays are semi – solid, tight, and rarely soft-plastic.

Plastic strength. The plastic strength of all clays decreases after leaching by more than 30%.

The strength of the shear. In experiments on diffusive leaching of salted clays, the strength characteristics of clays are reduced due to strong wetting, loosening and softening, which corresponds to the data obtained by a number of researchers. Thus, the specific adhesion decreases by 6-15 times in montmorillonite clays and by 2.0-3.5 times in illite-chlorite clays, by the angle of internal friction up to 3 times for montmorillonite clays and 1.5 times for illite-chlorite clays compared to saline clays [1].

Table 1. Quantitative changes in the composition and properties of saline and unsalted clay rocks during diffusion leaching.

| Indicators of composition and properties | Neogene marine salted clays [1,5] | Quaternary polygenetic saline clay rocks [5] | Non-saline Sarmatian clays does not contain pyrite | containing pyrite |
|-----------------------------------------|-----------------------------------|---------------------------------------------|--------------------------------------------------|-----------------|
| Content of dispersed (less than 0.005 mm fraction), % | 70.0 | 24.1 (7) | 30.8 (20) | 36.1 (10) |
| (microaggregate analysis)                | 72.5 | 24.5 | 46.4 | 35.2 |
| Aggregation coefficient of the dispersed fraction (less than 0.005 mm) | 1.10 | 7.40 (7) | 1.97 (20) | 1.93 (10) |
| Water-soluble salt content, %            | 0.68 (12) | 1.56 (9) | 0.17 (20) | 0.19 (10) |
| Leaching rate at the end of the experiment (average) | 0.41 (11) | 0.46 (9) | 0.43 (20) | 0.38 (10) |
| The content of gypsum, %                 | 0.12 (10) | 5.22 (6) | 0.15 (20) | 0.13 (10) |
|                                           | 0.22 | 3.08 | 0.10 | 0.41 |
| The content of carbonates, %             | - | 4.00 (4) | 9.54 (20) | 14.11 (10) |
|                                           | 2.68 | 8.47 | 15.60 |
| Humidity                                 | 0.31 (12) | 0.20 (8) | 0.23 (20) | 0.31 (10) |
|                                           | 0.29 | 0.30 | 0.44 | 0.52 |
| Density of “dry” soil, g/cm³             | 1.51 (11) | 1.61 (8) | 1.67 (20) | 1.50 (10) |
|                                           | 1.30 | 1.48 | 1.26 | 1.11 |
| The angle of internal friction, degrees  | 19 (13) | 22 (8) | 16.6 (20) | 13.0 (10) |
|                                           | 12 | 14 | 15.0 | 12.7 |
| Specific adhesion, MPa                   | 0.10 (11) | 0.14 (8) | 1.32 (20) | 1.08 (10) |
|                                           | 0.06 | 0.03 | 0.39 | 0.47 |

Note: in the numerator – the value before leaching, in the denominator - after leaching, in parentheses - the number of definitions.
For some quaternary clays, the specific adhesion during leaching decreases by 1.5-3.5 times [5]; for Sarmatian clays-by 2.0-3.0 times; for rocks of the lower Neogene up to 2.0 times. The angle of internal friction decreases accordingly: 1.3-3.5 times; 1.5-4.0 times; 1.5-5.0 times.

A comprehensive study of the engineering and geological properties of saline clays has shown that diffusive leaching results in the loss of non-water-resistant structural bonds, reduced mineralization of pore waters, increased hydration and water-holding capacity. Clays are softened and, as a result of changes in physical condition, the shear resistance of leached clays decreases sharply, which was previously noted in [1].

When leaching the swelling differences of saline clays, the decrease in the mineralization of pore waters leads to an increase in the thickness of the diffuse shells of clay particles, which contributes to their wedging action: a significant swelling pressure develops in the clays.

3. Changes in the composition and properties of unsalted clay rocks during leaching

The analysis of the features of changes in the composition and properties of unsalted clay rocks during diffusion leaching was performed using the following indicators: the content of the dispersed fraction, the aggregation coefficient of the dispersed fraction, the content of water-soluble salts, the content of gypsum, the degree of leaching, the content of carbonates, humidity, the density of the "dry" soil, the angle of internal friction, specific adhesion. Quantitative changes in the composition and properties of unsalted, as well as saline, clay rocks during diffusion leaching are shown in table 1.

The content of the dispersed fraction (less than 0.005 mm) and the coefficient of its aggregation. Marine unsalted sarmatian clays with plasticized-coagulation type of structural bonds (aggregation coefficient on average about 2.0) do not contain pyrite, when leaching, they are dispersed due to the removal of cementing salts and, first of all, gypsum. At the same time, the content of the dispersed fraction increases significantly (by about 30%) and its aggregation coefficient decreases as much. Similar processes also occur during leaching of plastered quaternary clay rocks (table 1.).

Marine unsalted sarmatian clays with plasticized-coagulation type of structural bonds containing pyrite do not change the content of the dispersed fraction during leaching. It may rise or fall slightly. All salted clay rocks behave in the same way. Accordingly, the aggregation coefficient may fluctuate slightly in both directions. It is characteristic that this is not related to the content of gypsum in the rock: its amount can either increase during leaching or decrease.

The content of water-soluble salts. When all clay rocks are leached, their salinity decreases. The minimum absolute decrease in salt content occurs for unsalted sarmatian clays that do not contain pyrite – on average by 20% of the outcome at the end of the test, which corresponds to the degree of leaching on average 0.43. the maximum decrease in salt content by 2.5-3.0 times takes place for saline clay rocks, but the degree of leaching at the end of the experiment does not exceed 0.46 on average.

The content of gypsum. The amount of gypsum in marine clay rocks is determined by: primary-its presence in seawater during sedimentation, secondary-the oxidation of pyrite during weathering (leaching) of clays in the post-genetic stage. Before the leaching of neogene marine clays, the gypsum content in all three groups of rocks was approximately the same-0.12 - 0.15%. In leached samples, the gypsum content decreased by about one-third only in sarmatian unsalted clays that do not contain pyrite. In the other two groups, its content increased by 2-3 times due to the formation and accumulation of secondary gypsum in the rock. When leaching saline quaternary clay rocks containing mainly secondary gypsum formed during continental salinization, its content decreased by an average of 45%.

The content of carbonates. The change in the content of carbonates during the leaching of clay rocks is subject to the dependence identified for gypsum: in samples that do not contain pyrite in the initial state, their number decreases. For unsalted sarmatian clays by 10-20%, for quaternary clay rocks by 1.5–2.0 times. In samples with pyrite inclusions, the amount of carbonates increases by 10-30% during leaching.
**Humidity.** The maximum increase in humidity by 1.5-2.0 times occurs for sarmatian unsalted clays and saline quaternary clays. For neogene saline clays, this indicator changes slightly in both directions during leaching.

*The density of the "dry" soil* during leaching of all clays decreases by 10-30%, which is a consequence of their loosening and swelling. Unsalted sarmatian clays containing pyrite are most decomposed (up to PD =1.40-1.50 g / cm³).

*Strength.* In general, the strength of all clay rocks during leaching decreases: by the angle of internal friction - from insignificant to 2 times; by the specific adhesion by 1.5–5.0 times. To assess the degree of influence of watering on the strength characteristics of clay rocks, the term "coefficients of resistance to flooding" is used, as the ratio of the value of the strength index of the leached sample to the strength index of the sample of natural humidity [5]. The coefficients of resistance to flooding according to a number of authors [7-12] are shown in table 2.

This fact is explained by the fact that the strength of clay rocks, other things being equal (humidity and density), significantly depends on the nature of the structural relationships between soil particles and the degree of soil aggrandizement. In samples of clays that do not contain pyrite, soil dispersion occurs during leaching and its aggregation coefficient decreases. And in samples of clays containing pyrite, new chemical compounds are formed during leaching: gypsum, amorphous silica, iron oxides, etc., which contribute to the aggregation of soil particles.

**Table 2.** Quantitative changes in the composition and properties of saline and unsalted clay rocks during diffusion leaching.

| Clay rocks and their degree of salinity                                      | coefficients of resistance to flooding |
|---------------------------------------------------------------------------|----------------------------------------|
| **Unsalted sarmatian clays that do not contain pyrite (Olyansky Y I [7-11])** | K_c 0.32 (15)  K_p 0.61 (9)  K_{p_e} 0.05 (5) |
| **Non-saline sarmatian clays containing pyrite (Olyansky Y I [7-11])**     | K_c 0.51 (9)      K_p 0.74 (8)      K_{p_e} 0.09 (7) |
| **Salted sarmatian clays of the Central Caucasus (Pakhomov S I, Monyushko A M [5])** | K_c 0.38 (3)     K_p 0.29 (4)     K_{p_e} 0.40 (4) |
| **Quaternary saline clays of the Central Caucasus (Zatenatskaya NP [1,2])** | K_c 0.12 (3)    K_p 0.46 (3)    K_{p_e} 0.04 (4) |
| **Syrtic saline clays of the East Volga region (Zatenatskaya NP [1,2])**   | K_c 0.30 (1)    K_p 0.71 (1)    K_{p_e} 0.03 (1) |
| **Salted khalyn clays of the Northern Caspian sea (Zatenatskaya NP [1,2])** | K_c 0.45 (2)    K_p 0.75 (2)    K_{p_e} 0.53 (2) |
| **Salted Neogene clays of the Central Caucasus (Pakhomov S I, Monyushko A M [5])** | K_c 0.69 (4)    K_p 0.52 (6)    K_{p_e} 0.34 (5) |
| **Salted Neogene clays of the Maikop**                                    | K_c 0.07 (1)    K_p 0.71 (1)    K_{p_e} 0.10 (1) |
| **Unsalted Sarmatians-meotic clays of the Prut – Dniester interflaue type I** | K_c 0.22 (21)  K_p 0.55 (21)  K_{p_e} 0.05 (15) |
| **II for resistance to flooding (Olyansky Y I [3, 6])**                   | K_c 0.31 (39)  K_p 0.67 (39)  K_{p_e} 0.06 (21) |
| **III for resistance to flooding (Olyansky Y I [3, 6])**                  | K_c 0.44 (31)  K_p 0.88 (31)  K_{p_e} 0.08 (22) |
|                                                                                   | K_c 0.33 (91)* K_p 0.71 (91)* K_{p_e} 0.06 (58)* |

Note: the first value is the average, with the number of definitions in parentheses; * - weighted average values for the sarmatian-meotic strata as a whole.

**4. Conclusions**

The main differences in changes in the composition and properties of unsalted and saline clay rocks during diffusion leaching are as follows:

1. Unsalted sarmatian clays that do not have pyrite in their composition are close to saline Quaternary clay rocks of various genesis in terms of chemical transformations and quantitative changes in their composition and properties during diffusion leaching.

2. Unsalted sarmatian clays containing pyrite are similar to saline marine clays of different ages, with the same degree of dispersion and aggregation of the clay fraction.
3. In general, non-pyrite clays are less stable (more sensitive) to water loss, due to their greater moisture content, a more significant change in the degree of dispersion and a significant decrease in the aggregation of the clay fraction.

4. The change in strength indicators for sarmatian clays that do not have pyrite in their composition is: up to 2 times - by the angle of internal friction and up to 4.5 times - by the specific adhesion. For those with pyrite, these indicators are equal: up to 1.5 times and up to 2-3 times, respectively.

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