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THIXOTROPIC PROPERTIES OF LATVIAN CLAYS

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Abstract. *This research studies Latvia originated Devon (Tūja, Skaņkalne), quaternary (Ceplīši), Jurassic, (Strēļi) and Triassic (Vadakste) deposit clays as well as Lithuania originated Triassic (Akmene) deposit clays. Thixotropic properties of clay were researched by measuring relative viscosity of clay in water suspensions.*

Relative viscosity is measured with a hopper method. It was detected that, when concentration of suspension is increased, clay suspension's viscosity also increases. It happens until it reaches a certain boarder point when viscosity increases significantly – a dramatic rise is shown on the curve. It means that clay particles make a lace-like, easily broken structure. Impact of chemical reagents on clay suspensions' thixotropic properties is researched. Experimental results obtained on the new materials with thixotropic properties will allow precise definition of production technologies and usage of a new approach in development of motivation products. Likewise, the results will make an important investment in establishing a thixotropic material description methodology.

Keywords: *clays, concentration, suspension, thixotropy, viscosity.*

Introduction

In the meantime, clay minerals are widely used in various fields of manufacturing and agriculture. In manufacturing, they are used as adsorbents for cleaning and clarifying wines, various juices, as well as waste waters. Also they are used in building as bonding and forming materials. In agriculture, clay suspensions are used as fortifiers of sand zones and for improvement of hydrophilie and adsorption properties of soil dispersions. Another interesting property of clay, thixotropy, is far less known [1].

The word thixotropy, which was first introduced by Freundlich, is put together by the two Greek words "thixis" (stirring, shaking) and "trepo" (turning, changing) [2].

Thixotropy is an ability of the "clay – water" system to restore its structure after some time, when it was influenced mechanically. This is a reverse isothermal transition sol↔gel and it is characteristic to the clays of smectyte type. Thixotropic properties are more characteristic to the clay suspensions of expansive type. These clays can be used for preparation of boring solutions, in cosmetology, medicine, etc.

In the latest years, with the field of clay usage expanding, a necessity of broadening clays' variety, assign them certain properties like high viscosity, thixotropic properties as well as substituting currently used imported materials by locally originated ones.

In water suspensions, clays exist in form of plates. In water solution, clay surfaces have a negative charge, but their edges carry positive charges. If concentration of suspension is high enough, then spaces between the plates grow smaller, making the plates collide so that weakly positive plate edges are drawn to the negatively charged clay plate surfaces. A lace-like three dimensional structure, called "House of cards", is formed. Thanks to such structure, expansive type clays have high thixotropic properties.

Materials and methods

Objects of this research are Latvia originated Devon (Tūja, Skaņkalne), quaternary (Ceplīši), Jurassic, (Strēļi) and Triassic (Vadakste) deposit clays as well as Lithuania originated Triassic (Akmene) deposit clays. Clay fraction of Latvian and Lithuanian Triassic sediment contains the following clay minerals: smectyte (67-80%), illyte (6-25%), chlorite (0-25%) and kaolinite (2-5%) [3].

Description of the researched clay samples is given in Table 1. From the studied clays, two series of clay suspensions are prepared: suspensions of the first series are prepared from clay samples which are visually cleared from additions, crashed in a mortar, dispersed and swollen in a distilled H_2O for 1 month. Swollen clays in suspension form are sieved and dried in 100°C temperature, by that obtaining a fine clay fraction with particle size < 63 µm and a 50% clay suspension in distilled H_2O.

Suspensions of the second series are prepared from clay samples which are visually cleared from additions, crashed in a mortar and, as concentrated suspensions, mechanically activated in a planetary ball mill for 20 min, in a 250 rpm speed. Obtained concentrated suspension is diluted with distilled water up to 50% clay suspension.

Table 1.

Characteristics of clay samples

Name of clay deposit	Period	Layer thickness of taken samples (m)	Humidity (%)
Strēļi	Jurassic	2,5 – 3,5	30
Tūja	Devon	0,1 – 0,2	20
Skaņkalne	Devon	2,0 – 3,0	19
Ceplīši	Quaternary	2,2 – 3,0	24
Vadakste	Triassic	-	-
Akmens	Triassic	4,8 – 7,7	-

It is known that viscosity, thixotropic properties and stability of clay suspensions often depends on the solid phase and mineral contents. Since the mentioned properties are coherently changing due to the solid phase contents of clay suspensions, by using the dilution method, from 50% suspensions there were 15, 20, 30 and 40% suspensions prepared and kept in a quiescence state for 24 hours in order to achieve an equilibrium condition. On the next day the system was stirred again and the conditional viscosity was defined by the conic funnel method. For this, 300 ml of the mixture was put in a funnel and the outflow time of 200 ml of suspension in a 20 ^{0}C temperature was detected. Based on the obtained data, variation of relative viscosity was calculated, depending on the solid phase concentration, using the following formula (1):

$$\eta_{relative} = \frac{t_1}{t} \tag{1}$$

where t_1- outflow time of the clay solutions, sec.

t- outflow time of 200 ml of distilled water (10 sec.)

pH of the clay suspensions is measured using a "HANNA HI 8424 pH meter".

Results and discussion

Studying suspensions of the first series, it was found that, with a suspension concentration increasing, a clay suspension's relative viscosity also increases. It happens until the moment when the viscosity increases significantly, a dramatic rise is shown on the curve. It proves that the clay particles form a lace-like, easily breakable structure and demonstrate thixotropic properties. Concentration of clays from the Strēļi and Akmene deposits lies within the suspension boundaries of 33 % - 39%, but clays from the Skaņkalne, Ceplīši and Tūja - from 39% up to 45%.(see figure 1.)

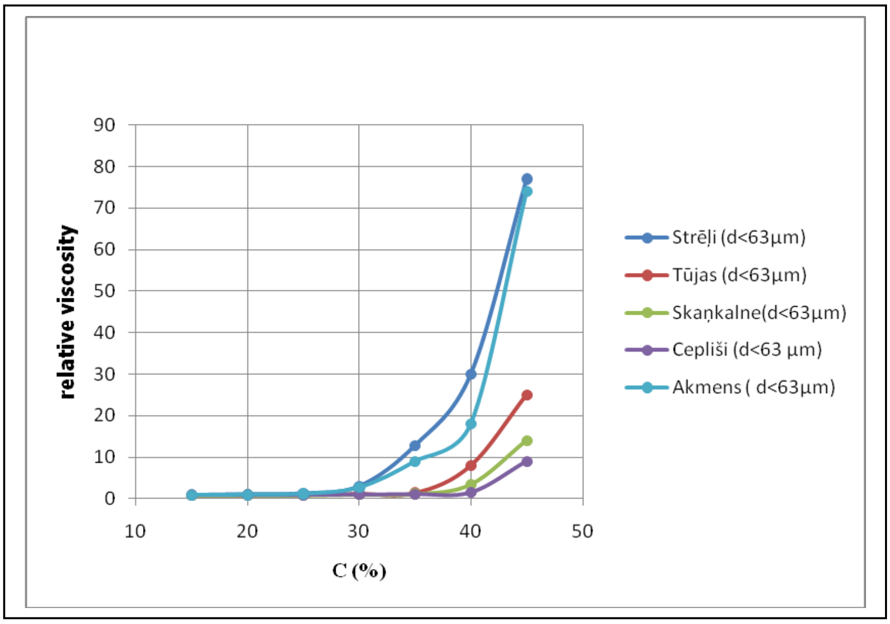

Fig.1. **Dependence of relative viscosity of the natural clay samples from the clay concentration in suspensions**

Fig.2 shows dependence of relative viscosity of the mechanically activated clay samples from the clay concentration in suspensions. Obtained results testify that while solid phase concentration of mechanically activated clays increases viscosity of the clay sample suspensions dramatically increases starting from 35% concentration.

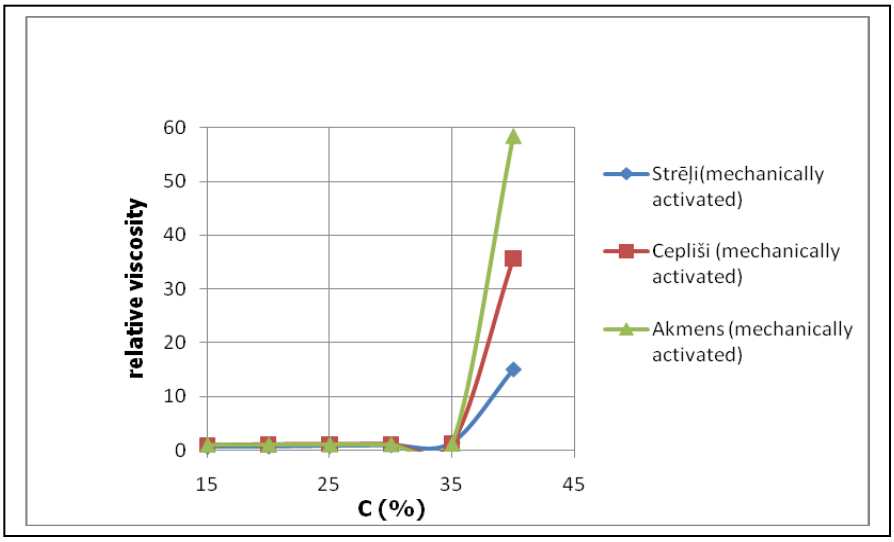

Fig.2. **Dependence of relative viscosity of the mechanically activated clay samples from the clay concentration in suspensions**

This is because not only clay sample dispersity increases as a result of mechanical activation, but also its reactivity. Dispersity of clay minerals is the most important criteria that determine its main physical chemical properties: thixotropic structurization, adsorption ability, coagulation, ion exchange, etc.

Thixotropic properties of clay suspensions are amended, modifying the samples with sodium carbonate (Na_2CO_3) and methylcellulose. It is defined that modification of clay suspensions with methylcellulose (0,1%) increases concentration of structurization. However, modification of clay suspensions with sodium carbonate (0,1%) lowers concentration of structurization (Fig.3) [4].

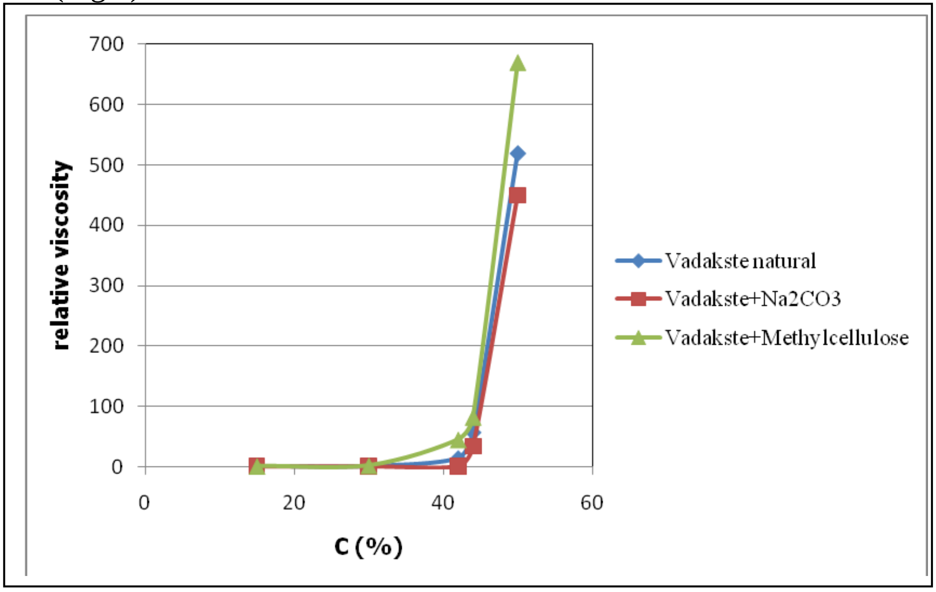

Fig.3. **Dependence of relative viscosity of Vadakste deposit clay samples from the modifier**

While mixing sodium carbonate with a clay sample, there is almost no exchange of Ca^{2+} onto Na^{+}. Their interaction occurs only after putting clay powder in the water, but mechanically adsorbed salts weakly interacts with clay particles. Methylcellulose is a highly molecular organic soluble material. It gives a serious impact on the contents of water. Breaking the contents of clear water by its hydrophilic fragment and structuring it with hydrophobic groups, it structurizes the water around itself in a specific way by forming thixotropic systems [5].

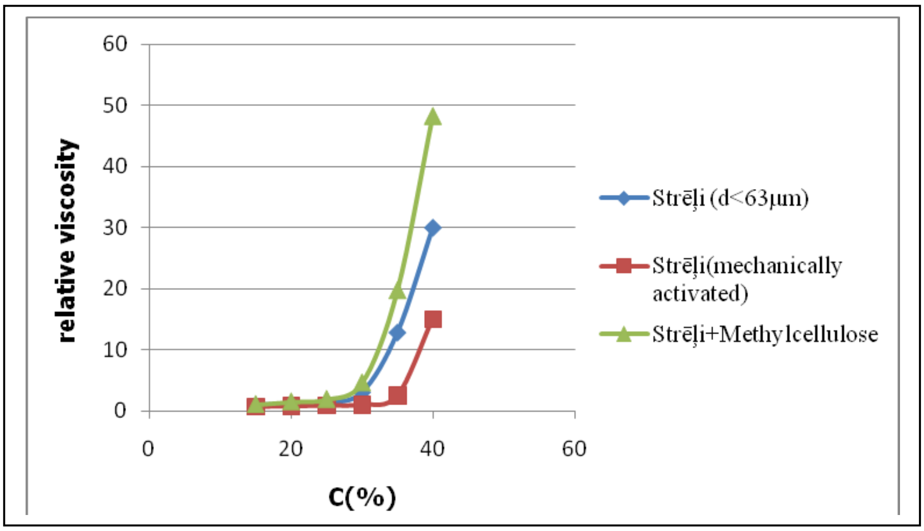

Fig.4. **Dependence of relative viscosity of Strēļi deposit clay samples from the modifier**

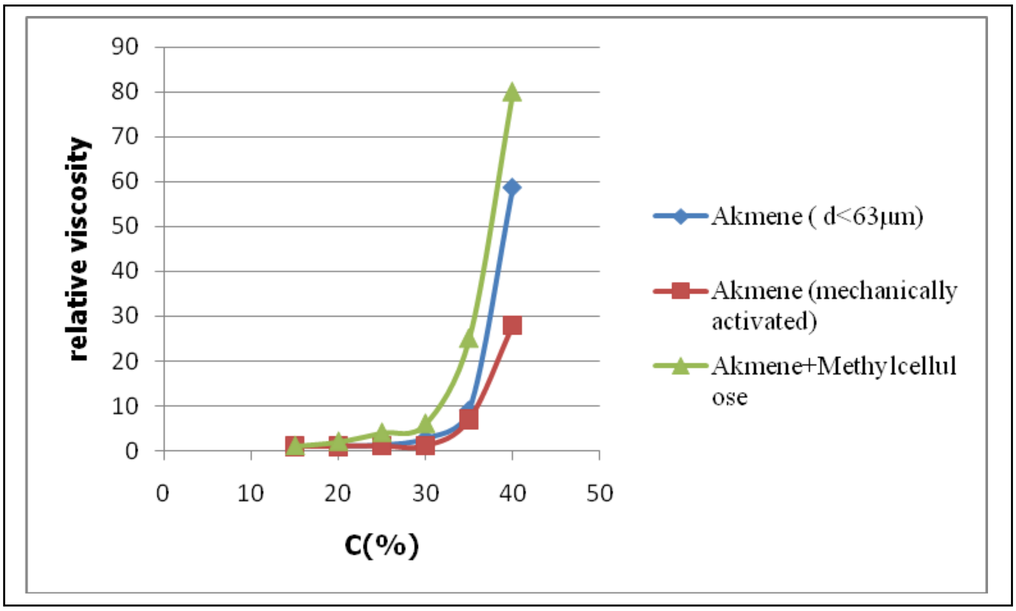

Fig.5. **Dependence of relative viscosity of Akmene deposit clay samples from the modifier**

The largest conditional viscosity is found at the clay samples modified by 0,1 % metilcellulose (Fig.4). Similar regularity is detected at the clays of Akmene deposit. (Fig.5)

Conclusions

1. It is found that Latvian originated clays have thixotropic properties.
2. It was found that modifying clay suspensions with methylcellulose (0,1%) increases the structurization concentration. In the same time, modifying clay suspensions with sodium carbonate (0,1%) lowers the structurization concentration.

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