Investigation of Formation Laws of Clays Composition under High Pressures

Valeriy V. Seredin[1], Alexander V. Rastegaev[2], Vladislav I. Galkin[3], Panova E.G.[4*], Tatyana Yu. Parshina[5]

[1]Professor and Head of engineering geology department of Perm state national research university
[2]Professor of oil and gas geology department of Perm national research polytechnic university
[3]Head of oil and gas geology department of Perm national research polytechnic university
[*4]Professor of geochemistry department, institute of Earth science, Saint- Petersburg state university
[5]Graduate student of engineering geology, department of Perm state national research university

Abstract— *It is found experimentally, that while building-up of pressure applied to natural clay, observed is general tendency of clay fraction content decrease and pulverescent fraction content increase. In montmorillonite natural clay, granulometric changes progress more intensively, than in kaolinite one. Within the pressure range of 0 – 125MPa processes of change of natural clay fractional compositions progress more intensively, than at higher pressures. Under pressures within the ranges of 125-750MPa and 800-2200MPa revealed is different intensity of natural clay fractional compositions formation. Based on pressure index, three classes are defined; each is featuring different intensity of aggregation and dispersion processes progressing. While compression of natural clay defects are formed on crystallite surfaces, increasing energy potential of crude ground. Additional energy enables formation of molecular attractive forces, which cause particles aggregation.*

Keywords— ***Clay, Pressure, Granulometric Analysis, Fraction, Kaolin, Montmorillonite.***

I. INTRODUCTION

Natural clay properties are defined, to a large extent, by specific area of particle active surface, which can be controlled by granulometric or micro-aggregative ground compositions. In the processes of sedimentation, diagenesis, hypergenesis and technogenesis, «primary» particles of natural clays are transformed to «secondary» particles, forming micro-aggregates.

The issues of micro-aggregates formation in grounds are presented in the following studies [Krivosheeva et al., 1977; Osovetsky, 1993; Osipov, Sokolov, 2013; Savko, 2015]. Thus, the consider of information on formation of granulometric and micro-aggregative composition of natural clays during the processes of their natural formation and transformation. In previously investigations the data on natural clays, exposed to technogenic effect by the following solutions $MgCl_2$, $CaCl_2$, KCl and NaCl [Seredin et al., 2013; Seredin, 2014]. Authors concluded that aggregation process is connected with concentration of salt solution and mineral composition of particles. «Primary» particles of natural clays, exposed to oil contamination are connected between each other by electrostatic forces, which are determined by contamination volume and type of hydrocarbons [Boiko et al., 2009; Seredin, Yadzinskaya, 2014; Ilic et al., 2016].

Effect of mechanical factor is of importance, for example, effect of pressure on formation of aggregates in dispersed crude grounds [Krivosheeva et al 1977; Stefani et al., 2014; Friedlander et al., 2016]. The studies carried out [Sergeev, 1946] exhibited, that under pressures to 200 MPa, observed is insignificant change of crude ground aggregative compositions. Under pressure of 300 MPa applied to pulverescent ground, content of fine sand fraction increased from 13% to 51%, pulverescent fraction from 5% to 23%, and clay one from 2,15% to 5,42%. Hence it appears, that formation of clay aggregates at natural conditions as the result of mechanical exposure, progresses in rather limited volumes. While testing of blanket loams under pressures of P=2000 MPa and P=3660 MPa analogous results were received [Sergeev, 1946 a]. Procedures of prediction of ground granulometric compositions regarding not only earthy grounds [Boiko et al, 2009], but moon ones as well [Korolyov, 2016] are being developed based on experimental investigations.

The above mentioned discloses, that issues of pressure effect on formation of natural clay micro-aggregative compositions are studied not thoroughly enough. In this connection, the aim of the study is investigation of formation of natural clay micro-aggregative compositions exposed to high pressure.

II. SUBJECT, TESTING METHODS AND INVESTIGATION PROCEDURES

Subjects of investigation are montmorillonite and kaolinite natural clays. Under the results of X-ray diffraction analysis, montmorillonite natural clay consists (mass. %) of: montmorillonite – 75; kaolin - 3,6; quartz - 11,4; albite - 6,7; calcite - 3,3. Kaolinite natural clay contains (mass. %): kaolin - 76,7; montmorillonite – 15,6; quartz - 7,7.

High pressure device (was developed and produced to apply pressure to clay samples (Fig 1). Test spaces of the device (pos. 3, Fig.1) were produced out of hard-alloy material, their area constituted $S=0,75sm^2$. Press PLG-20 mark was used as loading device.

Preparation of clay samples for granulometric analysis was provided as follows: initial clayey ground (powder) was grinded in mortar by pistil. It was followed by mounting of the ground sample of about 0,2 g mass in testing space (pos. 3, Fig.1) of the device. Then press (pos. 6, Fig .1) was used to apply vertical pressures to the ground under the following scheme: the first stage - initial material (P=0 MPa), the second and subsequent stages – vertical pressure was increased by P=10-50 MPa. Maximum pressure constituted P=2200 MPa. Then upper holder (pos. 2, Fig.1) traveled relative to lower holder (pos. 1, Fig.1) by 90° by turning handles (pos. 4, Fig.1).

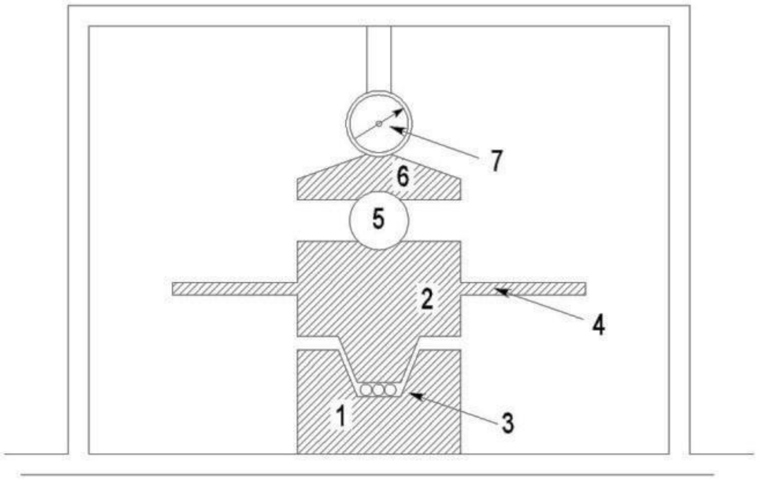


FIG.1. SCHEME OF DEVICE TO STUDY GROUNDS AT HIGH PRESSURES
1-lower holder; 2-upper holder; 3-test space of 0,75 sm² area;
4- handles to turn upper holder; 5-centering ball; 6-upper plate of loading device (press); 7- recorder to record load transferred to ground.

Natural clay granulometric composition was defined using laser diffraction-type analyzer «Analizette-22 MicroTec plus» under the procedure, described in [Seredin et al, 2017]. The device capabilities allow to provide diagnostics of 0,08 µm to 20000 µm size particles. In the studies of [Lepoytevin et al., 2014; Sun D et al., 2015] it was disclosed, that fine clay fraction, the sizes of which are lower, than 1 µm, defines, to a large extent, physicochemical properties of clays. That is why, on the basis of the device capabilities and significant effect of fine-dispersed particles on ground properties, we investigated the following fractions: $F_{<0,1}$, $F_{0,1\text{-}0,2}$, $F_{0,2\text{-}0,5}$, $F_{0,5\text{-}1}$, $F_{1\text{-}2}$, $F_{2\text{-}5}$, $F_{5\text{-}50}$.

There were carried out 319 identifications of granulometric composition of montmorillonite and 385 – of kaolinite natural clays. To evaluate changes of clay crystal lattice parameters there was provided X-ray diffraction analysis using the diffractometer «D2 Phase Bruker». The device characteristics: X-ray tube with copper anode (radiation – Cu Kα, λ=1,54060 Å), generator, voltage – 30 кW, current strength – 10 мA; linear detector – LYNXEYE; filter – Ni.

Representative sample hanging was abraded with alcohol in agate mortar to the sizes of 20-40 мсм, it was followed by its mounting in cuvette, and then diffraction pattern survey was provided. The survey conditions: divergent slot 0,2 mm, Soller's slots – primary 2,5°, secondary 2,5°; angular range 5 to 70° 2θ; impulse rate increase at each point 1,0 sec; pitch – 0,02°. The survey of oriented preparations was carried out within the interval of 4 to 35º 2θ.

The oriented preparations were produced out of clay fraction aqueous suspension by deposition on degreased slides, followed by drying at room temperature. One sample (air-dry) was surveyed, two next were additionally treated: saturation with glycerin during 24 hours, ignition in muffle furnace during 1 hour at the temperature of 600˚C.

The program «Diffrac Eva» was used for processing of curves, measurement of basal reflection width at height midpoint, as well as its area.

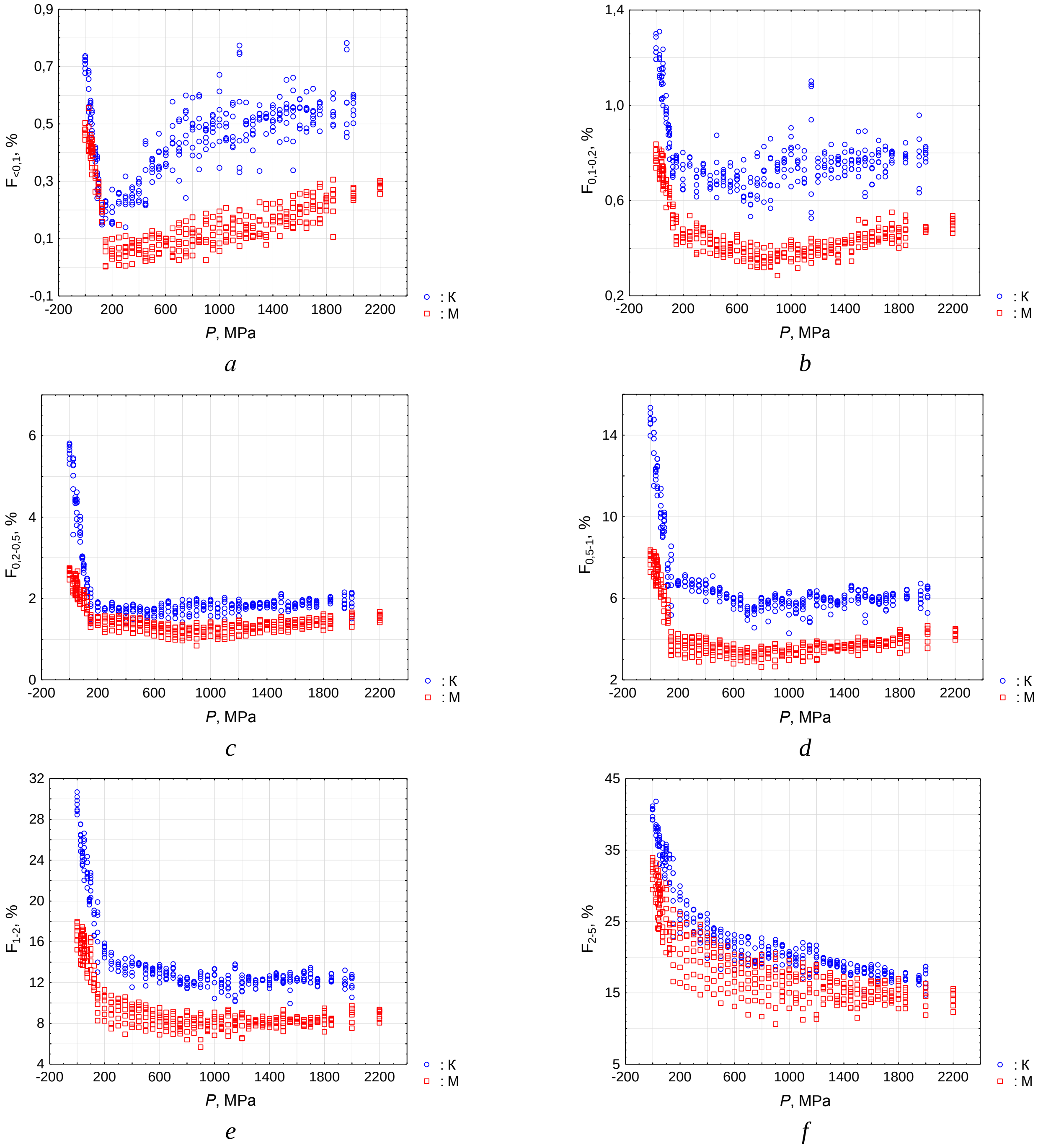
III. RESULTS AND DISCUSSION

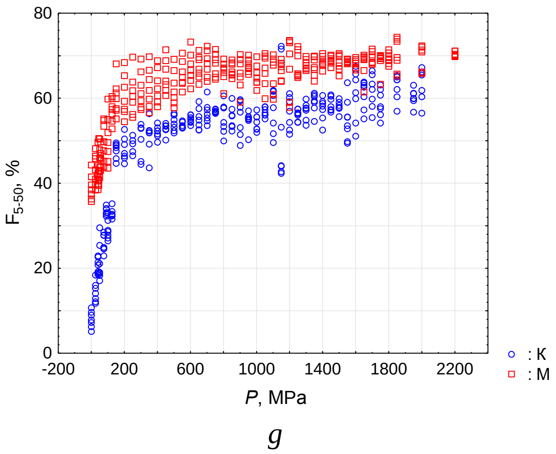
The study was carried out in successive steps**.**

At the first stage investigated was effect of natural clay mineral compositions on change of ground fractional compositions, subjected to pressure.

Granulometric studies revealed, that in initial samples of montmorillonite and kaolinite natural clays, fraction content, accordingly, is as follows (mass %): $F_{<0,1}$ - 0,48 and 0,70; $F_{0,1\text{-}0,2}$ - 0,77 and 1,22; $F_{0,2\text{-}0,5}$ - 2,66 and 5,54; $F_{0,5\text{-}1}$ -8,30 and 14,8; $F_{1\text{-}2}$ -17,73 and 30,10; $F_{2\text{-}5}$ - 32,95 and 41,22; $F_{5\text{-}50}$ - 37,11 and 6,42.

Change of clay fractional compositions at pressure build-up is shown in Fig. 2.





К – kaolin,
M – montmorillonite

FIG. 2. CHANGE OF FRACTIONAL COMPOSITION OF MONTMORILLONITE (M) AND KAOLINITE (К) OF NATURAL CLAYS UNDER PRESSURE. FRACTIONS: *a* - $F_{<0,1}$, *b* - $F_{0,1\text{-}0,2}$, *c* - $F_{0,2\text{-}0,5}$, *d* – $F_{0,5\text{-}1}$, *e* - $F_{1\text{-}2}$, *f* - $F_{2\text{-}5}$, *f* - $F_{5\text{-}50}$

It is evident in figure, that correlation fields have approximate behavior for different fractions. However, fraction correlation fields $F_{<0,1}$–$F_{2\text{-}5}$ of kaolinite natural clay are positioned above applicable fields of montmorillonite natural clay, and on the contrary, for $F_{5\text{-}50}$ fraction. The above fact reveals, that pressure effects differently formation of fractional composition of kaolinite and montmorillonite natural clays that is: mineral composition of natural clays effects significantly change of clay fraction contents in ground, when compressed.

Statistical methods [Galkin, 2013] were used to confirm the conclusion on effect of natural clay mineral compositions on formation of their granulometric composition. The matter of them is that, if mineral composition effects change of crude ground fraction contents under pressures, statistical discrepancies will be observed between samples of kaolinite and montmorillonite natural clays. Measure of discrepancy is to be evaluated as per Student's criterion (t). In case, when the calculated value (t_p) is higher, than the tabulated one ($t_т$), it is considered, that mineral composition effects change of ground fraction contents under pressures. Student's criterion constitutes $t_т$=0,03 at the degrees of freedom $к=n_1+n_2-2=704$ and the significance level α=0,05. Calculated statistical parameters are exhibited in table 1.

TABLE 1
CLAY STATISTICS

Fractions, %	Kaolinite natural clay		Montmorillonite natural clay		Calculated value of Student's coefficient, t_p	Identification of samples, %		
	Mean	Stat. deviation	Mean	Stat. deviation		Kaolinite natural clay	Montmorillonite natural clay	Total
$F_{<0,1}$	0,45	0,14	0,18	0,12	25,9	80,0	85,9	83,0
$F_{0,1\text{-}0,2}$	0,79	0,15	0,47	0,12	29,2	93,4	85,0	89,1
$F_{0,2\text{-}0,5}$	2,18	0,94	1,51	0,40	11,8	42,3	83,4	63,3
$F_{0,5\text{-}1}$	6,96	2,29	4,26	1,42	17,8	83,6	83,4	83,5
$F_{1\text{-}2}$	14,64	4,54	9,67	2, 80	16,5	67,5	82,1	75,0
$F_{2\text{-}5}$	23,20	6,64	18,81	5,33	9,1	44,6	74,6	59,9
$F_{5\text{-}50}$	49,96	13,96	62,69	9,20	-13,5	58,4	81,8	70,4
Z	-1,76	1,02	1,68	0,98	-42,9	97,0	93,4	95,2

The table demonstrates, that calculated values of Student's coefficient for each studied fraction are higher, than $t_т$=0,03, so it can be concluded, that mineral composition effects significantly formation of crude ground fractional compositions subjected to pressure. Student's criterion reveals that samples are statistically different.

Linear discriminant analysis was used for quantitative estimation of differentiation. Calculation results of samples identification are shown in table1. The table exhibits, that maximum difference between kaolin and montmorillonite is observed for fractions $F_{0,1\text{-}0,2}$ and $F_{<0,1}$, and minimum – for fraction $F_{2\text{-}5}$. The rest of the fractions have intermediate position.

For them, t-criterion changes from 9,1 to 17,8, and total identification correctness – from 59,5 to 83,5%. It should be mentioned, that for prevailing majority, fractions of montmorillonite natural clay are identified better, than fractions of kaolinite natural clay.

Maximum difference of kaolinite natural clay from montmorillonite natural clay is observed as the result of complex analysis of all the fractions using step-by- step LDA. LDF expression is as follows:

$$Z = 3.32537 - 7.50608F_{0,1\text{-}0,2} + 3.15488F_{0,2\text{-}0,5} - 0.93596F_{1\text{-}2} + 0.32878F_{2\text{-}5},$$

at R = 0,86, χ = 854,3, multidimensional centers of groups Z_K = -1,76, Z_M = 1,68.

The calculations indicate that degree of sample difference of kaolinite natural clay from montmorillonite natural clay is maximum as per t-criterion (Table 1) and identification correctness, regarding both – total and each class value.

Thereby, it was found experimentally and proved statistically, that formation of micro-aggregative composition of kaolinite and montmorillonite natural clays has different scenarios, when compressed with shear. It can be explained from the position of mineral crystal lattice structures. One tetrahedral sheet and one octahedral sheet forming structural layer provide kaolin structure. They are connected between each other by hydrogen bonds, strength of which constitutes 5-40 кJ/mole [Osipov, Sokolov, 2013], that is why, kaolin crystal is featuring sufficient rigidity in common case. As to montmorillonite natural clay, structural layers consisting of two tetrahedral and one octahedral sheets are connected between each other by molecular bonds, strength of which twice and more as lower, than of hydrogen ones. Due to the abovementioned, montmorillonite crystal rigidity is lower, than that of kaolin. Therefore, processes of aggregation and dispersion progress more intensive in montmorillonite natural clays at application of vertical load and shear, compared to kaolinite natural clays. The result of this is that clay fraction content in kaolinite natural clay varies not so significantly, as in montmorillonite natural clays.

The second stage included investigation of pressure effect on general laws of natural clay micro-aggregative compositions change (revealing of classes).

Changes of natural clay fractional compositions at pressure build-up are shown in Fig 2. It is evident, that building-up of pressure to P=125 MPa leads to significant reduction of clay fraction ($F_{<5}$) contents and increase of pulverescent ($F_{5\text{-}50}$) fraction content. Content of clay fractions changes differently directed, and pulverescent one – increases under pressure build-up to P=750 MPa. Further building-up of pressure to P=2200 MPa results in increase of clay fraction contents and chaotic change of pulverescent fraction content.

Thus, with regard to qualitative feature, it can be assumed, that pressure effects formation of granulometric composition of natural clays. Two terminal pressures P=125 MPa and P=750 MPa are revealed, at which aggregation and dispersion processes have different intensity of progressing.

Linear discriminant analysis (LDA) was used to confirm the assumption on availability of terminal pressures of P=125 MPa and P=750 MPa, the main point of which is that, if boundaries between classes are acceptable, then there should be maximum identification between them (classes) [Galkin, Silaycheva, 2013]. For this purpose, all samples were divided to three classes under the “pressure” criterion. Class 1 includes the experimental data (n=61) obtained at P=0÷125 MPa inclusive, class 2 – the data (n=91) at P=150÷750 MPa inclusive and class 3 – the data (n=167) at P=800÷2200 MPa.

Two discriminant functions for each were provided for kaolinite and montmorillonite natural clays: the first one – to validate the boundary between Cl.1 and Cl. 2 ($Z_{1\text{-}2}$), the second – between Cl. 2 and Cl. 3 ($Z_{2\text{-}3}$). The natural clay fractional compositions data were used for calculations.

For kaolinite natural clay the following functions were obtained:

$$Z_{K\,1\text{-}2} = -43,0310 - 3,0265F_{<0,1} - 1,0016F_{0,1\text{-}0,2} + 1,9803F_{0,2\text{-}0,5} + 1,5040\,F_{0,5\text{-}1} - 0,3170\,F_{1\text{-}2} + 0,2595F_{2\text{-}5} + 0,6258\,F_{5\text{-}50}$$

Multidimensional centers of classes: $Z_{Cl.1}$ = -4,54344 and $Z_{Cl.\,2}$ = 2,79596,

R = 0,96, χ^2 =52,01.

$$Z_{K\,2\text{-}3} = -32,4909 + 21,3266F_{<0,1} + 11,5974F_{0,1\text{-}0,2} + 9,8014F_{0,2\text{-}0,5} + 1,0194\,F_{0,5\text{-}1} - 1,7571\,F_{1\text{-}2} + 0,6667F_{2\text{-}5} - 0,0143F_{5\text{-}50}$$

Multidimensional centers of classes : $Z_{Cl\,2}$ = -3,26488 and $Z_{Cl.3}$ = 1,8437,

R = 0,93, χ^2= 60,96.

For montmorillonite natural clay LDF are as follows:

$Z_{M\ 1\text{-}2}$ = -38,8093 – 0,7017$F_{<0,1}$ – 3,0345$F_{0,1\text{-}0,2}$ - 1,6975$F_{0,2\text{-}0,5}$ +1,7205$F_{0,5\text{-}1}$ + 2,4931$F_{1\text{-}2}$ - 0,4997$F_{2\text{-}5}$ + 0,3155 $F_{5\text{-}50}$

Multidimensional centers of classes: $Z_{Cl.1}$ = 5,17712 and $Z_{Cl.2}$ = -3,58416,

R = 0,98, χ^2 = 50,55.

$Z_{M\ 2\text{-}3}$ = 61,7964 + 41,3331$F_{<0,1}$ – 6,8428$F_{0,1\text{-}0,2}$ – 12,5794$F_{0,2\text{-}0,5}$ +2,2471$F_{0,5\text{-}1}$ – 0,2790 $F_{1\text{-}2}$ – 0,5695$F_{2\text{-}5}$ – 0,6605$F_{5\text{-}50}$

Multidimensional centers of classes: $Z_{Cl.2}$ = -2,96914 and $Z_{Cl.3}$ = 1,60828,

R = 0,91, χ^2 = 56,69.

Discriminant function calculations exhibited, that correct identification of all the samples constitutes 100%.

Thereby it is proved, that pressure terminal values P=125 MPa and P=750 MPa are well-grounded choice. That means, that each class has different intensity of aggregation and dispersion processes progressing, that is why conditions of natural clay fractional compositions formation are featuring their individual specific character as well.

The third stage concerned study of pressure effect on change of natural clay micro aggregative compositions, with regard to classes revealed *(inside classes).* Correlation analysis was provided, the essence of which is that, if observed are statistical relations ($r>r_T$, where r – pair correlation coefficient) between natural clay fractional compositions (F) and pressure (P), it is considered, that pressure effects formation of clay micro-aggregative compositions. It should be mentioned, that the tabulated value of correlation coefficient constitutes r_T=0,25 at α=0,05 and n=61 for class 1, r_T=0,20 at α=0,05 and n=91 for class 2 and r_T=0,17 at α=0,05 and n=167 for class 3. Let's consider correlation analysis results for each class.

Class 1 (P=0-125 MPa): mean content of clay fractions is lower, than that of initial sample (table 2). This change, probably, concerns clay particle aggregation processes, resulting in increase of pulverescent fraction $Ф_{5\text{-}50}$ content.

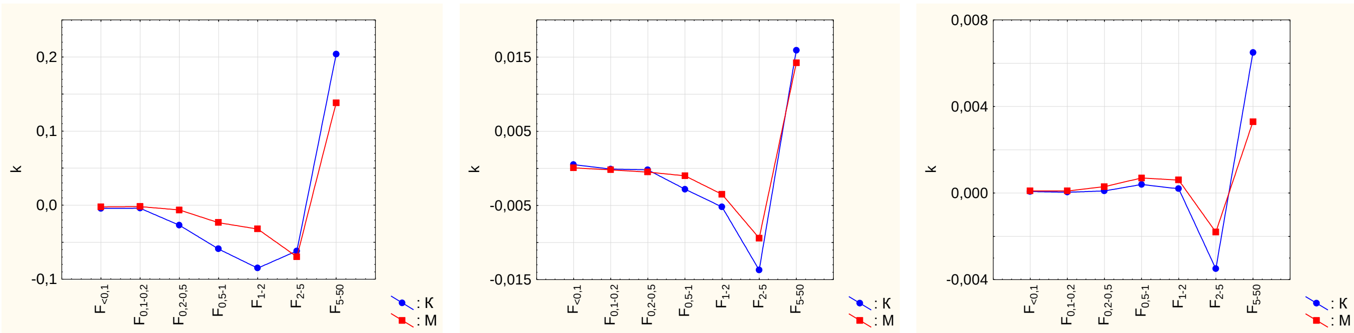
TABLE 2
MAIN STATISTICAL CHARACTERISTICS OF CLAYS

Fraction	Class	Kaolinite clay					Montmorillonite clay				
		$\bar{x}$	σ	r	a	k	$\bar{x}$	σ	r	a	k
$F_{<0,1}$	Cl.1	0,44	0,18	-0,98	0,7163	-0,0043	0,37	0,09	-0,93	0,5047	-0,0023
	Cl.2	0,32	0,11	0,83	0,1013	0,0005	0,07	0,04	0,36	0,0395	0,000069
	Cl.3	0,52	0,08	0,34	0,4190	0,000074	0,17	0,06	0,77	-0,0047	0,0001
$F_{0,1\text{-}0,2}$	Cl.1	1,01	0,17	-0,95	1,2735	-0,0042	0,69	0,08	-0,87	0,8030	-0,0019
	Cl.2	0,70	0,06	-0,46	0,7638	-0,0001	0,42	0,05	-0,70	0,4976	-0,0002
	Cl. 3	0,76	0,08	0,18	0,7033	0,000041	0,42	0,05	0,81	0,2618	0,0001
$F_{0,2\text{-}0,5}$	Cl.1	3,90	1,11	-0,97	5,5854	-0,027	2,23	0,29	-0,80	2,5963	-0,0064
	Cl.2	1,74	0,14	-0,29	1,8336	-0,0002	1,36	0,15	-0,62	1,5705	-0,0005
	Cl.3	1,85	0,13	0,38	1,6461	0,0001	1,33	0,15	0,69	0,9355	0,0003
$F_{0,5\text{-}1}$	Cl.1	11,20	2,44	-0,96	14,8988	-0,0591	6,96	0,99	-0,88	8,3198	-0,0236
	Cl.2	6,27	0,67	-0,78	7,5343	-0,0028	3,53	0,36	-0,55	4,0035	-0,001
	Cl.3	5,90	0,38	0,35	5,3675	0,0004	3,67	0,34	0,75	2,7079	0,0007
$F_{1\text{-}2}$	Cl.1	23,43	3,60	-0,94	28,7528	-0,085	14,97	1,67	-0,71	16,8207	-0,0322
	Cl.2	13,66	1,44	-0,68	16,0368	-0,0052	8,87	1,11	-0,59	10,4361	-0,0035
	Cl.3	12,18	0,65	0,08	11,9696	0,0002	8,18	0,64	0,32	7,4068	0,0006
$F_{2\text{-}5}$	Cl.1	35,72	2,85	-0,86	39,5856	-0,0617	27,67	3,51	-0,73	31,6779	-0,0697
	Cl.2	23,38	3,18	-0,81	29,6140	-0,0137	19,14	3,23	-0,55	23,3908	-0,0094
	Cl.3	18,86	1,57	-0,79	23,6591	-0,0035	15,40	1,92	-0,34	17,8553	-0,0018
$F_{5\text{-}50}$	Cl.1	23,02	8,70	0,93	10,2629	0,2036	46,31	6,32	0,80	38,3612	0,1381
	Cl.2	52,57	3,69	0,81	45,3052	0,0159	64,07	4,65	0,57	57,6770	0,0142
	Cl.3	57,69	4,83	0,47	48,7852	0,0065	67,93	2,93	0,42	63,3412	0,0033

Notes: $\bar{x}$ – mean value, σ – standard deviation, r – correlation coefficient, a –free term of the equation, *k* – angular coefficient, tangent of line inclination in equation of P and F relation.

Calculations revealed that statistical relations are provided between P and F, the evidence of which is significant coefficients of pair correlation (Table 2). Availability of negative values r between P and $F_{<5}$ confirms our conclusion that, content of clay fractions is reduced, if pressure increases. Positive values r between pressure and content of pulverescent fraction, on the contrary, prove that build-up of pressure causes increase of $F_{5\text{-}50}$ content.

To evaluate degree of pressure effect on change of investigated fraction contents, there is used index *k* – angular coefficient, which is the tangent of line inclination in equation of pressure P and F relation. It can be interpreted as follows: the higher are *k* values; more is effect of pressure on change of investigated fraction content. Calculation results are presented in Table 2 and Fig. 3.



Cl.1 Cl.2 Cl.3

FIG. 3. DEPENDENCE OF PRESSURE EFFECT DEGREE ON CHANGING OF INVESTIGATED FRACTION CONTENTS FOR KAOLINITE AND MONTMORILLONITE NATURAL CLAYS REFERRING TO CLASSES 1, 2 AND 3

The figure illustrates, that less is particle size, less is effect of pressure on these fraction contents change, meanwhile, the most sensitive to pressure is pulverescent fraction $F_{5\text{-}50}$, and less sensitive – clay fraction $F_{<0,1}$. It should be mentioned, that fractions $F_{1\text{-}2}$ and $F_{2\text{-}5}$ of montmorillonite and kaolinite natural clays, accordingly, are subjected to pressure more among all the clay fractions.

Rate of clay fraction contents change at pressure increase in kaolinite natural clay is higher, compared to montmorillonite one; higher values of *k* index are evidence of the abovementioned (Fig. 3).

Class 2 (P=150÷750 MPa): similar to class 1, reduction of content of clay fraction $F_{<5}$ and increase of pulverescent fraction $F_{5\text{-}50}$ are observed (Table 2). For fraction $F_{<0,1}$ different law is exhibited: build-up of pressure results in increase of $F_{<0,1}$ content, conditioned by dispersion processes of another fractions. Increase of $F_{5\text{-}50}$ content is connected with aggregation processes of clay particles to the sizes of pulverescent fraction.

There are statistical relations between P and F, significant coefficients of pair correlation prove it (Table 2). Hence it appears that pressure effects significantly formation of clay fractional compositions. The largest effect pressure has on formation of fraction $F_{5\text{-}50}$, the least – on formation of fraction $F_{0,1\text{-}0,2}$ (Fig.3).

Among all clay fractions, the most sensitive to pressure is fraction $F_{2\text{-}5}$. Meanwhile, pressure effects more kaolinite natural clay, compared to montmorillonite one, higher values of *k* index are evidence of the above mentioned.

Class 3 (P=800÷2200 MPa): effect of pressure on change of clay fractional compositions is basically different from classes 1 and 2. While pressure building up, content of all the fractions, except $F_{2\text{-}5}$ increases, confirmation of this are positive values r. There are statistical relations between P and F, significant coefficients of pair correlation are evidence of the above (Table 2). The largest effect pressure has on formation of fraction $F_{5\text{-}50}$, and the least – on formation of $F_{<0,1}$fraction.

Among all clay fractions, similar to foregoing classes, the most sensitive to pressure is fraction $F_{2\text{-}5}$. Meanwhile, pressure effects kaolinite natural clay more significant, compared to montmorillonite one, higher values of *k* index are evidence of the above mentioned.

Thus, reduction of clay fraction content and increase of pulverescent one – is the general tendency, while pressure build-up. Alongside with this law, each class shows local changes of clay fractional compositions content, subject to pressure. So, class 1 exhibits, that build–up of pressure P leads to decrease of clay fraction ($F_{<5}$) content and increase of pulverescent one. Class 2, taking into the account the abovementioned law (of class 1), demonstrates inversion only for the fraction of less, than 0,1 мсм, build-up of pressure causes increase of $F_{<0,1}$ content. Concerning class 3, formation of fractional composition is provided based on opposite to classes 1 and 2 scenario, that is, build-up of pressure results in increase of all fractions content, and F_{2-5} fraction, on the contrary is decreased.

The fourth stage included study of conditions of natural clay microaggregative compositions formation, when compressed. Change of content of natural clay ground fractional compositions are connected with particles aggregation and dispersion processes. Aggregation of particles is effected by pressure (compression) being exhibited as physicochemical processes, causing formation of new structural relations under the attractive forces [Osipov, Sokolov, 2013; Zhu et al., 2016]. Forces of compression and shear also effect dispersion (grinding) of particles, resulting in destruction of structural relations and grinding of particles.

The following assumption is the basis of clay particles aggregation process, caused by pressure applied to ground: when clay is compressed with shear (by displacement of device upper holder relative to lower one) additional energy centers should be provided on surface of ground particles. Due to free energy, structural relations are formed between particles, causing their aggregation.

To prove the abovementioned assumption, it was required to choose evaluation criterion of clay particle surface energy state. The investigation results analysis [Shlykov, 2006; Cora et al., 2014; Zhu et al., 2016] revealed, that it is available to use as the above criterion – the size of coherent –scattering region (CSR) of X-rays in the direction of ***c*** axis (crystallographic direction). This index correlates with particles structure (micro-assemblies) and their energy activity. Small values of CSR demonstrate that micro-assemblies have small sizes and are featuring high values of cation-exchange capacity, typical for kaolin [Shlykov, 2006]. Besides, the study [Radiography.., 1983; Trofimof et al, 2005] exhibited, that in case of CSR small value, there are, as usual, water molecules between micro-assemblies, which facilitate unrestricted displacement of sub-packings relative to each other, and this, in turn, leads to increase of particles energy activity. So, coherent–scattering region, expressed as Mк index (quantity of elementary layers in defect-free blocks) can be compared with cation-exchange capacity (CEC, as index of particle energy activity). In case of Mк > 40, CEC constitutes 2-5 mg-equiv/100 g, at Mк=40-25 capacity is increased to 6-12 mg-equiv/100 g, and at Mк<25 capacity takes the value of CEC>12 mg-equiv/100 g [Shlykov, 2006].

The results of diffractometer analysis carried out by us presented in table 3, do not conflict with the investigation Shlykov`s results.

TABLE 3
RESULTS OF CLAY DIFFRACTOMETER ANALYSIS

Clay	Pressure (P), MPa	Class	Diffraction angle, 2Θ	Interplanar spacing (d), Å	Half-width of basal reflection, B/2	Peak area (intensity of basal reflection)	Quantity of elementary layers in defect-free blocks, Mк
Montmorillonite	initial		6,061	14,570	0,574	4,988	16,6
	0-125	1	6,230	14,173	0,631	3,054	14,7
	150-750	2	6,243	14,148	0,600	1,836	15,6
	800-2200	3	6,202	14,242	0,523	0,961	17,7
Kaolinite	initial		12,348	12,162	0,386	4,271	26,3
	0-125	1	12,324	7,176	0,435	3,153	20,7
	150-750	2	12,321	7,178	0,441	2,953	20,3
	800-2200	3	12,323	7,177	0,476	2,577	18,8

The table exhibits, that when crude grounds are compressed, crystallite surfaces defectiveness (energy capacity) of montmorillonite natural clay is higher (M=14,7-17,7), than that of kaolinite natural clay (M=18,8-26,3). Hence it follows, that particle aggregation processes are more intensive in montmorillonite natural clay, than in kaolinite one. This conclusion conforms to the experimental data of the first stage of the studies.

Let's consider conditions of clay fractional compositions formation as per classes revealed.

Class 1. Extra energy centers are formed on crystallite surfaces at pressures from 0 to 125 MPa, due to defectiveness increase (displacement of crystal lattice vacancies or relative displacements of layers). Free energy of centers enables formation of molecular attractive forces, which cause aggregation of 0,1 мсм to 5 мсм particle sizes. Due to the abovementioned, there is observed decrease of clay fraction content and increase of pulverescent one in the experiment carried out. It should be mentioned, that if pressure range constitutes from 0 to 125 MPa, formation of extra energy centers on particle surfaces is more intense, than formation of 2 and 3 classes, numerical values of Мк index are confirmation of this.

Class 2. Defects on crystallite surfaces, probably, are «healed», at pressure build-up 125 MPa to 750 MPa in montmorillonite natural clay, that is why there is observed some increase of coherent–scattering region from Мк=14,7 – class 1 to Мк=15,6 – class 2. In kaolinite natural clays mean values of Мк practically do not change. Insignificant variation of Мк index confirms that energy potential on crystallite surfaces changes insignificantly as well. Thereby, clay particle aggregation processes are less intensive within the range of these pressures and in the first place effect change of fraction $F_{0,1\text{-}0,2}$ and $F_{1\text{-}2}$ contents.

Reduction of clay particles, except $F_{<0,1}$ fraction, reveals, that molecular attractive forces are formed between them causing their aggregation. It is important, that based on abovementioned law, for particle sizes of less, than 0,1 мсм, build-up of pressure results in increase of their content. The indication of this is, that energy on crystallite surfaces, composing $F_{<0,1}$ fraction, is realized in the form of electrostatic repulsion forces, that can lead to process of fraction particles dispersion. Meanwhile, the second scenario version is available: dispersion of larger fractions is provided, due to which content of $F_{<0,1}$ is increased.

Class 3. Pressures of 800 MPa to 2200 MPa cause further «healing» of defects on crystallite surfaces of montmorillonite natural clay, which is conditioned by some increase of coherent-scattering region from Мк=15,6 – class 2 to Мк=17,7 – class 3. This process reduces energy on crystallite surfaces. Kaolinite natural clays are featuring opposite law: CSR index is decreased from Мк=20,3 – class 2 to Мк=18,8 – class 3. Therefore, in kaolinite clay pressures of 800 MPa to 2200 MPa cause further deteriorations of crystallite surfaces, which are realized in the form of crude ground energy potential increase. Based on the results obtained, it can be concluded, that this class of montmorillonite natural clay is characterized mainly by dispersion processes and kaolinite one, on the contrary, by aggregation processes.

Thereby, compression of natural clay on crystallite surfaces causes mainly formation of the defects, which increase crude ground energy potential. Free energy enables formation of molecular attractive forces, which result in particles aggregation. Dispersion processes, being the result of particles grinding are provided in small volumes, which is not in conflict with the data [Sergeev,1946].

IV. CONCLUSION

1. It is found experimentally, that while building-up of pressure applied to natural clay, there is general tendency of clay fraction content decrease and pulverescent fraction content increase. Montmorillonite natural clay changes are more intensive, compared to kaolinite ones.
2. It is revealed, that processes of natural clay fractional compositions change are featuring higher intensity of progressing under pressures within the range of 0–125 MPa, than under higher pressures. It is revealed, that there is different intensity of natural clay fractional compositions formation under pressures within the range of 125-750 MPa and 800-2200 MPa. Thereby, three classes are identified regarding «pressure» index, each has different intensity of aggregation and dispersion processes progressing. Due to the abovementioned, conditions of natural clay fractional compositions formation have their individual specific character as well.
3. It is disclosed, that when clay is compressed, defects are formed on crystallite surfaces, which increase energy potential of crude ground. Extra energy enables to form molecular attractive forces, which cause particles aggregation. Dispersion processes, referring to particles grinding, progress in small volumes.

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