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Epigenetic Formation of Clay Surface Properties: Experimental Modeling

O A Sofinskaya* and R M Usmanov

Institute of Geology and Petroleum Technologies, Kazan Federal University,
Kremlevskaya str., 4/5, Kazan, 420008, Russian Federation

*Corresponding author email: ushik2001@mail.ru

Abstract. Quaternary diluvium soil samples were tested for particles' cohesion, contact angle, porosity and their geoenvironmental properties were compared. The effect of particle size, applied external pressure, hydration and the presence of organomineral surfactants on the soil surface properties of a clay preparation was evaluated. These characteristics determine the strength of clay particles' cohesion to each other and are important for the development of techniques for geoenvironmental management. The macroscopic wetting contact angle was estimated using the captive bubble method by the author's technique. An external pressure in excess of 40 kPa applied to a clay preparation on a glass substrate results in more than one layer of clay particles due to cohesion. It was observed that the thickness of the clay layer retained on the preparations due to cohesion decreases during hydration. This decrease is more noticeable for samples with particles up to 45 μm compared to samples containing larger particles up to 250 μm . The positive effect of organomineral surfactants on the cohesion of clay particles has been established. The addition of these surfactants initially leads to an increase in wetting heterogeneity.

1. Introduction

The clay surface properties determine maximum thickness of the adsorbed water film, which, in turn, determines the viscous friction of the flow, the hygroscopicity of the soil, the height of capillary rise, the disjoining pressure between the particles and hence the adhesion forces between adjacent clay particles and the soil strength [1]. In particular, surface properties appear as the wetting that occurs on the solid/liquid/gas interface. Wettability characterizes a preference of a solid surface to be in contact with one fluid (liquid, gas) rather than another depending on the balance of their free surface energies. In clays, by the change in the wettability one can judge about the change in surface free energy of clay particles. The change in the surface free energy of soil particles is of great importance in engineering geology, hydrogeology, agriculture and integrated management of territories, but the mechanisms of this process are studied insufficiently for the moment. The analysis of the spatial distribution of clay surface properties and their dependence on the range of factors is a basic problem for the development of methods for geoenvironmental management.

The most obvious ways to effect clayey particles' surface energy are changing the particles' hydration energy and the surface area involved into interphase interactions [1]. Both of these ways manifest themselves in interactions between clayey minerals and organic matter, which acts in the form of either surfactants or active biota. Herewith, the ambiguous effect of organic matter on the change in clayey particles' free energy is observed due to random orientation of organic matter molecules functional groups or clayey particles, by basal faces or edges relative to their interface, that creates variations in surface charge and roughness. In total, all these factors together cause high uncertainty in the state of clay and organic components of the system. As a result, the soil wettability



has a high spatial heterogeneity of various manifestation scales. For instance, according to the hypothesis of Bachmann et al., spatial orientations of organic matter molecules and their functional groups towards the mineral surface in soils changes during their accumulation and due to different genesis [2]. Thus, in soils with similar organic matter content, the surface can be completely hydrophilic to superhydrophobic. [3, 4]. In short, surface prehistory (or "memory") leads to an additional change in the surface energy of clay particles.

The common quantitative measure of wettability is the contact angle (CA). It is measured at the point of contact between the phases, tangentially to the interface, towards the polar liquid. Complete wetting is achieved when CA is 0° , while with partial wetting, CA is between $0-90^\circ$; non-wetting liquids creates CA between $90-180^\circ$. The ideal equilibrium CA (Young's angle) is a characteristic for smooth homogeneous surfaces:

$$\cos \theta_Y = \frac{\sigma_{13} - \sigma_{12}}{\sigma_{23}}, \quad (1)$$

where σ_{13} , σ_{12} , σ_{23} are interfacial tensions at the solid – gas, solid – liquid, and liquid – gas interfaces, respectively. Modern techniques allow to determine CA on rough heterogeneous surfaces, but only as a macroscopic apparent CA characterizing the surface energy only at a certain point of the surface [5]. This angle is connected the angle from equation (1) using the Cassie – Baxter equation:

$$\cos \theta_{CB} = \sum \lambda_i \cos \theta_{Yi}, \quad (2)$$

where θ_{Yi} is an Young's angle for the matter i , including air, λ_i – is the surface fraction occupied with the matter i .

The apparent CA can vary greatly with texture and chemical composition within a single sample, i.e. the certain quantitative characteristic of the rock wettability is fundamentally impossible. Thus, to study the wettability of heterogenic surface, it is advisable to use a statistical approach based on representative sample of measured contact angles. From the point of view of mathematical statistics, at least 20 points characterized on the studied surface for rock wettability representative measurements is necessary. The most convenient characteristic that satisfies this condition is CA measured by one of the modifications of the drop shape method. Particularly, the drop shape method modifications such as the sessile drop and the captive bubble methods are widely used. The captive bubble method [5] is based on the gas bubble attachment on solid surface immersed in liquid; the sessile drop method involves the deposition of a liquid drop on solid surface in a gas environment. The task of adapting these methods to work with heterogeneous porous samples remains unresolved: the drop installation on a porous rock sample is accompanied by its spreading and absorption with time; the application of the captive bubble method without special surface preparation causes particles flaking in the liquid.

A routine scheme for the preparation of rock powder specimens for CA measuring using drop shape methods is empirically developed and includes the following operations: crushing a rock sample, spreading and fix powder onto flat substrate with gluing, compaction of powder on the flat substrate applying pressures in the range of 0.5 kPa - 500 MPa [6, 7]. The described way of rock powder specimens preparing for measuring CA are suitable to use in the sessile drop method, mainly on rock surfaces having CA of more than 50° .

The aim of our study is to evaluate the effect of particle size, applied external pressure, hydration and the presence of organomineral surfactants on the surface properties of a clay preparation, which determine the adhesion strength of clay particles to each other and the geoenvironmental properties of clay soils. In this work we apply an alternative powder specimen preparation for CA measurement using the captive bubble method, which is suitable for hydrophilic clay samples.

2. Objects and Methods

2.1 Objects and Sampling

Soil samples were taken with a hand drill on the right bank at the mouth of the Sviyaga River, the right tributary of the Volga River, and consisted of Quaternary diluvium on the Urzhumian (~Wordian) Stage deposits of the Permian system (table 1). Such rocks are widespread in the Middle Volga region

and are common as load-bearing soils. Measurements of rock temperature during sampling were carried out using an infrared laser pyrometer. Rock temperatures in the deepest sampling zone were typical for a constant soil temperature layer in a given region. The engineering behavior of the soils is influenced by groundwater of infiltration origin. The clay of sample R with field water content of 12.7% was in a semi-solid state. The clay of sample RS with field water content of 18.3% was in a decompressed state due to deep weathering.

Table 1. Samples and sampling description.

Samples	Description of sampled rocks	Sampling depth, m	Ground temperature, °C
D	Dolomite + limestone	1.40 – 1.60	+13.8 - +16.1
M	Rose marl	1.90 – 2.20	+9.9 - +13.1
R	Variegated carbonate clay	2.40 – 2.80	+4.0 - +5.5
RS	Weathered carbonate clay from rockslide site on the slope of the northward exposition (azimuth 190°)	0 – 0.15	+12.0 - +12.4

2.2 Specimen Preparation

The rock samples were subjected to the action of factors simulating epigenesis: crushing, decompaction/ re-compaction, hydration, the effect of organic surfactants. Samples were crushed, sieved separately through 45 and 250 microns to prepare two according options. The powders were spread onto flat glass slide covered by double sided scotch with rubber gluing layer, then one of the following external pressures was applied: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 kPa. Pressures of this range are known to be not destroying clayey particles and approximately equally reducing the porosity of clays of different composition [1]. After that, a flat substrate with glued clayey particles was shaken by gentle tapping and weighed. These operations were repeated several times until the weight of preparation stabilizes. Finally, the preparations obtained were saturated with hygroscopic moisture in an environment of 98-100% relative humidity in order to displace air from their surfaces [5].

Sample R was treated for 10 days with the mixture of organic surfactants. An extract of humic substances from meadow chernozem soil was prepared by boiling the soil with 15% KOH; then, 1 ml was mixed with 1 L of a suspension containing 0.5 g of each of the following chemicals: yeast extract, casein hydrolysate, proteose peptone, glucose, starch. The suspension was homogenized by shaking and boiling, cooled to room temperature and distributed over sample volume at an amount of 50% in air-dry clay weight. After that, the sample was placed into laminar-box with short-term ozonation by UV to suppress microbial activity, and left to dry to an air-dry state.

The specimens obtained were compared on the following attributes: clayey particles' cohesion at dry and wet conditions, CA, porosity. Samples D, M, RS were investigated after sieving through 45 μm . The porosity was evaluated at a particles' size of up to 250 μm . The macroscopic CA was estimated using the captive bubble method [5] by the author's technique (is in the process of patenting). Measurements were carried out on digital images of air bubbles attached to the surface of clay specimens prepared as described.

2.3 Cohesion Tests

Cohesion forces between clay micro-aggregates were estimated based on the following indicators: 1) clay layer thickness of specimens, which reached constant weight before and after hydration, 2) flaking and flotation of clay specimen particles when hydrated. The clay layer thickness of specimen was determined as the minimum value of several measurements performed using a micrometer with an accuracy of $\pm 1 \mu\text{m}$. Flaking and flotation of clay specimen particles at the air bubble/water interface were observed when performing CA measurements.

2.4 Compression Tests

Compression tests were carried out at conditions identical to those at which CA and particles' cohesion were determined. Powder samples in an air-dry state were placed into the compression ring

of hardware complex ASIS 3.2 (Geotech, Russia). The ring with clay was placed into odometer, and automated tests were carried out according to the Incremental loading oedometer tests (ISO 17892-5: 2017). The test scheme consisted of applying external pressure from 5 to 50 kPa in steps, with a step of 5 kPa. At each step a consolidation stage was fixed until the deformation of a sample was less than 0.01 mm per 4 hours. At the end of the test for each loading step sample porosity was calculated using the ordinary procedure considering solid phase density of the clays 2.65 g/cm^3 and field water content.

3. Results and Discussions

3.1 Clay Particles' Cohesion

An external pressure of less than 10 kPa applied to the clay samples was insufficient to fix clay particles on substrate (fig. 1a). At the same time, at a distances less than 50 nm between the disjoining pressure is activated [1], hence the thickness of the clay layer during preparation procedure will stepwise increase with increasing applied pressure. The maximum compaction of the powder preparation was achieved at an applied pressure of 20-30 kPa, regardless of particle size range. Starting from the pressure of 30 kPa for clayey particles of up to 250 μm in size and 40 kPa - for 45 μm , obviously, the second clayey layer was formed.

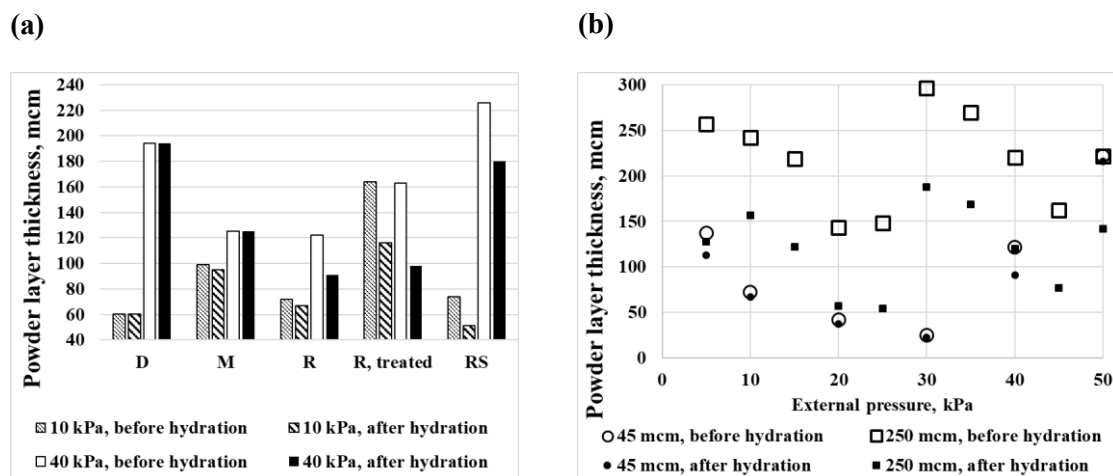


Figure 1. Powder layer thickness on specimens under different external pressure applied

When the specimen was placed into water for measurement, detachment and sedimentation of loosely bound particles from the surface of the preparation was visually observed, and the layer of powder in the preparation became thinner. For sample R with particle size range of up to 45 μm (fig. 1a) the clay layer retained on substrate was only slightly thinned. On the contrary, for a range of particle sizes up to 250 μm , a thinning of the clay layer was observed at all external pressures. So, attractive forces between particles dominate in disjoining pressure forces during hydration of powder with particle size range up to 45 μm that is quite consistent with the action of disjoining pressure forces: larger particles in the particle size range of up to 250 μm are mostly microaggregates developed along three spatial axes compared on those in size range of up to 45 μm . Consequently, the compensation of repulsive forces of disjoining pressure and gravity by the hydrostatic pressure of surrounding water in the case of particle size range of up to 250 μm was less expressed.

Comparison of various models of the epigenetic situation, when the powder specimen consists of several layers of particles (40 kPa, fig. 1b), showed that samples D and M are the most stable, i.e. the dominance of clay minerals prevents particles' cohesion. Treatment of sample R with organomineral surfactant suspension increased the particles cohesion in both the dry and the wet conditions. However, the best clayey particles' cohesion was obtained for sample RS. In both cases (R-treated and RS), clays contained organomineral complexes at a higher concentration than in other samples.

3.2 Wetting Contact Angle

The average CA values (fig. 2a) for sample R, calculated for more than 20 positions on the surface of the specimens, are slightly scattered around 48° , regardless the applied external pressure. Simultaneously, for specimens with particle size range up to $45\ \mu\text{m}$, the dispersion in CA measurements decreased with external pressure; for preparations with particle size range of up to $250\ \mu\text{m}$ the dispersion in CA measurements increased with external pressure from 5 to 15–20 kPa, then reached plateau. Based on point 3.1, it can be assumed that higher external pressures consistently reduce the gaps between particles of smaller size range (up to $45\ \mu\text{m}$) hence cohesion forces prevail in the disjoining pressure for multi-layer powder preparations due to the decreased distance between particles less than $100\ \text{nm}$ [1], and further, the anisotropy in particle orientation relative to substrate is formed. Thus, with increasing external pressure, the homogeneity of the surface of clay preparation increases, and the dispersion in the CA measurements decreases.

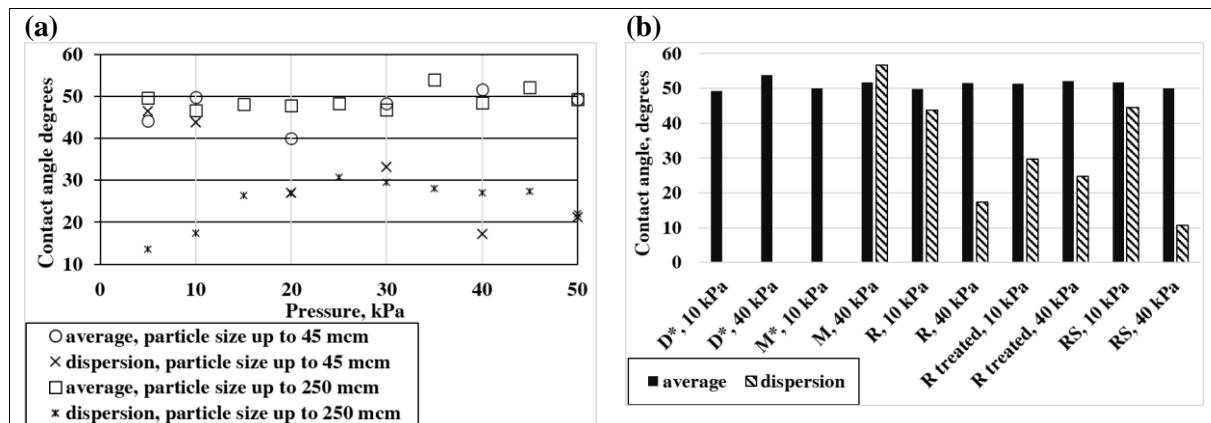


Figure 2. Wetting contact angle on the specimens under different external pressure applied
**For samples *D, *M non-robust values are given, because their tiny particles quickly formed colloidal system in water volume, so water in the measuring chamber turned into “milk”.*

The difference in epigenetic situations models (fig. 2b) did not affect on the mean CA values, however, it affected their dispersion. Accepting CA dispersion as an indicator of surface heterogeneity one can conclude that the surface of specimen RS was the most homogenous, and specimen M was pretty heterogeneous. The treatment of clay with suspension of organic surfactants (R-treated) increased surface heterogeneity. These two facts suggest that organic matter introduced into the soil has a non-uniform patchy spatial distribution (R-treated), but autochthonic organic matter (RS) has more uniform distribution. Based on significant decreasing in CA dispersion at an external pressure of 40 kPa it can also be assumed that in this case the influence of roughness factor on clay surface properties is partially excluded.

3.3 Clay Samples' Compression Tests

Inflection points were detected characterizing the beginning of the greatest compaction regime (fig. 3): at 10 kPa for sample R and at 20 kPa for sample RS. The data obtained on the change in the samples' porosity were substituted into Cassie-Baxter equation (2) as a fraction of substrate material for approximate calculations. CA for the substrate with rubber glue was 90° , herewith observed CA for clay surface about 40° - 50° could be formed only at sample porosity 0.1-0.4, and porosity values obtained should lead to CA 65° - 75° . Therefore, in the cases considerate, the porosity cannot be equated to a fraction of substrate material, i.e. the boundary clay specimens' layers were compacted more tightly than the underlying ones due to the preferred clayey particles' orientation in plane and filling the gaps.

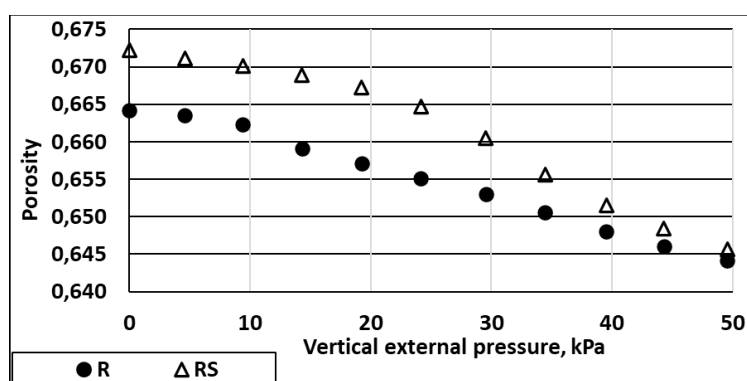


Figure 3. Clay samples' compaction under different applied external pressure

4. Conclusions

Maximum compaction of clay powder on the specimens was reached under applied external pressure of 20-30 kPa. Further, at 40 kPa, obviously, the second clayey layer was formed. Boundary clay specimens' layers were compacted more tightly than the underlying ones due to the preferred particle orientation in plane appeared and filling the gaps between particles. For particle size range of up to 45 μm , clay layer retained on substrate under hydration was thinning slighter than for ones of size range up to 250 μm . During the formation of the second layer of particles on specimens, the predominance of clay minerals broke the cohesion of the particles; the introduction of organomineral surfactants increased the cohesion of clay particles at dry and wet conditions. If these surfactants were fresh input into a clay, surface heterogeneity increased. Hypothetically the influence of roughness on the properties of the clay surface clearly diminishes at higher external pressure of 40 kPa. The wettability of all the considered powders of carbonate rocks practically coincided on average.

5. Acknowledgement

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