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# MASS CHANGE OF BOUND WATER IN CLAYS UNDER COMPRESSION

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# ИЗМЕНЕНИЕ МАСС СВЯЗАННОЙ ВОДЫ В ГЛИНАХ ПРИ СЖАТИИ

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#### Key words:

montmorillonite, kaolinite, clay, pressure, mass loss, thermal analysis, x-ray phase analysis, correlation matrix, regression analysis, colloid, mineral. In general, reliability of industrial and civil units is determined by strength and deformation properties of foundation soils of structures. On the one hand, calculated values of mechanical properties largely depend on technogenic load on a ground base, and on the other hand, on content of bound water in soils, especially clays. Many Russian and foreign scientists were engaged in evaluation of bound water in clays. Their works describe an effect of mineral composition, initial moisture and composition of clay exchange cations on thermal dehydration of bound water. It was found that the smaller the size of clay particles, the sharper dehydration curves diverge in a high-temperature area. The conclusion is drawn that there is no significant discontinuity in values of energy, corresponded to active centers on basal facies and crystal chips. The paper presents results of studies of change of properties of bound water in clays under influence of high temperatures and pressures. To researchers' mind, during compaction of clays saturated with water, free water of large pores is first to be removed, then under 1-3 MPa load osmotic water, and under pressure of more than 10 MPa structured hydrate layers begin to be removed. Closest to a hard surface water layers, which determine moisture content in clays, are not squeezed out at tens of megapascals, when monolayers at loads of hundreds of megapascals. As a result of studies conducted it was experimentally established that in kaolinite and montmorillonite clays content of film and absorbed water of the colloid, as well as surface water and water of hydroxyl groups of minerals varies with change in pressure magnitude. It is established that studied parameters influence total water loss differently, which is confirmed by various mathematical models. However, in all cases, except for montmorillonite subjected to pressure of more than 1000 MPa, the most important factor determining the overall loss of water mass is adsorbed water of minerals.

Ключевые слова:

монтмориллонит, каолинит, глина, давление, потеря массы, термический анализ, рентгенофазовый анализ, корреляционная матрица, регрессионный анализ, коллоид, минерал. Надежность промышленных и гражданских объектов определяется в основном прочностными и деформационными свойствами грунтов оснований сооружений. Расчетные значения механических свойств, с одной стороны, во многом зависят от техногенной нагрузки на грунтовое основание, а с другой – от содержания в грунтах, особенно в глинистых, связанной воды. Оценкой связанной воды в глинах занимались многие российские и зарубежные ученые. В их работах описано влияние минерального состава, начальной влажности и состава обменных катионов глин на термическую дегидратацию связанной воды. Приведены данные о влиянии размера частиц на вид кривых дегидратации. Выявлено, что чем меньше размер глинистых частиц, тем резче кривые дегидратации расходятся в области высоких температур. Сделан вывод о том, что в значениях энергий, соответствующих активным центрам на базальных гранях и на сколах кристаллов, нет большого разрыва. Представлены результаты исследований по изменению свойств связанной воды в глинах под действием высоких температур и давлений. По мнению исследователей, при уплотнении водонасыщенных глин в первую очередь удаляется свободная вода крупных пор, затем при нагрузках 1-3 МПа осмотическая вода, а при давлении более 10 МПа начинается удаление структурированных гидратных слоев. Ближайшие к твердой поверхности слои воды, определяющие влажность глин, не отжимаются при нагрузках в десятки мегапаскалей, а монослои - при нагрузках в сотни мегапаскалей. В результате проведенных исследований экспериментально установлено, что в каолинитовых и монтмориллонитовых глинах содержание рыхлосвязанной и прочносвязанной вод коллоида, а также воды поверхности и гидроксильных групп минералов изменяется в зависимости от величины давления. Установлено, что в образовании общей потери масс воды исследуемые показатели принимают различное участие, что подтверждают различные математические модели. Однако во всех случаях, кроме монтмориллонита, подверженного давлению более 1000 МПа, наиболее существенным фактором, определяющим общую потерю масс воды, является прочносвязанная вода минералов.

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# Introduction

Reliability of industrial and civil facilities is determined mainly by strength and deformation properties of soils that compose base of structures. On the one hand calculated values of mechanical properties of soils depend on artificial load on soil base [1], on the other hand they depend on content of bound water in soils (especially clayish) [2]. Many Russian [3-5] and foreign scientists [7-11] were engaged in evaluation of bound water in clays. Several works [5-6] describe an effect of mineral composition, initial moisture and composition of clay exchange cations on thermal dehydration of bound water. Data on effect of particle size on shape of dehydration curves are given in [7, 12]. It was found that the smaller size of clay particles, the sharper dehydration curves diverge in hightemperature area. The conclusion is drawn that there is no significant discontinuity in values of energy, corresponded to active centers on basal facies and crystal chips.

The papers [3-11] present results of studies of change of properties of bound water in clays under influence of high temperatures and pressures. To researchers' mind, during compaction of clays saturated with water, free water of large pores is first to be removed, then under 1-3 MPa load osmotic water, and under pressure of more than 10 MPa structured hydrate layers begin to be removed. According to data of authors [4-11], water layers closest to hard surface that determine moisture of clays, are not squeezed out under loads of tens of megapascals, and monolayers at loads of hundreds of megapascals.

However, despite the high scientific and practical value of the problem, there are not enough experimental studies. Comparative analysis of compression resistance of clays with different mineral and structural type could be a field of especial interest.

This paper describes changes in mass of bound water in kaolinite and montmorillonite clays under load.

A method for preparation of samples and determination of loss of bound water mass in clays is given in [5-6].

Following types of water mass loss are considered, %: film water  $-MS_{FW}$ , adsorbed water

in a colloid –  $MS_{AWC}$ , adsorbed water in a mineral –  $MS_{AWM}$ , hydroxyl groups in a mineral –  $MS_{HGM}$ , recrystallization of minerals –  $MS_{RCM}$  and total loss of bound water mass –  $MS_T$ . Normal stresses  $S_n$ , MPa is used as a load parameter. During processing of experimental data, statistical analysis was used.

At the first stage, influence of pressure on change in mass of bound water in clays was studied. Mean values were estimated by *t* criterion for kaolinite and montmorillonite. A difference in mean values is considered statistically significant if  $t_p > t_t$ . Comparison of mean values of studied parameters is given in Table 1. In this case estimation  $t_t = 1.98$  is carried at  $n_1 = n_2 = 96$  and degree of significance ( $\alpha = 0.05$ ). In addition, during statistical analysis of data studied, a correlation analysis was used (Table 2). The comparison showed that for the same loads, mean losses for certain water categories for kaolinite and montmorillonite are statistically different.

Table 1

Comparison of mean values of clay parameters

Parameter	Mean va variance of		Student's coefficient		
Falametei	kaolitine	montmo- rillonite	$t_p$ calculated	$t_t$ critical	
S <sub>n</sub> , MPa	$665.0\pm735.0$	$665.0\pm735.0$	0.0000	) < 1.98	
MS <sub>FW</sub> , %	$2.8 \pm 0.9$	$5.1 \pm 0.8$	18.285	7 > 1.98	
$MS_{AWC}$ , %	$0.40\pm0.22$	$0.96\pm0.24$	16.571	1 > 1.98	
$MS_{AWM}$ , %	$7.5 \pm 1.3$	$4.6 \pm 1.9$	11.588	1 > 1.98	
$MS_{HGM}$ , %	$1.46 \pm 0.81$	$2.98 \pm 1.07$	11.020	05>1.98	
$MS_{RCM}$ , %	$0.68\pm0.47$	_		_	
$MS_T$ , %	$12.8 \pm 2.9$	$13.7 \pm 3.4$	2.1187	7 > 1.98	

At the same time, a statistical difference for total water mass losses was also obtained, but not so significant (see Table 1). This indicates that when values of S<sub>n</sub> are in the interval of 0-2000 MPa losses in different types of water for kaolinite and montmorillonite occur according to different scenarios. In order to look over dynamics of changes in water loss parameters, it is needed to construct functions of change in water mass losses increase in  $S_n$  values. Quantitatively with these changes are estimated by calculations of values of r. In addition, it is needed to find values of r between analyzed types of water losses. Changes in values of MS<sub>FW</sub> versus S<sub>n</sub> are shown in Fig. 1, a.



Table 2

	Sn	$MS_{FW}$	$MS_{AWC}$	MS <sub>AWM</sub>	MS <sub>HGM</sub>	MS <sub>RCM</sub>	$MS_T$
Sn	1.00	<u>0.53*</u>	<u>0.56*</u>	-0.21*	-0.23*	-0.39*	-0.01
S <sub>n</sub>	1.00	0.54*	0.38*	0.71*	0.61*	_	0.75*
MS <sub>FW</sub>		1.00	0.42*	-0.38*	-0.39*	-0.39*	0.02
WISFW		1.00	0.37*	0.24	0.26	_	0.50*
MS			<u>1.00</u>	<u>0.43*</u>	0.07	<u>-0.02</u>	<u>0.55*</u>
$MS_{AWC}$			1.00	0.41*	0.36*	_	0.52*
MS				<u>1.00</u>	0.71*	<u>0.69*</u>	<u>0.69*</u>
MS <sub>AWM</sub>				1.00	0.92*	_	0.95*
MS					1.00	<u>0.78*</u>	<u>0.78*</u>
$\mathrm{MS}_{\mathrm{HGM}}$					1.00	_	0.93*
MC						1.00	<u>0.73*</u>
MS <sub>RCM</sub>						1.00	_
MS							1.00
MS <sub>T</sub>							1.00

Correlation matrix

R e m a r k s : \*- significant correlation links, kaolinite is a numerator, montmorillonite is a denominator.

Changes in values of MS<sub>FW</sub> depending on S<sub>n</sub> for kaolinite and montmorillonite are close, but displaced from each other. The dependence for kaolinite is located slightly lower than for montmorillonite. Note that there are almost linear trends of increase of MS<sub>FW</sub> both for kaolinite and montmrillonite before values  $S_n < 1000$  MPa. Then with increase in S<sub>n</sub> values of MS<sub>FW</sub> are maintained almost the same. This allows concluding that to extract the same mass of film water for kaolinite there is a need of bigger values of  $S_n$  than for montmorillonite. This is also proved by the mean values of MS<sub>FW</sub> for kaolinite and montmorillonite, given in Table 1. It has to be noted that values of coefficients of r between MS<sub>FW</sub> and S<sub>n</sub> are statistically significant. There is a stronger bond for kaolinite, than for montmorillonite. The dependence looks like

- for kaolinite:

$$MS_{FW} = 2.258 + 0.000837 S_n$$
,

- for montmorillonite:

$$MS_{FW} = 4.675 + 0.000701 S_{n}.$$

Note that these dependancies describe relationship between  $MS_{FW}$  and  $S_n$  only for  $S_n < 1000$  MPa, which is well described on Fig. 1, *a*.

Dependence of change in values of  $MS_{AWC}$  on  $S_n$  is shown in Fig. 1, *b*. It is seen that the same pattern as above is observed for  $MS_{AWC}$ , but with less loss of water mass. Data on mean values,

given in Table 1, indicate that mass loss of water is much lower. Values of coefficients r between  $MS_{AWC}$  and  $S_n$  are statistically important. There is a tighter bond for kaolinite, than for montmorillonite.

Dependance looks like:

- for kaolinite:

$$MS_{AWC} = 0.266 + 0.000204 S_n$$

- for montmorillonite:

$$MS_{AWC} = 0.863 + 0.000154 S_n.$$

It should be noted that these dependences well describe relationships between  $MS_{AWC}$  and  $S_n$  also only for values of  $S_n < 1000$  MPa, as seen in Fig. 1, *b*.

Dependance of change in  $MS_{AWM}$  on  $S_n$  is presented on Fig. 1, c. According to MS<sub>AWM</sub> there are significantly different in direction and value scenarios. There is a decrease in MS<sub>AWM</sub> for kaolinite at values of  $S_n < 1000$  MPa. There are at first increase in MS<sub>AWM</sub> for montmorillonite at values of  $S_n < 1000$  MPa and then decrease. Then there is a chaotic change in MS<sub>AWM</sub> both for kaolinite and montmorillonite. There are fundamental differences for kaolinite and montmorillonite under decrease of S<sub>n</sub> according to  $MS_{AWM}$ . Value of r coefficient between  $MS_{AWM}$ and S<sub>n</sub> for kaolinite is negative and looks like

$$MS_{AWM} = 7.775 - 0.000457 S_n$$
.

There is titgher and positive bond for montmorillonite

$$MS_{AM} = 3.129 + 0.00228 S_n$$
.

Value of  $S_n = 1000$  MPa devide selection into 2 classes that is seen on Fig. 1, *c*. Dependence of change in values of  $MS_{HGM}$  on  $S_n$  is shown in Fig. 1, *d*.

Values of  $MS_{HGM}$  for montmorillonite depending on  $S_n$ , in general are higher, than for kaolinite, especially when  $S_n > 1000$  MPa.  $MS_{HGM}$ changes randomly for kaoplinite with increase of  $S_n$ . There is a complex change in  $MS_{HGM}$  for montmorillonite with increase of  $S_n$ . Here are fundamental different changes for kaolinite and montmorillonite with increase of values of  $S_n$  as in case for  $MS_{AWM}$ . Values of *r* coefficients between  $MS_{HGM}$  and  $S_n$  are negative for kaolinite. There is a direct and tighter bond for montmorillonite. A dependance for kaolinite looks like

$$MS_{HGM} = 1.673 - 0.000308 S_n$$

Note that this dependence mainly describes data obtained for values of  $S_n < 1000$  MPa, as is seen in Fig. 1, *d*. The correlation for montmorillonites is statistically straight, tight and looks like

$$MS_{HGM} = 2.665 + 0.00107 S_n$$
.

Note that this dependence, on contrary, describes data better  $S_n > 1000$  MPa (see Fig. 1, *d*).

The dependence of change in values of  $MS_{RCM}$  on  $S_n$  is shown in Fig. 2.



Fig. 2. Dependance of  $MS_{RCM}$  change on  $S_n$  for kaolinite

An analysis of change in  $MS_{RCM}$  values versus  $S_n$  for kaolinites shows that in case dependence is consider as a whole, there would be a trend of decrease of  $MS_{RCM}$  values with increase in  $S_n$ . Such correlation would be statistically significant. However, if this dependence is considered in more detail, there would be two sub-dependencies observed. The first sub-dependence appear to be at  $S_n < 1000$  MPa, the second at  $S_n > 1000$  MPa.

Changes in  $MS_T$  values as a function of  $S_n$ , presented in Fig. 1, *d*, show that with increase of  $S_n$ , an  $MS_T$  value varies randomly for kaolinites which is proved by a low value of *r* coefficient r = -0.01.

However, there is a regular decrease of  $MS_T$  values at  $S_n < 1000$  MPa at in-depth analysis.

Then there is a sharp increase in  $MS_T$  values with following decrease again. There is quite complex change in  $MS_T$  values for montmorillonite with increase in  $S_n$ . Neverthelles, in general there is a tight positive trend, that is described as follows:

$$MS_{\rm T} = 10.934 + 0.00421 \, S_{\rm n}.$$

Consequantly, it was found that pressure affect mass loss in variety of bound water types in clays differently in direction. It was found that there is sudden change in loss of bound water mass at pressures of about 1000 MPa. Therefore, it can be assumed that at pressures up to 1000 MPa bound water is formed according to one scenario and to another scenarion at  $S_n > 1000$  MPa.

Therefore, legitimacy of existence of proposed hypothesis was studied in the second stage. The hypothesis says that distinguished ranges of values of  $S_n$  are statistically different by a set of indicators.

To do that a stepwise linear discriminant analysis (SLDA) was used. Possibilities of using such analysis to solve similar issues are given in [13-15]. For development of models it was assumed that the first sample (class 1) consists of values of  $S_n < 1000$  MPa and the second sample (class 2) consists of values of  $S_n > 1000$  MPa.

As a result of implimentation of this method, following linear discriminant function was obtained for kaolinite:

$$Z_{\rm k} = -11.6559 \text{ MS}_{\rm AWC} + 1.1717 \text{ MS}_{\rm AWM} - 0.9982 \text{ MS}_{\rm HGM} + 0.5777 \text{ MS}_{\rm FW} - 4.186$$
,

where R = 0.851,  $\chi^2 = 118.23$ , p = 0.000.

A mean value for the first class (sample) is  $Z_{k_1} = 0.923$  and for the second  $Z_{k_2} = -2.77$ .

The probabilities of experimental data, belonging to the second class  $P(Z_{\kappa_2})$ , were calculated using the function given above [16-17]. For the 2<sup>nd</sup> class mean value and variance are  $P(Z_{k_2}) = 0.982$  and  $\sigma_2^2 = \pm 0.059$ ,  $P(Z_{\kappa_1}) = 0.016$ and  $\sigma_1^2 = \pm 0.022$  for the 1<sup>st</sup> class. It has to be noted that there was 100 % of right recognition by this function.

As a result of this method implementation following linear discriminant function was obtained for montmorillonite:

$$Z_{\rm m} = 0.11299 \text{ MS}_{\rm AWC} - 1.07678 \text{ MS}_{\rm AWM} + 0.12472 \text{ MS}_{\rm HGM} + 2.863$$

at R = 0.860,  $\chi^2 = 125.018$ , p = 0.000.

A mean value for the first class (sample) is  $Z_{k_1} = 0.966$ , for the second class  $- Z_{k_2} = -2.90$ .

For this function, values of probability of experimental data, belonging to the second class, were calculated  $-P(Z_{k_2})$ . Mean value and variance for the 2<sup>nd</sup> class are  $P(Z_{k_2}) = 0.939$ and  $\sigma_2^2 = \pm 0.117$ ,  $P(Z_{k_1}) = 0.029$  and  $\sigma_1^2 = \pm 0.073$ for the 1<sup>st</sup> class. It has to be noted that there was 100 % of right recognition for both classes by this function.

Mean values of indicators for kaolinite and montmorillonite, taking into account division of samples into classes 1 and 2, obtained using LDF, (Table 3) are given below.

Table 3

Comparison of mean values of kaolinite and montmorillonite

Parameter	Mean values of va	Student's coefficient							
1 arameter	class 1	class 2	$t_p$ – calculated	$t_t -$ critical					
Kaolinite									
S <sub>n</sub> , MPa	$358.3 \pm 324.6$	$1725.0\pm349.4$	12.3988	> 1.98					
$MS_{FW}$ , %	$2.3\pm0.9$	$3.5 \pm 0.5$	3.1375 >	· 1.98					
$MS_{AWC}$ , %	$0.30\pm0.11$	$0.69\pm0.15$	9,0985 >	· 1.98					
$MS_{AWM}$ , %	$7.3 \pm 1.3$	$7.8 \pm 1.5$	1.2126 <	1.98					
$MS_{HGM}$ , %	$1.45 \pm 0.75$	$1.54\pm0.98$	0.3211 <	1.98					
MS <sub>RCM</sub> , %	$0.71\pm0.47$	$0.57\pm0.44$	0.8859 < 1.98						
$MS_T$ , %	$12.4 \pm 1.9$	$14.2 \pm 3.1$	2.3477 >	1.98					
	Mo	ntmorillonite							
S <sub>n</sub> , MPa	$358.3 \pm 324.6$	$1725.0\pm349.4$	12.3988	> 1.98					
$MS_{FW}$ , %	$4.8\pm0.6$	$5.9 \pm 0.4$	6.3182 >	· 1.98					
$MS_{AWC}$ , %	$0.90\pm0.21$	$1.07\pm0.25$	2.3980 >	· 1.98					
$MS_{AWM}$ , %	$4.1 \pm 1.2$	$7.9 \pm 0.9$	9.8450 >	· 1.98					
$MS_{HGM}, \%$	$2.71\pm0.48$	$4.01 \pm 1.70$	4.1605 >	1.98					
$MS_{RCM}$ , %	_	_	-						
$MS_T$ , %	$12.5 \pm 2.2$	$19.0 \pm 2.5$	8.5910 >	1.98					

There is a significant difference in loss of water mass in 1<sup>st</sup> and 2<sup>nd</sup> classes for kaolinite and montmorillonite under different loads. Quantitative evaluation of these differences was carried out using Student's *t* criterion [18]. Calculated values of *t* are given in Table 3, while the critical  $t_t = 1.98$ was calculated for  $n_1 = n_2 = 96$  and a significance level  $\alpha = 0.05$ .

There are statistical differences in  $MS_{FW}$ ,  $MS_{AWC}$ and  $MS_{T}$  for caolinite, that is proved by the values of  $t_p > t_t$ . Herewith, loss of bound water mass for the second class is higher than for the first.

There are statistical differences in all of indicators ( $t_p > t_t$ ) for montmorillonite. Herewith losses for the second class are much higher than for the first. It should be noted that for kaolinite losses in MS<sub>AWM</sub> for two samples (classes) statistically are not different. A maximum statistical difference is observed for montmorillonite. The values of *r* coefficients between studied parameters for kaolinite and montmorillonite with considered distinguished samples (classes) are given in Table 4.

Table 4

Correlation matrix

	Sn	MS <sub>FW</sub>	MS <sub>AWC</sub>	MS <sub>AWM</sub>	MS <sub>HGM</sub>	MS <sub>RCM</sub>	MS <sub>T</sub>
Kaolinite							
S <sub>n</sub>	1.00	<u>0.68*</u>	-0.18	-0.85*	-0.50*	-0.44*	-0.56*
3 <sub>n</sub>	1.00	-0.68*	-0.74*	-0.58*	-0.77*	-0.93*	-0.78*
MS <sub>FW</sub>		1.00	0.20	-0.61*	-0.55*	-0.43*	<u>-0.24</u>
MOFW		1.00	0.76*	0.38	0.27	0.68*	0.54
MS <sub>AWC</sub>			1.00	<u>0.39*</u>	<u>-0.16</u>	<u>-0.03</u>	<u>0.37</u>
WIDAWC			1.00	0.87*	0.69*	0.90*	0.92*
MS <sub>AWM</sub>				<u>1.00</u>	<u>0.68*</u>	<u>0.69*</u>	<u>0.85*</u>
IVIO <sub>AWM</sub>				1.00	0.85*	0.83*	0.96*
MS <sub>HGM</sub>					<u>1.00</u>	<u>0.78*</u>	<u>0.77*</u>
HUDHGM					1.00	0.88*	0.92*
MS <sub>RCM</sub>						<u>1.00</u>	<u>0.82*</u>
MORUM						1.00	0.95*
$MS_T$							<u>1.00</u>
mol							1.00
				orillonite			
S <sub>n</sub>	<u>1.00</u>	<u>0.55*</u>	<u>0.48</u>	<u>0.53*</u>	<u>0.38*</u>		<u>0.58*</u>
Un	1.00	-0.16	-0.47	0.48*	0.83*		0.79*
$MS_{FW}$		<u>1.00</u>	<u>0.02</u>	<u>0.69*</u>	<u>0.80*</u>		<u>0.83</u>
WIGFW		1.00	-0.29	-0.20	0.01		0.06
MS <sub>AWC</sub>			1.00	0.41*	0.19		0.36*
MIDAWC			1.00	0.75*	0.54		0.72*
MS <sub>AWM</sub>				1.00	<u>0.83*</u>		<u>0.97*</u>
WISAWM				1.00	0.42		0.73*
MS <sub>HGM</sub>					1.00		<u>0.91*</u>
					1.00		0.91*
$MS_{RCM}$							
$MS_T$							<u>1.00</u>
							1.00
Remarks: *- significant correlation bonds, in a							

R e m a r k s: \*- significant correlation bonds, in a nominator – class 1, in denominator – class 2.

Comparison of *r* values shows that there are significant differences both during division of kaolinite and montmorillonite into samples and inside of samples. For instance, correlation between  $S_n$  and  $MS_{AWM}$  is statistically significant and negative for the 1<sup>st</sup> and 2<sup>nd</sup> classes of kaolinites ( $r_{p_1} = -0.85 > r_t = 0.21$  and  $r_{p_2} = -0.58 > r_t = 0.21$ ), statistically significant and positive for

montmorillonites  $(r_{p_1} = 0.53 > r_t = 0.21$  and  $r_{p_2} = 0.48 > r_t = 0.21$ ). The same differences are observed for other parameters (see Table 4).

Thus, a pressure threshold  $S_n = 1000$  MPa is established. This pressure divides the population into two classes. Class 1 includes data obtained at pressures of  $S_n < 1000$  MPa, and class 2 – at pressures of  $S_n > 1000$  MPa.

Estimation of loss of various kinds of bound water in clays showed that they differ quite strongly between classes 1 and 2 in montmorillonite and kaolinite clays. Hence it can be assumed that their formation proceeds according to different scenarios.

Therefore, in the third stage, an effect of bound water of different kinds on total loss of water mass in clays was studied. To solve this problem, stepwise regression analysis was used [19-21]. The correlation coefficient (r) was used as the criterion that helps to evaluate influence of studied parameters on MS<sub>T</sub> values.

The possibility to apply this indicator is as follows: the higher r value, the more significant effect of this type of water on the total mass loss of  $MS_T$  [22-23]. In our case  $MS_T$  plays a role of dependent feature and  $MS_{FW}$ ,  $MS_{AWC}$ ,  $MS_{AWM}$ ,  $MS_{HGM}$ ,  $MS_{RCM}$  – independent. Following scenarios are considered:

- first (for kaolinite) - total selection, formed at pressures  $S_n = 0-2000$  MPa;

- second (for kaolinite) - selection 1, formed at pressures  $S_n < 1000$  MPa;

- third (for kaolinite) – selection 2, formed at pressures  $S_n > 1000$  MPa;

- fourth (for montmorillonite) - total selection, formed at pressures  $S_n = 0-2000$  MPa;

- fifth (for montmorillonite) - selection 1, formed at pressures  $S_n < 1000$  MPa;

- sixth (for montmorillonite) - selection 2, formed at pressures  $S_n > 1000$  MPa.

Built models are given in Table 5.

An analysis of data given in Table 5 shows that the formation of multidimensional models for calculation of MS<sub>T</sub> values occurs in a different sequence. For joint sampling in kaolinite clay (scenarion 1), the process of model formation begins with adsorbed mineral water (r = 0.867) and continue with parameters that characterise film colloidal water (r = 0.945), hydroxyl groups of a mineral (r = 0.993)and recrystallized mineralization (r = 0.998). A similar pattern was identified in scenario 2. Major part in variation of MS<sub>T</sub> in 3<sup>rd</sup> sce nario (at  $S_n > 1000$  MPa) is brought by the index of adsorbed mineral water (r = 0.846). At the second step, unlike option 1, an indicator that characterize mass loss during recrystallization of the mineral (r = 0.991). At the third step – MS<sub>HGM</sub> (r = 0.993)and the fourth –  $MS_{FW}$  (r = 0.999).

Thus, adsorbed water of mineral is major reason of total loss of mass of bound water [24]. Depending on pressure, second place belongs to film water (at  $S_n < 1000$  MPa) and recrystallization of minerals (at  $S_n > 1000$  MPa).

Table 5

Scenario		Free term	Types of bound water					
		Free term	MS <sub>FW</sub>	MS <sub>AWC</sub>	MS <sub>AVM</sub>	MS <sub>HGM</sub>	MS <sub>RCM</sub>	
First	coefficients	-1.05413	$\frac{1.13632^{*}}{0.945}$		<u>1.16559</u> 0.867	<u>0.98018</u> 0.993	<u>0.80678</u> 0.998	
	order to build the model		2		1	3	4	
Second	coefficients	-0.65403	<u>1.07218</u> 0.916		<u>1.12806</u> 0.847	<u>0.92678</u> 0.990	<u>0.91262</u> 0.999	
	order to build the model		2		1	3	4	
Third	coefficients	-0.093371	<u>1.05074</u> 0.999		<u>1.08152</u> 0.846	<u>0.90393</u> 0.993	<u>1.23638</u> 0.991	
	order to build the model		4		1	3	2	
Fourth	coefficients	0.008447	<u>1.02352</u> 0.922	<u>0.62194</u> 0.998	<u>0.34881</u> 0.867	<u>2.01826</u> 0.864		
	order to build the model		2	4	3	1		
Fifth	coefficients	0.581344	<u>1.09253</u> 0.989		<u>1.09294</u> 0.923	<u>0.82505</u> 0.995		
	order to build the model		2		1	3		
Sixth	coefficients	4.214447	0.82877 0.872			<u>2.11214</u> 0.862		
	order to build the model		2			1		

Multidimensional models for calculation of MS<sub>T</sub>

R e m a r k s. \*Nominator – coefficients at indexes in equations, denominator – value of correlation coefficient R.

Pressure influence formation of MS<sub>T</sub> much in montmorrilonite than in kaolinite clay.

Adsorbed mineral water has the most significant effect on formation of MS<sub>T</sub> in scenarion 5 (r = 0.923) in scenario 6 water of hydroxyl groups (r = 0.862). Second place by the influence on formarion of MS<sub>T</sub> according to scenarios 5 and 6 is taken by film water.

Thus, taking into account class division and depending on pressure studied parameters influence formation of MS<sub>T</sub> in kaolinite and montmorillonite differently. That fact is proved by different mathematical models [25-28]. Neverthelles, in all the cases (except scenario 6) the most significant factor that determines formation of MS<sub>T</sub> is adsorbed mineral water. For 6<sup>th</sup> scenario that is water of hydroxyl groups.

## Conclusion

1. It is determined that at the pressures less that 1000 MPa there is different in directions

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change in total mass of loss water. Total mass of loss water is decreased with increase in pressure in kaolinite clay and is increased in montmorillonite clay [29-30]. Under the pressures of 1000 MPa such laws do not work. The mathematical models that help to understand a mechanism of mass loss of water in clays depending on pressure are developed.

2. It is determined and proved mathematically that threshold equals to 1000 MPa, at which mass loss of water in clays between classes 1 and 2 are different. Taking into account class division and depending on pressure studied parameters influence total mass loss of water differently in caolinite and montmorillonite. That is proved by different mathematical models. Neverthelles, in all the cases except for montmorillonite affected by 1000 MPa, the most significant factor that determines change of total mass loss of water is adsorbed water of minerals.

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