

Obtaining of Clinoptilolitic Extrudates for Environmental Applications

I. Rheological Characterization for the Zeolitic Pastes

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The natural zeolites powders with high content of clinoptilolite can be used in the polluted water treatment processes. In order to bring these ceramic materials to the desired shape, for example by extrusion, all information about the rheological properties are imperative. The purpose of this paper is to present the rheological aspects regarding the obtaining of new natural zeolites based extruded materials, containing a high amount of clinoptilolite, an abundant material in Romania. The influence of two parameters was assessed: the amount of stearine and the presence of cationic surfactant, both at a constant solid fraction. It was noticed that all unmodified clinoptilolite based pastes present a tixotropic pseudoplastic non-newtonian fluid behaviour. As the stearine concentration in the composition of the pastes rises, their dynamic viscosity decreases; in parallel, the pseudoplastic character decreases and a viscoelastic effect appears. This behaviour confirms the lubricant function of the stearine for this system. The pastes become more workable by stearine adding. Applying the Ostwald de Waele rheological model, the parameters of this model for all the pastes were determined. The clinoptilolite pastes modified with cationic surfactant showed a more complex behaviour (dilatant with a viscoelastic element). The conclusion is that the cationic surfactant plays a binding role.

Key words: clinoptilolite, surfactant, rheology, ceramic pastes, extrudates

The rheological properties for the low molecular inorganic systems [1], organic systems [2] and macromolecular systems [3-8] are important directions of the national research.

Using the natural zeolites powders with a high content in clinoptilolite in the polluted water treatment processes imposes a special shape to these materials, compatible with the equipments in use. The most used technique for bringing a ceramic powder to the desired shape is extrusion. The size and the shape of the extrudates are heavily influenced by the rheological characteristics of the paste to be extruded [9].

The ceramic powders can become extrudable by mixing with a liquid phase, aiming to obtain a concentrated suspension with a high content in solid particles (a paste). The solid phase content in the paste is increased up to a threshold which provides the optimal flowing characteristics [10]. The rheological properties and the solid particles concentration for the extrudable pastes depend on the forces between particles; thus the control of these forces is essential for a good processing [11, 12].

The obtaining process of the extrudates involves a set of steps: mixing the inorganic powder with active additives, obtaining a water suspension, malaxating, extrusion and drying. The quality of the obtained extrudate depends on the choice of adequate additives and their presence in an optimal dosage; these proportions would correspond to a good rheological behavior of the pastes.

The experiments described in the present work had the purpose to achieve extrudate materials based on natural zeolites [15, 16] a raw material, rich in clinoptilolite, abundant in Romania. The extruded materials are designed for the decreasing of the organic pollutant content from residual industrial waters. The present paper constitutes a first approach of a more complex study and presents the

flowing properties of ceramic pastes, obtained both from unmodified clinoptilolite (CLN) and from cationic surfactant modified clinoptilolite (CLNM). The final purpose of the study is to develop adequate recipes for new extrudable materials.

Experimental part

Materials

The natural zeolite powder used in the experiments was delivered by SC CEMACOM SA and comes from the fields near Zalau (Marsid).

A multifunctional system of additives was used for the pastes casting. The micronized methyl ethyl cellulose (MEC) from Alfa-Aesar GmbH – Germany and the polyvinyl alcohol (PVA) from Fluka AG - Switzerland were used as binders, the type A olein, the magnesium stearate and the stearine flake (from SC SIN SA) were used as lubricants.

Characterization of the clinoptilolite powder

The granulometric distribution of the powder was determined on a Mastersizer 2000 v5.31 device. The phase composition of the powder was determined on Bruker D8 Advance diffractometer with the X-ray Bragg-Brentano method.

Obtaining the pastes

Two categories of pastes with a $62.4 \pm 0.3\%$ solid phase content were obtained, the zeolitic powder fraction being $57.1 \pm 0.4\%$ (the rest is represented by solid binders). From each category different formulas were prepared, as shown in table 1.

The natural zeolite powder used for the CLN type of pastes was conditioned by a 2 h drying at 105°C , in a thermostat controlled stove.

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Table 1
RECIPES FOR THE PREPARATION OF CLINOPTILOLIT

Paste Code	Solid compounds							Liquid compounds			liquid / solid			
	mass g	zeolite %	Mg stearat %	PVA %	MEC %	Stearine %	Σ solid g	Σ admixture g	Olein %	Water %		Σ liquid g		
CLN 1	64.00	57.50	1.56	1.56	1.56	0	39.80	62.18	3.00	4.69	0.31	37.50	24.20	0.61
CLN 2	64.20	57.32	1.56	1.56	1.56	0.31	40.00	62.31	3.20	4.98	0.31	37.38	24.20	0.61
CLN 3	64.40	57.14	1.55	1.55	1.55	0.62	40.20	62.41	3.40	5.28	0.31	37.27	24.20	0.60
CLN 4	64.80	56.79	1.54	1.54	1.54	1.24	40.60	62.65	3.80	5.86	0.31	37.04	24.20	0.60
CLNM 1	64.00	57.50	1.56	1.56	1.56	0	39.80	62.18	3.00	4.69	0.31	37.50	24.20	0.61
CLNM 2	64.20	57.32	1.56	1.56	1.56	0.31	40.00	62.31	3.20	4.98	0.31	37.38	24.20	0.60
CLNM 3	64.40	57.14	1.55	1.55	1.55	0.62	40.20	62.41	3.40	5.28	0.31	37.27	24.20	0.60
CLNM 4	64.80	56.79	1.54	1.54	1.54	1.24	40.60	62.65	3.80	5.86	0.31	37.04	24.20	0.60

PVA – Polyvinyl alcohol
Mg stearate – Magnesium stearate
MEC – Methyl ethyl cellulose

For the CLNM type of pastes, the dried zeolitic powder was treated with an aqueous solution (0,06M) of cationic surfactant with high molecular weight (benzyl dimethyl tetradecyl ammonium chloride, fig. 1). Then the powder was rinsed to remove the surfactant excess and was dried in the same conditions as the first powder.

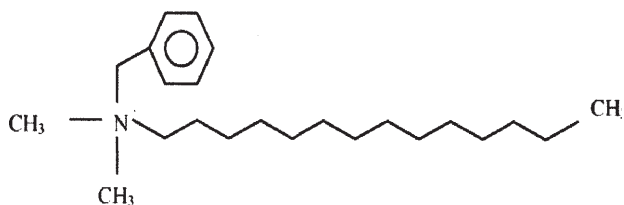


Fig. 1. Cationic surfactant - benzyl dimethyl tetradecyl ammonium chloride

The solid materials were premixed, followed by the addition of water and liquid lubricant in small portions. The mixing was performed at room temperature with a laboratory mixer at 100 rpm.

The homogeneity of the pastes was controlled by comparing the theoretical density, calculated using the mixing rule, with the experimentally determined one [13].

Rheological characterization

The viscosities of the two pastes categories were determined at 25°C with a Reotest 2 rotational viscosimeter, with two coaxial cylinders, which is the device generally used for this kind of pastes [11, 12].

The measurements regarding the apparent dynamic viscosity η were performed by increasing and then decreasing the shear rate, in order to observe the presence of any hysteresis. The hysteresis proves the time

dependence of the dynamic viscosity. Processing the experimental data, the following characteristic parameters were computed: the dynamic viscosity (η) and the shear stress (τ) for various values of shear rate ($\dot{\gamma}$). Finally, the viscosity curves and the characteristic flowing curves were drawn.

Results and discussions

The granulometric distribution of the clinoptilolite powder is presented in figure 2. The powder contains mainly 20 – 40 μm particles, but the variation range is larger: 0.5 -200 μm due to the very diverse composition.

Table 2 gives the phase composition of the powder. These results show that, beside the clinoptilolite (present in a proportion of 72.6%), the powder contains also albite (12.4%), biotite (10%), and the remaining of 5% is quartz and cristobalite.

CLN pastes

Four pastes based on unmodified clinoptilolite (CLN) were prepared (as one can observe in table 1). They differ only on the amount of added stearine: CLN 1 contains 0% stearine, CLN 2 0.5%, CLN 3 1% and CLN 4 2% stearine. For every paste the dependence of the viscosity and shear stress on the shear rate variation was assessed.

Figure 3a shows the influence of the shear rate on the dynamic viscosity and figure 3b the same influence on the shear stress, both for the CLN 1 paste (without stearine).

The experimental measurements were performed increasing and then decreasing the shear rate. Figures 3a and 3b reveal the pseudoplastic flowing with hysteresis for CLN 1, proving that CLN 1 is a thixotropic pseudoplastic fluid. The other 3 pastes (containing different quantities of

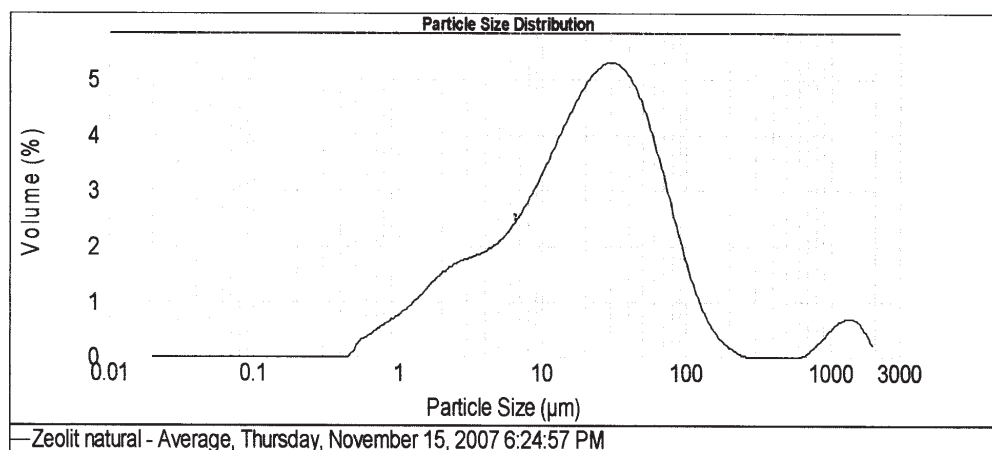
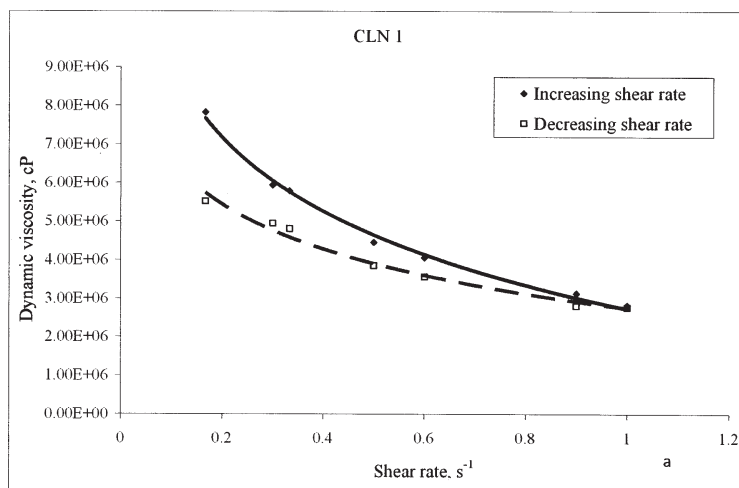


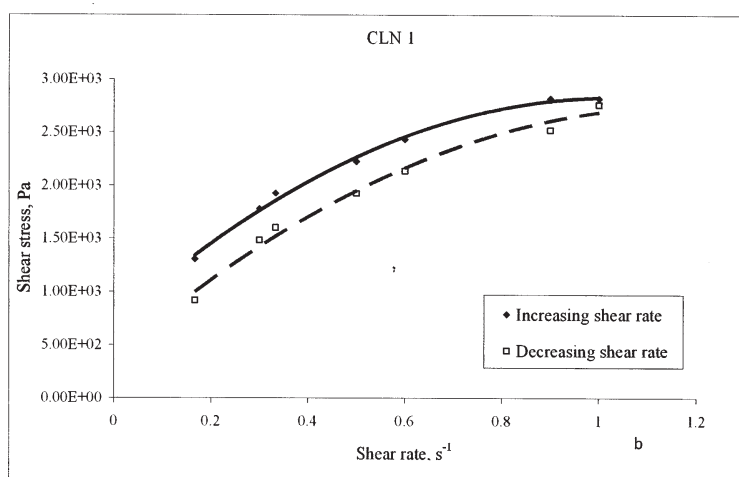
Fig. 2. Granulometric distribution of the clinoptilolite powder

Table 2
PHASES COMPOSITION OF THE CLINOPTILOLITE POWDER

Formula	Compound name	Content, %
$\text{Ca}_{1.24}\text{Na}_{1.84}\text{K}_{1.76}\text{Mg}_{.2}\text{Al}_6\text{Si}_{30}\text{O}_{72}(\text{H}_2\text{O})$	Clinoptilolite	72.6
$\text{Na}(\text{Si}_3\text{Al})\text{O}_8$	Albite	12.4
$\text{K}(\text{Mg}, \text{Fe}^{+2})_3(\text{Al}, \text{Fe}^{+3})\text{Si}_5\text{O}_{10}(\text{OH}, \text{F})_2$	Biotite	10.0
SiO_2	Quartz	2.3
SiO_2	Cristobalit, high	2.0
SiO_2	Cristobalite, low	0.8
Amorphous	Yes	



a



b

Fig. 3. Hysteresis for the CLN 1 paste:

- a) Dynamic viscosity variation
b) Shear stress variation with the increase and decrease in shear rate.

stearine) have a similar behavior to CLN 1 (data not shown).

Figure 4 presents the dynamic viscosity dependence on the shear rate (only for the increasing values of the shear rate) for all four clinoptilolite pastes (CLN). On this diagram one can notice the influence of stearine concentration upon the viscosity. All these pastes present a pseudoplastic non-newtonian fluid behaviour. Also, figure 4 reveals, the fact that, when the stearine concentration is increasing, the dynamic viscosity is decreasing for the low shear rate range, in parallel with the drop of the flowing pseudoplastic behaviour. These phenomena suggest the lubricant function of the stearine in this system.

The variation of the shear stress with the stearine concentration, for all 4 CLN pastes, is presented in figure 5. The CLN 1 paste, with 0% stearine, has a shear stress variation specific to the pseudoplastic fluids: a convex curve with positive slope. For the CLN 2 case, it is visible that the shear stress follows a parabolic trend, having a maximum at 1.5 s^{-1} . The ascendant segment of the parabola is specific to the pseudoplastic fluids, but the

descendant one is not. Adding stearine to the clinoptilolite powder clearly influences the pseudoplastic behaviour of the paste, inducing a viscoelastic effect. The viscoelastic fluids have a partial viscous and partial elastic behaviour, dissipating only a part of the received energy (the viscous component), thus conserving another part (the elastic component); when the stress is discarded, they recover the energy [14].

Also figure 5 shows that the CLN 3 paste has a complex behavior, the initial pseudoplastic behaviour combines with the viscoelastic one induced by the presence of stearine. The CLN 4 curve confirms the fact that the rheogram is strongly modified by the addition of stearine.

An overview on the figure 5 reveals the global influence of the stearine in the system: at the stearine concentration increasing, the shear stress is decreasing and the shear stress variation with the shear rate becomes more complex, acquiring a partial viscoelastic character. The pastes become more workable due to stearine addition.

Literature data [14] show that the most simple equation giving a fair description of the behaviour of these fluids is

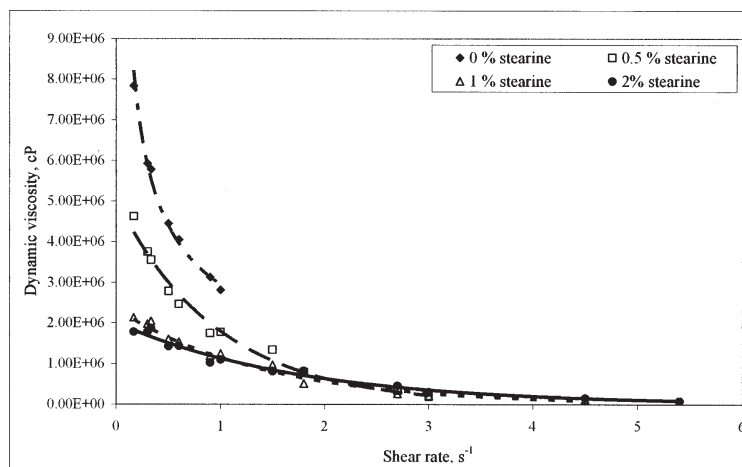


Fig. 4. Influence of the stearine concentration on the CLN paste viscosity

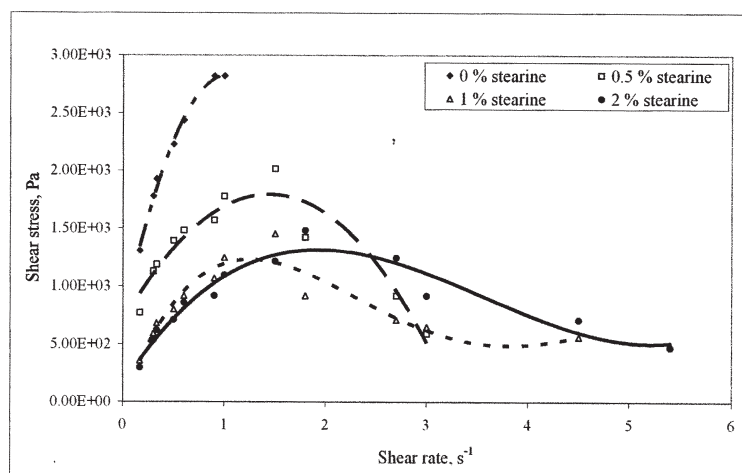


Fig. 5. Shear stress variation with the stearine concentration for CLN pastes

the Ostwald de Waele model, known also as the “power law” model.

$$\tau = k \cdot \dot{\gamma}^n \quad (1)$$

where k is the flow consistency index ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-n-2}$) and n the flow behaviour index.

Applying this model to the figure 5 curves (shear stress variation with the shear rate), the rheological parameters of all four pastes can be determined with a good precision. These parameters are presented in Table 3. The parameter n offers important information, confirming the previous remarks.

It is well known that for $n=1$ the fluid is newtonian, for $n < 1$ is pseudoplastic and for $n > 1$, it is dilatant [14].

All the unmodified CLN pastes are described by n values below 1. The last two pastes (CLN 3 and CLN 4), containing 1 and 2% stearine, have higher values of the flowing index

n (about 0.6) compared to 0.4 for CLN 1 and CLN 2. A higher flowing index, its approaching towards 1, symbolizes that the pseudoplastic character decreases and the workability increases (for extrusion, for example).

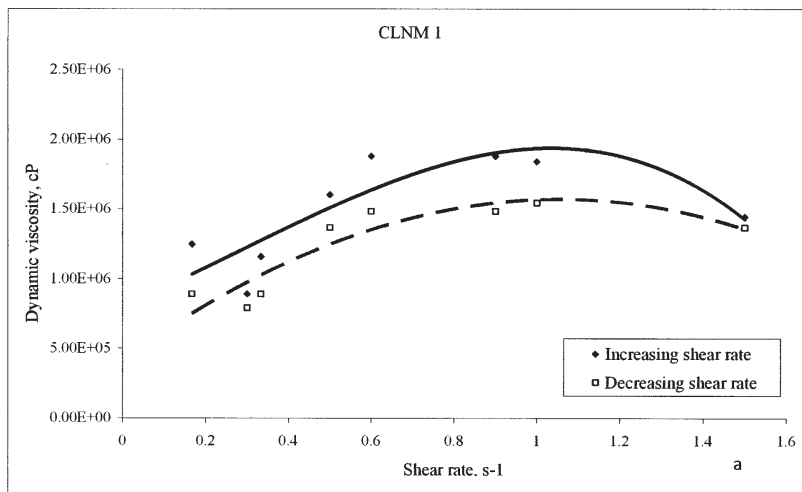
CLNM pastes

The rheological studies on modified clinoptilolite (CLNM) were performed with pastes prepared with the same recipes and the same procedure as in the case of unmodified clinoptilolite. The pastes were encoded as: CLNM 1 (0% stearine), CLNM 2 (0.5% stearine), CLNM 3 (1% stearine) and CLNM 4 (2% stearine).

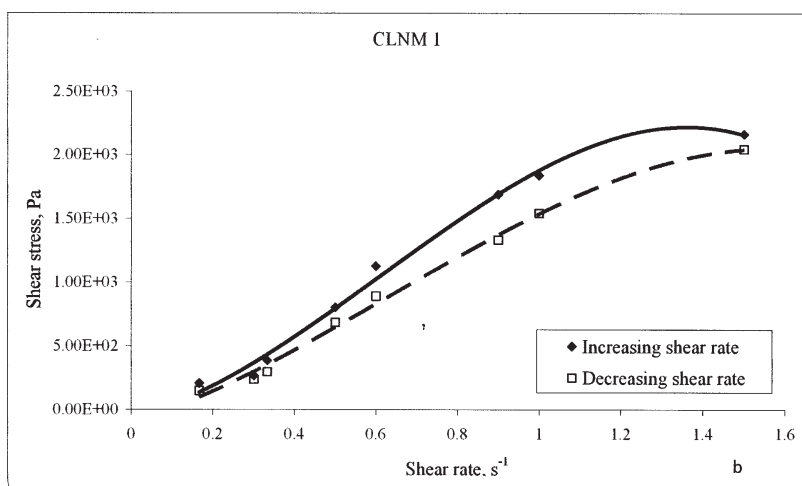
In the case of CLNM 1 paste with modified clinoptilolite without stearine, the rheological measurements were performed for the increasing and then decreasing shear rate so that the time influence could be observed. The presence of a hysteresis was noticed, which can be

Table 3
RHEOLOGICAL PARAMETERS OF THE CLINOPTILOLITE PASTES

Paste	Behaviour/ Rheological model	Rheological parameters	Workability
CLN 1	Pseudoplastic tixotropic fluid / Ostwald de Waele model (power law)	$k = 2953.2 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1.5709}$ $n = 0.4291$	satisfactory
CLN 2	Pseudoplastic tixotropic fluid / Ostwald de Waele model (power law)	$k = 1761.3 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1.5922}$ $n = 0.4078$	satisfactory
CLN 3	Pseudoplastic tixotropic fluid / Ostwald de Waele model (power law)	$k = 1205 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1.385}$ $n = 0.615$	Good
CLN 4	Pseudoplastic tixotropic fluid / Ostwald de Waele model (power law)	$k = 1052.6 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1.3954}$ $n = 0.6046$	Good



a



b

Fig. 6. Hysteresis for the CLNM 1 paste:
a) Dynamic viscosity variation and
b) shear stress variation with the shear rate increasing and decreasing

observed in figure 6 (a and b) and which indicates a strong thixotropy.

Figure 7 shows the dynamic viscosity variation with the increase of the shear rate and figure 8 shows the shear stress variation with increasing shear rate for all four CLNM pastes. By comparing the CLNM 1 curve from figure 7 with that of CLN 1 from figure 4, it appears that modifying the clinoptilolite by adding the cationic surfactant influenced the flowing behaviour. For the modified zeolite the flowing behaviour is dilatant at low shear rate values and with a pronounced viscoelastic component at high shear rate values.

Figure 8 indicates for all CLNM pastes a rheological behaviour without yield stress, with monotonous, but non-linear, increase of the shear stress with the shear rate. In

conclusion, the CLNM 1 paste has a dilatant behaviour with a viscoelastic component and it displays thixotropy.

In figures 7 and 8 one can observe that CLNM 2 paste (containing 0.5% stearine) has a dilatant behaviour at low shear rate range and with a viscoelastic influence at high shear rate range; in the case of the CLNM 3 paste it is noticed that at 1% stearine the rheological behaviour is somewhat different, at low shear rate range the rheological behaviour being pseudoplastic. The CLNM 4 paste has a similar behaviour as CLNM 1 and 2: dilatant at very low shear rates and viscoelastic at higher shear rates.

Looking at the curves presented in Figures 7 and 8, some conclusions can be drawn about the influence of the stearine concentration on the dynamic viscosity variation and on the shear stress for the CLNM pastes: at 0.5% and

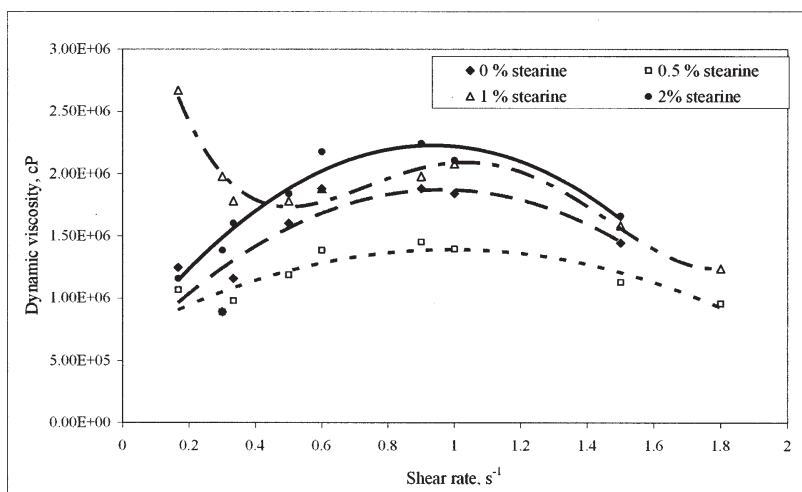


Fig. 7. Viscosity variation with the stearine concentration for CLNM pastes

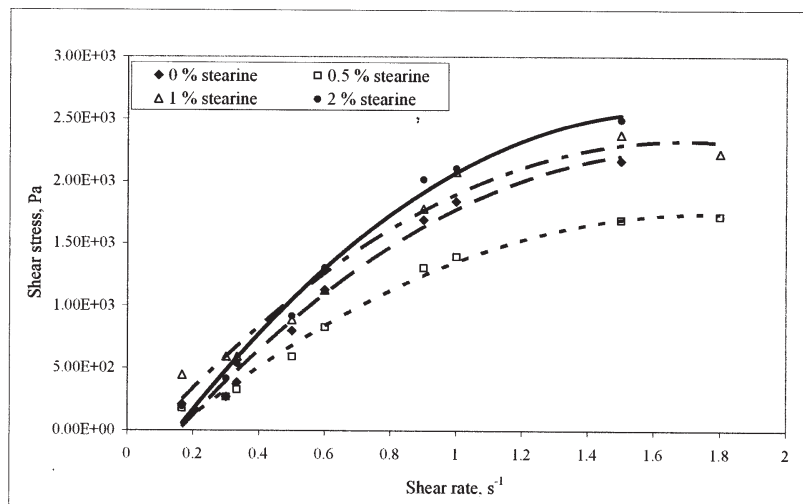


Fig. 8. Shear stress variation with the stearine concentration for CLNM pastes

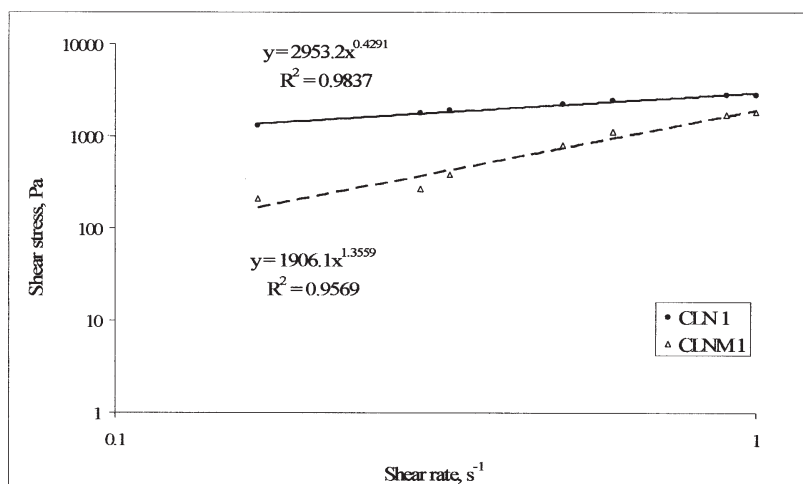


Fig. 9. Logarithmic diagram for CLN 1 and CLNM 1 rheological parameters determination

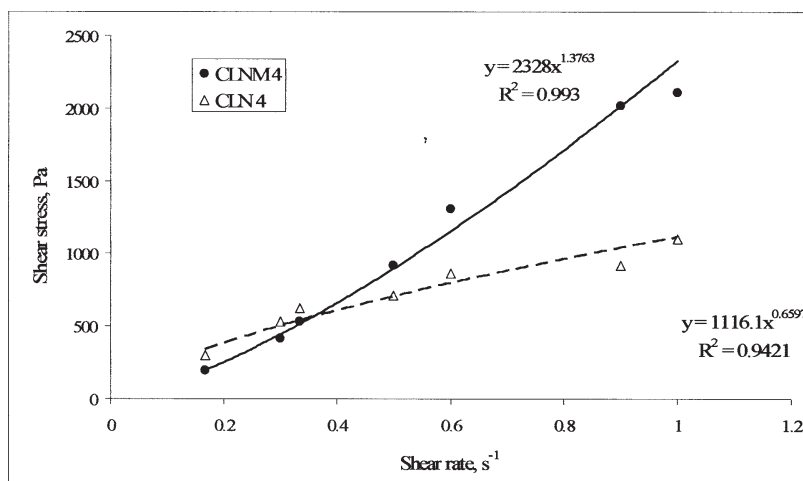


Fig. 10. Logarithmic diagram for CLN 4 and CLNM 4 rheological parameters determination

2% stearine, the behavior is similar to that from the case of the absence of stearine (dilatant with a viscoelastic component). At 1% stearine the flowing behaviour is more complex: pseudoplastic at the beginning, then dilatant and viscoelastic. A strange phenomenon is that the paste containing 0.5% stearine has a lower dynamic viscosity than in the absence of stearine (CLNM1), but the pastes containing 1% and 2% stearine have a higher dynamic viscosity than CLNM1, probably due to particle association.

Another way to represent the shear rate influence on the shear stress is using a logarithmic diagram, from which the model parameters can be easily calculated and where the "power law" model is a straight line. This kind of diagram is presented in figure 9, for the CLN 1 and CLNM 1. The first noticeable detail in the logarithmic diagram is the

slope of the straight line. If the slope is smaller than 1 (like for CLN 1 and CLNM 1 in fig. 9), the fluid is pseudoplastic.

In order to obtain additional information about the modified clinoptilolite based fluids, the Ostwald de Waele model can be applied for CLN 4 and CLNM 4 as it is shown in figure 10. Applying this model to the curves in figure 8, the model parameters for all four pastes are determined with a good precision. The parameters are presented in table 4. Once more, the flowing index n gives useful information. The CLNM 1, 2 and 4 pastes have a preponderantly dilatant behavior ($n > 1$), while the CLNM 3 paste is preponderantly a pseudoplastic fluid ($n < 1$).

Experimentally, it was discovered that the pastes workability is improved when the flowing index n is closer to 1 (CLNM 2 and 3, table 4).

Table 4
RHEOLOGICAL PARAMETERS OF THE MODIFIED CLINOPTILOLITE PASTES

Paste	Behaviour/ Rheological model	Rheological parameters	Workability
CLNM 1	Dilatant tixotropic fluid / Ostwald de Waele model (power law)	$k = 1906.1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-0.6441}$ $n = 1.3559$	satisfactory
CLNM 2	Dilatant tixotropic fluid / Ostwald de Waele model (power law)	$k = 1284.2 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-0.8496}$ $n = 1.1504$	Good
CLNM 3	Pseudoplastic tixotropic fluid / Ostwald de Waele model (power law)	$k = 1786.1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1.1361}$ $n = 0.8639$	Good
CLNM 4	Dilatant tixotropic fluid / Ostwald de Waele model (power law)	$k = 2328 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-0.6237}$ $n = 1.3763$	satisfactory

Conclusions

All the CLN pastes present a pseudoplastic non-newtonian fluid behaviour and thixotropy. While the stearine concentration in the paste composition increases, the dynamic viscosity and the pseudoplastic flow behaviour decrease. A viscoelastic behaviour appears also along with the increase in stearine. All these phenomena suggest the lubricant role of the stearine in this system.

The CLN pastes become more workable due to the stearine addition. Applying the Ostwald de Waele model, the rheological parameters for all four pastes were determined with reasonable accuracy. The flowing index $n < 1$ is a proof of the pseudoplastic character previously announced.

For CLNM pastes a more complex behavior was observed (dilatant with a viscoelastic component), a strong thixotropy being present. Using again the "power-law" model, it was proved that CLNM containing 0, 0.5 and 2 % stearine have a preponderantly dilatant behaviour ($n > 1$), while the CLNM 3, containing 1 % stearine is preponderantly a pseudoplastic fluid ($n < 1$).

When the flowing index n is approaching to 1, the pseudoplastic (if $n < 1$) or the dilatant ($n > 1$) behaviour decreases and the workability improves.

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