Modification of clays subjected to different stages of lithogenesis under microbial activity

O A Sofinskaya¹, R M Usmanov¹, E A Korolev¹

¹Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, Russian Federation
E-mail: ushik2001@mail.ru

Abstract. A comparative study of the influence of microorganisms on physical-chemical clays’ properties at different lithogenetic stages concerned the formation of contact strength between particles was carried out. Natural samples were taken for experiments: dolomite-clay marl from outcrop, the Jahorina mountains, the Dinaric Alps, Bosnia and Herzegovina; alluvial loam from spring, West side of the Onega Lake, Konchezero village, Karelia Republic, Russia; bentonite from the Biklyan deposit, Tatarstan Republic, Russia; phyllite from outcrop, Les Sybelles, Rhone Alps, France. The microbial community was added into moistened clays for 2–4 months. Before and after the experiments such analyses were conducted: X-ray powder diffractometry, determination of water content in clays, maximum hygroscopicity, dry bulk density, total organic carbon, macroscopic wetting contact angle, liquid and plastic limits; incremental loading oedometer test, ion chromatography of filtrate. The microbial activity enhanced the hydrophilicity of marl and phyllite. Multidirectional factors of toughness formation acted in clays subjected to stages between sedimentogenesis and late diagenesis, among which organic matter content dominated.

1. Introduction

The purpose of the study was to examine the influence of physical-chemical factors on the compressive strength of clays at different stages of their formation. These factors include the clay particles structure, their ability to retain water films, the hydrophilicity of their interfaces, the presence of cations and organic matter, the activity of microbial community. Strength and deformation characteristics of clays depend on the ratio of the potential energy of particle adhesion to each other and the kinetic energy caused by external influences [1]. Consequently, an impact on particles adhesion forces changes the compressibility of clays. Particularly, it is expressed by the modification of the surface energy of clay particles using surfactants. For example, surfactants are released into clays as products of microbial activities (polysaccharides, proteins, nucleic acids) recharging the surface of clay minerals [2, 3]. The latter process depends on the interfacial tension of biofilms determined by the combination of phases in clays, taxa of microflora as well as stage of microbial activity [4, 5]. There are three types of contacts between clay particles: point to point, coagulation and physisorptive ones [1]. Each of these types appears under certain conditions and certain stages of clay formation [6]. Young clay deposits as well as sedimentary rocks under weathering (e.g. marls) are characterized by the predominance of the weakest long-range coagulation contacts. As clays pass diagenesis the number of more durable short-range coagulation contacts increases (e.g. bentonite clays). Lithification during catagenesis causes the clay
overconsolidation and cementation and the appearance of phase contacts (e.g. phyllites, argillites). In addition, the presence of cations in interlayer spaces of clay minerals affects the strength of contacts between particles and manages their hydrophilicity. With higher hydrophilicity less hydrophobic contacts between the particles are possible and the toughness of the clay matter increases. The presence of cations with a large ionic radius contributes to a decrease in hydrophilicity, and vice versa [6]. The study tested the hypothesis that microorganisms - lithobionts are able to affect the strength of contacts between clay particles.

2. Objects and methods

Natural samples - representatives of various stages of clay lithogenesis were taken for experiments (table 1): 1) the weathered sedimentary rock was dolomite-clay marl from outcrop, 2) the rock at the stage between sedimentogenesis and diagenesis was alluvial loam from spring, 3) the rock at the late diagenesis stage – bentonite from mine, 4) the rock at the catagenesis stage - phyllite from outcrop. The microbial community consisted of microorganisms - lithobionts isolated from oil-contaminated soil and the commercial inoculum based on aerobic and anaerobic heterotrophs (Bacillus, Streptomycetes, Lactobacillus) producing viscous biopolymers and releasing phosphorus and potassium from insoluble organic compounds. The culture medium with the microbial community was inoculated into clays to create a dry weight concentration of 1 %. Clays crushed, sieved through 250 microns, moistened to state of full water capacity and thoroughly mixed were placed into sealed containers for 2-4 months. Before and after the experiments such analyses were conducted: X-ray powder diffractometry, X-ray images decoding using Crystallographic and mineralogical database WWW-MINCRYST (http://database.iem.ac.ru/mincryst/rus/index.php); determination of water content in clays (ISO 11465:1993), maximum hygroscopicity (the Nicolaev’s procedure), dry bulk density (ISO 11272:2017), organic carbon by sulfochromic oxidation (ISO 14235:1998), macroscopic wetting contact angle [7], liquid and plastic limits (ISO 17892-12:2018); incremental loading oedometer test (ISO 17892-5:2017) using the hardware complex ASIS 3.2 (Geotech, Russia). The loading oedometer tests excluding the possibility of the specimen expansion were carried out after specimen was completely saturated with water in the oedometer ring at a fixed packing density. The calculation of the oedometric deformation modulus was carried out according to the formulas:

\[ E_i = \frac{\Delta P_i}{\Delta \varepsilon_i} \]  
\[ \varepsilon_i = \frac{\Delta h_i}{h_i} \]

where \( \Delta P_i \), \( \Delta \varepsilon_i \) – are the pressure difference and the difference in relative deformations between the beginning and the end of the i-th load stage, \( h_i \) – is the height of specimen in the oedometer ring, \( \Delta h_i \) – is the absolute deformation of specimen at the i-th load stage.

The macroscopic clay wetting contact angle was estimated using the captive bubble method on clay powders pressed under a pressure of 10 kPa and immersed into water [7]. To assay the mobility of some cations filtration experiments in 3 ml microlysimeters packed with experimental clays compared to samples treated using the antiseptic Basic Green 4 were performed. The filtrate composition dynamics was determined by ion chromatography on an analyzer Dionex ICS 1600.

3. Results and Discussions

The liquid limit for sample “A” was 0,76 of its full water capacity, for sample “B” – 0,93 of its full water capacity, as the plastic limits for the same samples were 0,53 and 0,57 of their full water capacities, respectively. After the treatment with the microbial community sample “A+” lost its resilience at 0,74
and sample “B+” at 0.98 of their full water capacities. The plastic limit achievement by sample “A+” is observed at the same moisture that by sample “A”, but by the sample “B+” it occurred at the higher moisture than by sample “B” (0.63 of its full water capacity). Thus, the strength of coagulation contacts in sample “A+” decreased while in sample “B+” increased due to microbial activity compared to the initial options. The microbial activity in sample “B+” and the complete removal of organic matter from sample “B” enhanced the oedometric deformation modulus (figure 1) calculated as in equation (1).

**Table 1.** Scheme of experiment design.

| Sample     | Sign | Treatment type                                           | Origin                                      |
|------------|------|----------------------------------------------------------|---------------------------------------------|
| Marl       | M    | Initial sample                                           | the Jahorina mountains, the Dinaric Alps, Bosnia and Herzegovina |
|            | M+   | Microbial community within culture medium, 1% to abs.dry weight, during 130 days |                                            |
| Alluvial loam | A    | Initial sample                                           | West side of the Onega Lake, Konchezero village, Karelia Republic, Russia |
|            | A+   | Microbial community within culture medium, 1% to abs.dry weight, during 70-100 days |                                            |
|            | Aa   | Antiseptic, during 100 days                              |                                            |
| Bentonite  | B    | Initial sample                                           | The Biklyan deposit, Tatarstan Republic, Russia |
|            | B+   | Microbial community within culture medium, 1% to abs.dry weight, during 70-100 days |                                            |
|            | Ba   | Antiseptic, during 100 days                              |                                            |
|            | B0   | Organic matter combusting under 600°C                    |                                            |
| Phyllite   | F    | Initial sample                                           | Les Sybelles, Rhone Alps, France            |
|            | F+   | Microbial community within culture medium, 1% to abs.dry weight, during 130 days |                                            |

**Figure 1.** The toughness of bentonite under different experimental conditions.
However, the microbial community did not change the total organic carbon in sample “B+” (table 2), that is, the contact strengthening between bentonite particles could occur due to the change in surface properties of organic matter during its biotransformation.

According to X-ray diffraction analysis, sample “A” had the larger contents of muscovite and kaolinite than sample “B”, which had montmorillonite as the dominant phase. The ability to keep the hydration shell on surface decreases in the sequence: kaolinite → muscovite → montmorillonite [6], therefore, on the average, it was larger for sample “A” than “B”. At the same time, montmorillonite has a much more developed internal surface, which affected its highest hygroscopicity (table 2). Maximum hygroscopicity increased significantly in samples “M+” and “F+” compared to “M” and “F”, i.e. herewith the ability to keep water films and adsorbed water as well as capillary condensation increased (table 2).

### Table 2. The main characteristics of clays before and after the experiments.

| Samples | The main minerals | Associated minerals | Maximum hygroscopicity, % in abs. dry weight | Total organic carbon, % in abs. dry weight | Wetting contact angle at the clay – water – air interface, degrees | Liquid limit – Plastic limit, % |
|---------|------------------|---------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------------------------|-----------------------------|
| M/ M+   | Chlorite, muscovite, albite, dolomite | calcite, pyrite | 4.2/ 5.1±0.3 | 0.33/ 0.81±0.01 | 56°/ 41°±5° | - |
| A/ A+   | Albite, muscovite, chlorite, kaolinite, microcline | pyrite, amphibole | 5.4/ 5.6±0.3 | 3.42/ 2.49±0.01 | 48°/ 60°±5° | 12.2/ 11.1 |
| B/ B+/ Ba | Montmorillonite, muscovite, kaolinite, microcline | clinohlorite | 16.9/ 17.2±0.9 | 0.88/ 0.85±0.01 | 47°/ 50° | 23.2/ 23.0 |
| F/ F+   | Chlorate, muscovite, mixed-layer | microcline | 2.4/ 6.3±0.2 | 0.9/ 1.36±0.06 | 68°/ 50°±6° | - |

The increase in hygroscopicity possibly occurred due to sites possessed high wetting contact angle (reached 88°) disappeared from the specimens’ surfaces after the experiment. The hydrophilicity of the sample “B+” surface did not change while for sample “A+” it decreased. To separate factors impacting the surface hydrophilicity from each other — time of hydration and microbial activity — bentonite samples inoculated with microflora and antiseptically treated were compared. Average wetting contact angles on the surface of initial, inoculated and antiseptically treated samples “B”, “B+” and “Ba” did not differ (table 2). Herewith, the biofilm formed with the inoculate itself was tested on the smooth glass surface: the biofilm did not significantly affect the glass average wetting contact angle, but formed separate sites where the contact angle reached 89°. Sites with reduced hydrophilicity were also formed on surfaces of samples “A+” (up to 84°) and “B+” (up to 68° compared to 52° on “B”). Hydrophobic surface could be formed by microorganisms, rather, in the inhabited clay pores. Most pores in clays are smaller than they require (>2-5 microns) and therefore these pores remained unaffected by biofilms. Thus, biofilms could not affect the macroscopic wetting contact angle of clays directly, but are able to
take part in the formation of clay hygroscopicity releasing biosurfactants. In practice, the microbial community caused the hydration of external and internal surfaces of samples “M4+” and “F+” as well as the partial hydrophobization of mesopores in sample “A+” increased. The effect of the inoculation on the hydration of sample “B+” was not observed in the study.

According to data obtained in the microlysimetric experiment, the treatment by microorganisms enhanced the mobility of K+, Ca2+, Na+ cations in samples “A+” and “B+” and accelerated Mg2+ outflow in sample “B+”, compared to samples “Aa” and “Ba”, respectively (table 3).

At the same time, there no decrease in the strength of sample “B” due to the higher mobility of some cations occurred in the experiment, i.e., possibly, they were replaced by other cations. Besides, microorganisms could release substances neutralized the surface charge of minerals amplifying hydrophobic contacts and their total strength. In sample “A+” the outflow of Mg2+ ions was slowed down compared sample “Aa”, consequently, cations in the interlayer spaces of muscovite could substitute by magnesium. Among the main cations, magnesium has the smallest ionic radius and the largest ability for ion-dipole interactions [6], so these substitutions could cause increase in hydrophilicity of internal space and appropriate decrease in the contact strength after sample “A+” had been moistened.

Table 3. Total ion outflow during 100 days of microlysimetric experiments with the microbial community, mg.

| Samples | Ca2+ | Mg2+ | Na+ | K+ | SO42- | Cl- | PO43- | F- | Br |
|---------|------|------|-----|----|-------|-----|-------|----|----|
| A+      | 3.358| 0.664| 0.577| 2.803| 0.938 | 2.696| 0.008 | 0.049 | 0.002 |
| Aa      | 2.088| 0.579| 0.263| 1.120| 0.775 | 0.906| 0.001 | 0.018 | 0.001 |
| B+      | 5.441| 1.267| 5.798| 1.160| 8.329 | 3.638| 0.000 | 0.089 | 0.071 |
| Ba      | 2.134| 0.448| 3.142| 0.514| 9.686 | 2.452| 0.000 | 0.018 | 0.001 |

4. Conclusions

The microbial activity enhanced the hydrophilicity of both the external and the internal surface of marl and phyllite. It was detected that in clays subjected to stages between sedimentogenesis and late diagenesis, the strength of contacts between particles was not associated either with macroscopic surface properties or with hygroscopicity. Most likely, multidirectional factors of toughness formation acted in clays, among which organic matter content dominated: its complete removal from clay enhanced the compressive strength of bentonite; the organic matter transformed by microorganisms strengthened bentonite, but reduced the strength of unconsolidated alluvial loam.

Acknowledgments

This work is supported by Russian Foundation for Basic Research, project number 20-05-00151

References

[1] Urjev N B 2018 High-concentration dispersed systems and materials (Moscow, Russia: Techpolygraphcentr) (in Russian)
[2] Sergeeva I P et al 2013 Cationic electrolyte adsorption layers on hydrophilic and hydrophobic surfaces Colloid J. 75 202-206
[3] Tarasevich Yu I et al 2013 A microcalorimetric study of the interaction between water and poly(hexamethylene-guanidine)-modified kaolinite surface Colloid J. 75 117-120
[4] Wan J and Wilson J L 1994 Visualization of the role of the gas-water interface on the fate and transport of colloids in porous media Water Res. Res. 30 11-23
[5] Mitik – Dineva N et al 2009 Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus aureus Attachment Patterns on Glass Surfaces with Nanoscale Roughness Current Microbiology 58 268-273
[6] Osipov V I and Sokolov V N 2013 Clays and their properties. Composition, structure and formation of properties (Moscow, Russia: GEOS)
[7] Drelich J W 2019 Contact angles: from past mistakes to new developments through liquid-solid adhesion measurements Adv. in Colloid and Interface Sci. 267 1–14