Rheological Characterization and Extrusion of Suspensions of Natural Zeolites

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Abstract:
A rheological characterization and extrusion of aqueous suspensions of natural zeolites were carried out in this work. Preparation of suspensions followed similar routes to those used for the colloidal processing of ceramic powders. The suspensions were prepared at different volume fractions (v/v%) ranging from 5 to 61 v/v% for a pH value of 7. The suspensions showed a Newtonian behavior for solid contents up to 20 v/v% and shear thinning at higher solid loads. For solid contents above 35 v/v%, the suspensions exhibited hysteresis and a yield stress that growth exponentially with the solid load. The appearance of a yield stress and its fast growing at relatively low solid concentration, as compared to other type of ceramic suspensions, is attributed to several factors as inter-particle interactions, the presence of relatively large particles and to the influence of their irregular morphology. Also, a breaking stress was measured for solid contents above 35 v/v%, which characterizes a failure of the structure of the suspensions after yielding. This breaking stress determines the onset of slip flow of the suspensions, which is interpreted in this work as a signal of good extrusion characteristics. Finally, inexpensive and free of surface defects tubes were obtained from natural zeolites.

Zusammenfassung:
Eine rheologische Charakterisierung und Extrusion wässriger Suspensionen natürlicher Zeolithe wurden in dieser Arbeit durchgeführt. Bei der Herstellung der Suspensionen wurden ähnliche Methoden angewandt wie bei der kolloidalen Verarbeitung von keramischen Pulvern. Die Suspensionen wurden bei unterschiedlichen Volumenanteilen (v/v%) hergestellt, die von 5 bis 61 v/v% bei einem pH-Wert von 7 reichten. Die Suspensionen wiesen ein Newtonsches Verhalten bei einem Füllstoffgehalt bis 20 v/v% und strukturviskoses Verhalten bei höheren Füllstoffgehalten auf. Für Füllstoffgehalte oberhalb von 35 v/v% wiesen die Suspensionen Hysteresis und eine Fließgrenze auf, die exponentiell mit dem Füllstoffgehalt wuchs. Das Auftreten einer Fließspannung und ihr ausgeprägtes Wachstum bei relativ niedrigen Füllstoffkonzentrationen, verglichen zu anderen keramischen Suspensionen, wird verschiedenen Faktoren zugeschrieben wie den Partikel-Partikel-Wechselwirkungen, der Gegenwart von relativ großen Partikel und des Einflusses ihrer heterogenen Morphologie. Darüber hinaus wurde eine Bruchspannung für Füllstoffgehalte oberhalb von 35 v/v% gemessen, die ein Versagen der Struktur der Suspension oberhalb der Fließgrenze andeutet. Die Bruchspannung bestimmt den Beginn des Gleitfließens der Suspensionen, was in dieser Arbeit als ein Kennzeichen für gute Extrusionseigenschaften gedeutet wird. Kostengünstige und von Oberflächendefekten freie Röhren wurden mit natürlichem Zeolith erhalten.

Résumé:
Une caractérisation rhéologique et l'extrusion de suspensions aqueuses de zéolites naturelles ont été entreprises dans ce travail. La préparation des suspensions est semblable à celles utilisées pour le traitement colloïdal des poudres de céramique. Les suspensions ont été préparées à des fractions volumiques différentes allant de 5 à 61 %v/v et à un pH 7. Les suspensions présentent un comportement Newtonien pour des fractions solides allant jusqu'à 20 %v/v, et rhéo-amincissant pour des fractions supérieures. Au-dessus de 35 %v/v, les suspensions montrent une hystérésis et une contrainte seuil qui croît exponentiellement avec la charge solide. L'apparition d'une contrainte seuil et sa croissance rapide pour des concentrations relativement faibles en solide par rapport à d'autres types de suspensions céramiques, sont attribuées à différents facteurs tels que les interactions inter-particules, la présence de particules relativement grandes, et à l'influence de leur morphologie irrégulière. De plus, une contrainte de fracture a été mesurée pour des fractions en solide supérieures à 35 %v/v, qui caractérise la rupture de la structure des suspensions au-dessus du seuil. Cette contrainte de fracture détermine le début de l'écoulement de glissement des suspensions, qui est ici interprété comme un signe de bonnes caractéristiques d'extrusion. Enfin, des tubes peu coûteux et sans défauts de surface ont été obtenus à partir de zéolites naturelles.

Key words: powder suspensions, natural zeolites, extrusion, yield stress

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1 INTRODUCTION

Natural or mineral zeolites are crystalline hydrated aluminosilicates of alkaline metals (Na, K, Li) and alkaline-earth metals (Ca, Ba, Mg). Structurally, zeolites are complex inorganic polymers based on three-dimensional frameworks of silica and alumina tetrahedra linked to each other by sheared oxygen ions [1]. The aluminosilicate framework of a zeolite has a negative charge, which is balanced by positively charged cations. The interconnected voids of these frameworks may reach as much as 50% of the volume of the zeolite and normally accommodate the cations and water molecules. The diameter of the interconnecting channels in a natural zeolite ranges between 3 and 8 Å [2] and the structural formula of a zeolite is given by $M_x/_n[(AlO_2)_x(SiO_2)_y]wH_2O$ where n is the valence of the cation M, w is the number of water molecules per unit cell and $x + y$ is the total number of tetrahedra per unit cell [1].

Natural zeolites have exceptional physical-chemical properties that arise from their tridimensional porous structures, which permit the transfer of ions and the selective sorption of molecules. Natural zeolites may be used as "molecular sieves" to separate ions from aqueous solutions by ionic exchange [3, 4] and to separate mixtures of gases in hydrocarbon reactions [1, 5–6], amongst many other applications [7–10]. In addition, natural zeolites are inexpensive as compared to synthetic ones and can be also used as supports for catalysts. Natural zeolites are found in different parts of the surface of earth as well as in the sea bed. The characteristics of a zeolite deposit are determined by their genetic mode of occurrence and by variables such as temperature, geographic location and ash/water properties. More than 40 types of natural zeolites have been identified, being some of the most common the clinoptilolite, mordenite, chabacite and erionite. Clinoptilolite-heulandite, mordenite and erionite are the most abundant natural zeolites in the Mexican territory [11]. However, the use of Mexican natural zeolites (MNZ) is very limited due to the lack of a systematic physical-chemical characterization and identification of suitable powder processing techniques. Thus, it is necessary to identify the most appropriate forming methods if a massive processing of this kind of materials is intended. In particular, knowledge of the rheological behavior of zeolite suspensions is required to select the most appropriate consolidation technique.

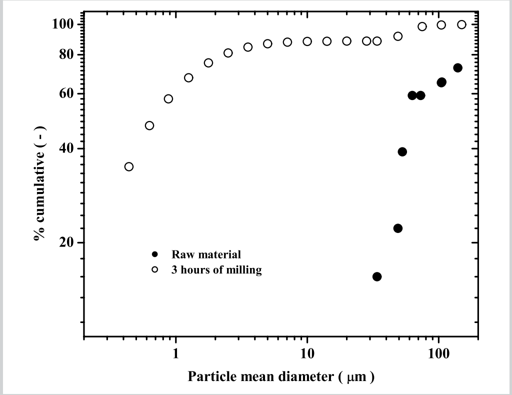
Colloidal processing of ceramics is a powder processing technique that has received great attention in the last decades, since it allows the fabrication of products with high densities and homogeneous microstructures [12]. Colloidal processing requires the preparation of stable suspensions with dominating repulsive forces between particles to maintain their dispersion during preparation and consolidation [13]. Repulsive forces can be produced by electrostatic, steric or electrosteric mechanisms [14 – 16]. Typically, anionic dispersants are used due to their easier availability and lower cost as compared to cationic ones. The solid content, particle size distribution, shape, and colloidal stability of the dispersed particles, all together determine the flow behavior of the system [17]. At the end, the rheological behavior of the suspension determines the most suitable forming process among the traditional ceramic shaping technologies (namely, slip-casting, tape-casting, and extrusion). On the other hand, the resulting mechanical and thermal properties of the product depend on the characteristics of the processed suspension, mainly through the microstructure and density of the product before firing (green product).

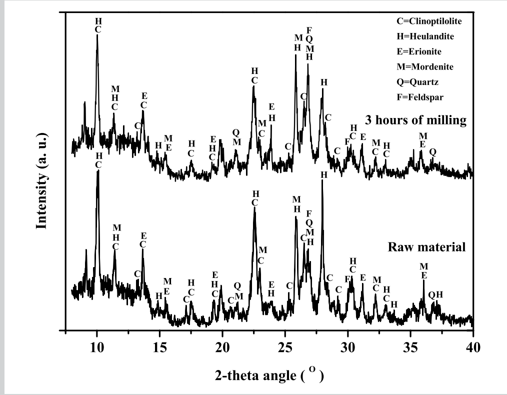
Since interactions between particles have a pronounced effect on their flow behavior, rheological methods are very useful to investigate the properties of powder suspensions. Typical flow behavior of powder suspensions and pastes includes non-Newtonian viscoelastic characteristics as shear thinning, shear thickening, time dependency (tixothropy) and even finite yield stresses and slip at high solid contents. The yield stress determines the shape retention of the product after processing. Meanwhile, slip of the suspension at solid boundaries must be considered not only for proper rheological characterization [18], but also for the extrusion of free of defects ceramic compounds. Graczyk and Gleissle [19] have pointed out the properties that are important for extrusion of ceramic compounds; namely, yield stress, permanent deformation and cohesion of the materials during and after deformation, which may be quantified by rheological measurements. These authors carried out capillary rheometry studies of γ-alumina compounds and showed that the best extrusion results are obtained when little or no shear deformation (slip) occurs in the sample.

Figure 1 (left): Negative cumulative percent as a function of particle mean diameter for the raw material and three hours of milling.

Figure 2: XRD spectra of the MNZ for raw material and 3 hours of milling.

Table 1: Chemical composition of MNZ, values are given in wt.% of oxides (LoI = loss on ignition).





The extrusion of synthetic and natural zeolite monoliths and tubes has been recently reported by some authors [20 – 22], but almost not attention has been paid to their suspension rheology. In fact, information in the literature regarding the rheological behavior of aqueous suspensions of zeolites, in particular natural zeolites, is scarce. McIntire and Filisko [23] have recently studied the squeeze flow of suspensions of zeolites at low concentrations in silicon oil, with a focus on the effect of particle aggregation on suspension rheology. These authors tested different empirical models for spherical particles in order to describe the viscous behavior of the suspensions. However, due to the relatively uncontrolled process of obtaining natural zeolite particles as compared to synthetic ones, a distribution of sizes and shapes is usually obtained, which strongly influence the rheological behavior of suspensions. Thus, a complex rheological behavior is expected for zeolite suspensions with increasing particle concentration. Therefore, it is the aim of this work to analyze the rheological behavior of aqueous suspensions of MNZ in a wide range of concentration. For this purpose, the technique of colloidal processing of ceramics has been used. This approach, to our knowledge, has not been previously used to prepare zeolite suspensions. The results from this study are expected to help in the establishment of directions for the appropriate processing of zeolite suspensions, and as an application, the extrusion of tubes made up of MNZ is presented. Details of the research are given below.

2 EXPERIMENTAL

2.1 CHARACTERIZATION OF POWDERS

The MNZ mined stones used in this work were obtained from the region of Catano-Etla, Oaxaca, in the south of México. The zone is covered by volcanic rocks of intermediate to acid composition (> 62% SiO_2) and is part of a formation known as Suchilquitongo, with an age corresponding to the Miocene, approximately 15 million years.

The stones were dry ball-milled and mixed up to reach particle sizes smaller than 105 μm. This maximum size was chosen in order to have an aspect ratio of about ten, at least, between the gap of the rheometer and the average size of the particles to produce consistent rheometrical results. The particle size distribution (PSD) was not purposely targeted, instead the particles used were those obtained under fixed milling time conditions, three hours in this case. The density of the milled particles was 2223.6 kg/m^3. The negative cumulative percentage of particle sizes for the raw powders, and for the 3 h milled powders are shown in Figure 1. The particle size distribution for the milled powders seems to be consistent with a bimodal distribution having 80 wt.% of particles smaller than 3 μm and approximately 20 wt.% of particles at sizes between 30 and 105 μm.

The particles were characterized by X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer equipped with CuKα radiation (35 KV, 25 mA). The XRD patterns were recorded with a scanning velocity (2θ) of 2°/min and the identification of phases was carried out by comparison of the peaks with the JCPDS files 025-1349 (clinoptilolite), 022-0854 (erionite), 60-239 (mordenite), 21-131 (heulandite), feldspar (025-0618) and 033-1161 (quartz). The XRD analysis of the MNZ powders revealed typical patterns of a clinoptilolite-heulandite type zeolite, being this the major mineralogical phase of the MNZ. The estimated amount of clinoptilolite in the rocks ranged between 60 and 85 wt.%. In addition, there were

Oxide	Raw material	3 hours of milling
SiO_2	65.7	65.6
Al_2O_3	11.5	11.45
Na_2O	5.36	5.56
K_2O	2.44	2.44
MgO	1	1.1
CaO	1.34	1.35
Fe_2O_3	1.66	1.74
LoI	10.35	10.19
Si/Al	5.71	5.73

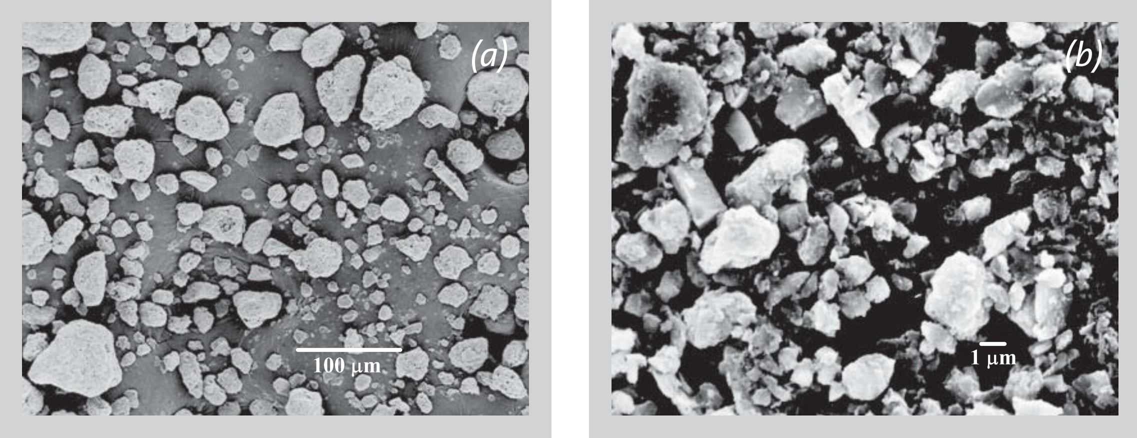


Figure 3 (above): SEM micrographs of MNZ. (a) Powders without milling (raw material) and (b) Powders after three hours of milling.

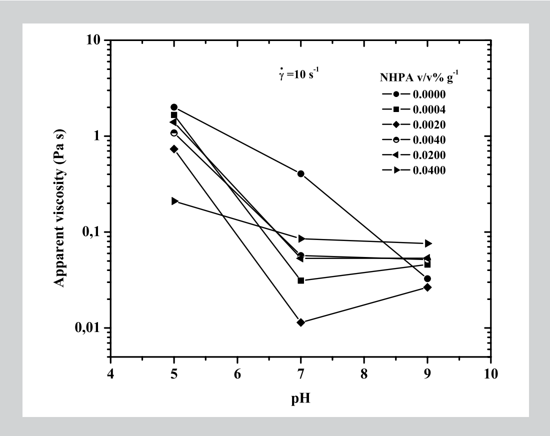


Figure 4 (left below): Apparent viscosity as a function of pH for a suspension with ϕ = 30 v/v% and various contents of NHPA at 10 s^{-1}. Continuous lines between experimental points are drawn in order to show the trend of data.

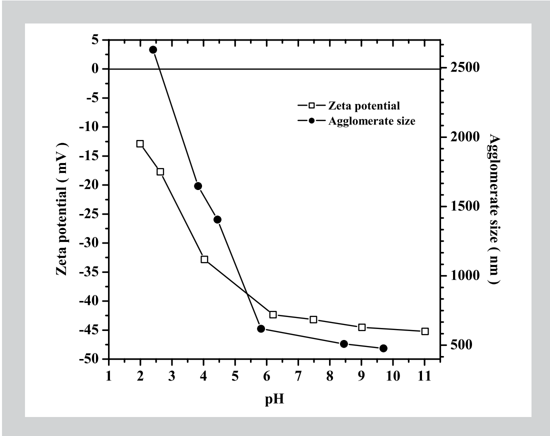


Figure 5 (right below): Zeta potential and agglomerate size of the powders as functions of the pH. Continuous lines between experimental points are drawn in order to show the trend of data.

found mordenite and erionite as second and third main phases, respectively, and some quartz and potassium aluminum silicate sanidine feldspar as impurities (see Figure 2).

A chemical analysis of the MNZ was done with an atomic absorption spectrophotometer (Perkin Elmer 403). The results for the raw and milled powders are shown in Table 1. The Si/Al ratios of two samples were 5.71 to 5.73, respectively, which are consistent with a clinoptilolite phase of sedimentary type [1]. The milling did not introduce significant amounts of contaminants to the powder, which does not contain toxic elements. Raw and milled particles were observed in a scanning electron microscope (SEM, Jeol JSM-630). Two selected images are shown in Figure 3 for the raw and milled for 3 hours powders, respectively. It may be seen that the particles exhibited irregular morphology and variable sizes.

2.2 PREPARATION OF SUSPENSIONS

Aqueous suspensions of MNZ were prepared at the desired solid volume concentration ϕ, pH and dispersant concentration in bottles of polyethylene of 250 ml capacity, which were agitated by putting them between two counter-rotating rollers at 159 RPM during 24 hours. After this, air was extracted from the samples with a vacuum pump during 10 minutes.

In order to determine the conditions for optimal dispersion of the powders, a study of the influence of pH and amount of dispersant on the viscosity of a 30 v/v% suspension was performed at a temperature of 22 ± 0.5°C. The pH values were controlled in the range between 5.0 and 9.0 by dosing small amounts of HNO3 and NaOH, meanwhile ammonium polyacrylate (NHPA) was used as an anionic dispersant, which is available as an aqueous solution at a concentration of 39 – 41 v/v% (Darvan C®, Vanderbilt). The concentration of dispersant was controlled in the range from 0 to 0.041 v/v%.

A pre-shear at a rate of 900 s^{-1} was supplied to the samples for 60 s before measurements. The viscosity measurements as a function of pH for different concentrations of dispersant at 10 s^{-1} are shown in Figure 4. It may be seen from the plot that the values of the pH and NHPA that gave the best dispersion of particles were 7 and 0.002 (v/v%)/g of zeolite, respectively.

The stability of the suspensions was evaluated by zeta potential measurements. The zeta potential of the MNZ particles in suspension and the agglomerate size at different pH values from 2 to 10 was measured using a ZETA-PLUS zetameter (Brookhaven Instrument Corporation BI-MAS). In order to avoid sedimentation of large particles within the zetameter cell, a sample of the milled powder was classified by gravitational sedimentation to reach particle sizes smaller than 0.7 μm. A sample of 0.45 g of the classified MNZ powder was dispersed in 1 l of deionized water containing

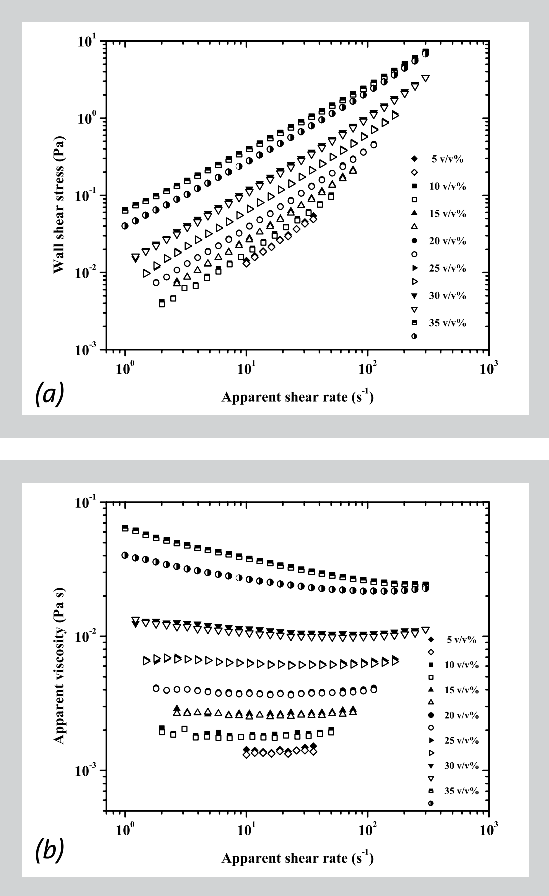


Figure 6: (a) Shear stress and (b) apparent viscosity, as functions of the apparent shear rate for suspensions with 5 ≤ ϕ ≤ 35 v/v%. Increasing and decreasing shear rate cycles are plotted, filled and hollow symbols correspond to up and down directions, respectively.

0.01 M of $NaNO_3$ to maintain the ionic strength of the suspension. The suspensions were prepared in Nalgene flasks and maintained for 24 hours under mechanical stirring. The pH was adjusted in aliquotes of 100 ml by adding HNO_3 at 11.5 M (Química Meyer, México) and NaOH at 2.5 M (Fermont, México). The results of zeta potential measurements shown in Figure 5 indicate a negative charge of the clinoptilolite in almost the whole pH range studied and becomes more negative with increasing the pH. Such a negative charge has been attributed to substitution of Al^{3+} for Si^{4+} within the clinoptilolite lattice due to grinding [1, 24 – 25]. The isoelectric point (IEP) of the suspension was not observed in the pH range studied, in agreement with previous results by Ersoy and Çelik [25] for clinoptilolite. It is observed from Figure 5 that the agglomerate size decreases rapidly as the pH increases, and that for pH > 6 the particle size tend to reach and asymptotic value, in agreement with good electrostatic dispersion of the particles.

Table 2 (below): Aqueous suspensions of MNZ (all numbers in v/v%).

Sample	Solid loading [v/v%]	Amount of dispersant [v/v%]	Amount of water [v/v%]
SMNZ-1	5	0.022	94.978
SMNZ-2	10	0.044	89.956
SMNZ-3	15	0.067	84.933
SMNZ-4	20	0.089	79.911
SMNZ-5	25	0.111	74.889
SMNZ-6	30	0.133	69.867
SMNZ-7	35	0.156	64.844
SMNZ-8	40	0.178	59.822
SMNZ-9	45	0.2	54.8
SMNZ-10	50	0.222	49.778
SMNZ-11	52	0.231	47.769
SMNZ-12	54	0.24	45.76
SMNZ-13	61	0.271	38.729

2.3 RHEOLOGICAL MEASUREMENTS

A detailed study of the effect of solids loading on the rheological behavior of MNZ suspensions was carried out once the optimum combination of concentration of dispersant and pH were determined (0.002 (v/v%)/g of zeolite and 7, respectively). Thirteen samples with the characteristics reported in Table 2 were prepared and analyzed under steady shear flow using a stress controlled Paar Physica UDS 200 rheometer with two Couette cells (Z2-DIN and Z3-DIN) and a parallel plate one of 0.0025 m in diameter. The use of three measurement cells was necessary in order to cover the wide range of viscosities resulting from the ample interval of concentrations analyzed in this work. In particular, the parallel plate cell was only used for the suspension with the highest concentration (61 v/v%). The flow experiments were carried out in a shear rate range from 0 to 1000 s^{-1} at a temperature of 25°C. The limit in the shear rate was determined by the presence of hydrodynamic instabilities at low solid contents as well as by slip at the rotating cylinder at high solid contents. Logarithmic ramps and cycles of increasing and decreasing shear stress were performed in order to obtain the flow curves and evidence of thixotropy for the higher concentrations. The experiments were run twice in order to check reproducibility of data.

2.4 EXTRUSION OF TUBES MADE UP OF MNZ

Extrusion of tubes was performed with two concentrated suspensions or pastes of MNZ (ϕ = 61 v/v%) one being pure and the other containing low viscosity (300 – 550 mPa·s) methyl cellulose, as organic binder, at a concentration of 1.5 wt.% (Methocel® MC Fluka). This type of cellulose binder has been used by other authors for the extrusion of zeolites pastes [20 – 22]. The binder provides cohesion among particles and produces an increase in the yield stress of the suspension. The pastes were prepared in a Hobart

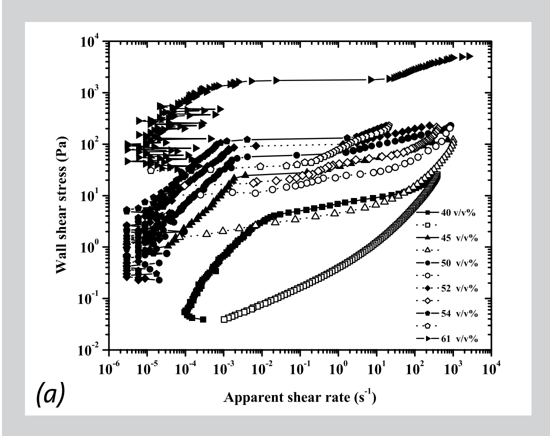
A-200 mixer at room temperature and the extrusion was performed by using a Göttfert Rheotester 1000 capillary rheometer with a 0.012 m barrel at T = 30°C. For this purpose, a tubing die was adapted to the rheometer and three different extrusion speeds (0.434, 0.694 and 0.868 mm/s) were tested.

3 RESULTS AND DISCUSSION

3.1 STEADY SHEAR FLOW

The flow and viscosity curves obtained for the suspensions with different solid contents are plotted in Figures 6 and 7. The data in the flow curves are the average of two measurements, whose uncertainty is comparable to the size of the symbols used to represent the data. Several interesting characteristics are observed in these plots. First, it can be seen from Figure 6 that the flow behavior is almost Newtonian up to ϕ = 20 v/v%, which suggests that inter-particle interactions are negligible. The apparent increase in viscosity at high shear rates within this range of solids concentration is due to the onset of flow instabilities in the Couette cell. For suspensions with 25 v/v% $\leq \phi \leq$ 35 v/v%, the viscosity curves in Figure 6b display a shear thinning behavior, which is enhanced when the solid load is increased in this range. There is a competition between the effects of inter-particle mechanical contacts and lubrication (by the suspending medium) of the inter-particle spacing in this flow regime. It seems that in this concentration range the inter-particle spacing is well lubricated, which determines the reduction in viscosity as the shear rate is increased. Due to their shear thinning behavior and the absence of a yield stress (see below), suspensions of MNZ in this concentration regime are suitable for slip casting.

At still higher solid contents (ϕ > 35 v/v%), inter-particle spaces are reduced and less lubricated while particle-particle mechanical contacts become more frequent. These facts, along with the irregular geometrical characteristics of the MNZ change the rheological behavior of the suspensions from a purely viscous shear thinning fluid (Figure 6) to a viscoplastic one (Figure 7), for which, a critical shear stress (yield stress τ_y) is required for the onset of flow (see below). Summarizing the observations in terms of the solid load, the MNZ suspensions stabilized at pH 7 with 0.002 v/v% of NHPA g^{-1} of zeolite, are characterized by the rheological regimes presented in Table 3.



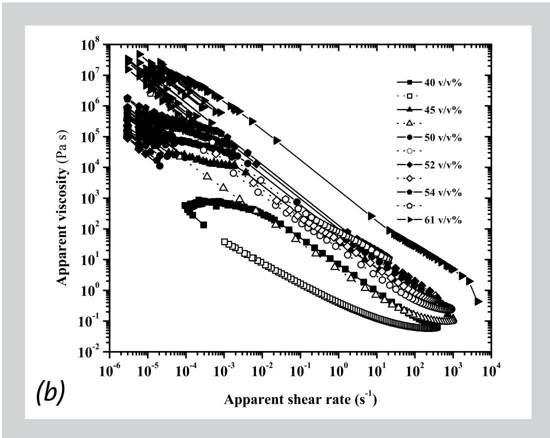


Figure 7: (a) Shear stress and (b) apparent viscosity, as functions of the apparent shear rate for suspensions with 40 $\leq \phi \leq$ 61 v/v%. Increasing and decreasing shear rate cycles are plotted, filled and hollow symbols correspond to up and down directions, respectively. Continuous lines between experimental points are drawn in order to show the trend of data.

3.2 SHEAR STRESS CYCLES, HYSTERESIS AND YIELD STRESS

Shear stress cycles were performed on the MNZ suspensions and the results are also included in Figures 6 and 7. The return flow curve for the 61 v/v% suspension is not shown because the sample was expelled from the rheometer at high shear rates. It can be seen from these Figures that hysteresis cycles or thixotropy are present for suspensions with ϕ > 30 v/v% (see Figure 6a), and that the area of the cycle, which represents the energy necessary to break any existing structure, increases along with ϕ. This behavior for high solid contents suggests strong mechanical inter-particle interactions at low shear rates that give rise to a yield stress (see next paragraph).

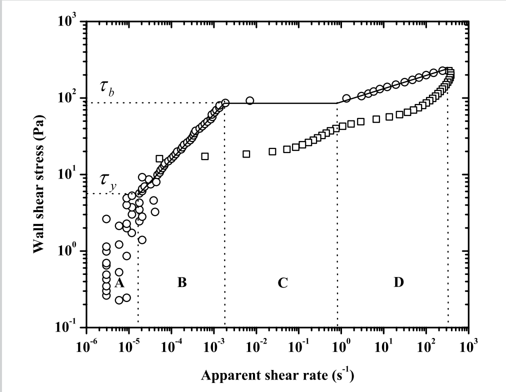
Thixotropic systems are often characterized by a yield stress; this was measured in this work when obtaining the flow curves in Figure 7a by

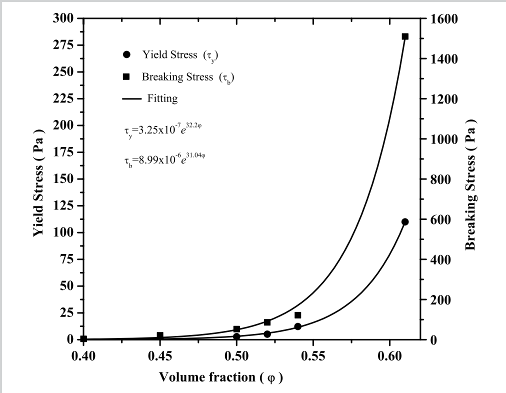
Table 3 (below): Different rheological regimes in MNZ suspensions.

Solids loading φ [v/v%]	Rheological behavior
φ < 20	Newtonian
20 < φ < 35	Shear thinning
35 < φ	Viscoplastic

Figure 8 (above): Flow curve for a suspension with ϕ = 52 v/v% showing four different regions, the static yield τ_y and breaking τ_b stress values. Continuous lines between experimental points are drawn in order to show the trend of data.

Figure 9: Static yield τ_y and breaking τ_b stress values as functions of the volume fraction.





controlling the shear stress. It is noteworthy that such a detailed flow curves cannot be obtained from shear rate controlled experiments, as has been recently shown by Pavlinek et al. [26]. In most cases, shear rate controlled measurements underestimate the yield stress value. It is interesting to note that the flow curves for suspensions with ϕ > 40 v/v% in Figure 7a resemble those recently reported by Paumier et al. [27] for clay materials, as well as the yielding behavior described by Pavlinek et al. [26] for electrorheological silica suspensions. In agreement with Pavlinek et al., the flow curves for suspensions with ϕ > 40 v/v% of MNZ may be divided into four regions, as it is illustrated independently for ϕ = 52 v/v% in Figure 8 (this graph has been separated so as not to make Figure 7a crowded). Region A is related to a solid-like behavior of the suspensions, where the shear stress increases with negligible deformation. As the shear stress is further increased the suspensions start to deform and flow (region B) at a critical shear stress τ_y, also known as the static yield stress value, which increases with the solid content (see below). Region B is limited by a "breaking stress" τ_b where a sudden increase of several orders of magnitude in the shear rate occurs (region C). This critical stress is related to a sudden failure of the structure of the suspension in the neighborhood of the rotating cylinder. Visual inspection showed that the failure was localized close to the rotating cylinder, and that the rest of the suspension exhibited a solid-like behavior that suggests a sort of cohesive failure. At still higher shear stresses in region D, there seems to be flow, but the behavior is more likely related to the dynamic friction or slip between a small amount of suspension attached to the cylinder and the rest of the fluid. Thus, the behavior described in this section clearly prevents the processing by slip casting of suspensions with ϕ > 40 v/v%, and suggests their transformation by extrusion means.

As previously mentioned, thixotropy and yield stresses in suspensions are usually linked to the existence of structures at rest. There are however, different ways by which a well dispersed suspension may exhibit a yield stress. One of these ways arises when coarse particles are immersed in a suspension with a preponderant content of fine particles. Ancey and Jorrot [28] showed that the addition of coarse particles in a colloidal suspension usually induces an increase of the yield stress. These authors proposed two mechanisms to account for the increase in the yield stress, they consist of depletion of particles at low concentrations (ϕ < 40 v/v%), as well as the development of coarse particle networks at higher concentrations, respectively.

From the PSD presented in Figure 1, it may be seen that the particles used in this work conform with the description in the previous paragraph, namely, almost 80 wt.% of the particles range around colloidal size and the rest corresponds to relatively coarse micrometric particles. For the suspensions with $\phi \geq$ 40 v/v% in this work, the percentage of coarse particles seems to dominate the rheological behavior, very likely via mechanical contacts. Moreover, the irregularity of the MNZ particles (see Figure 3) is expected to produce poor packing, more restrictions to their movement, and then to enhance the yield stress of the suspensions. Under such conditions, yielding requires overcoming stronger inter-particle mechanical forces. This may explain the existence of thixotropy and yield stresses at relatively low solids content, as compared to those observed in suspensions of purely colloidal particles [16, 29]. Therefore, in agreement with Ancey and Jorrot [28], the presence of coarse particles strongly affects the rheology and yielding behavior of the suspensions.

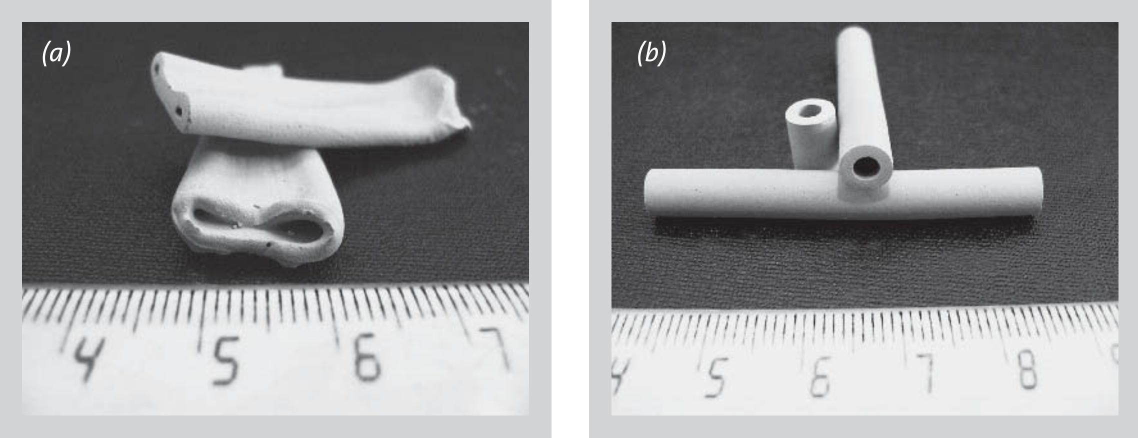


Figure 10 (above): Photographs of tubes obtained by extrusion of a suspension with 61 v/v% of MNZ at 30°C. (a) Green tubes without binder. (b) Green tubes with binder. The scale corresponds to 1 cm.

3.3 DEPENDENCE OF τ_y AND τ_b ON SOLIDS CONTENT

Figure 9 shows the measured τ_y and τ_b values as functions of the solid concentration for suspensions with $\phi \geq 40$ v/v%. It may be seen that τ_y grows exponentially with ϕ, or equivalently, with a decrease in the liquid content (see [30]). When ϕ is increased, there is a decrease in the liquid surrounding the particles, which results in poor lubrication of the inter-particle spacing, stronger particle-particle interactions and then an increase in the yield value. The yield stress versus ϕ relationship can be very well fitted by an exponential function given by:

$$\tau_y = 3.25 x 10^{-7} e^{32.2\varphi} \quad (1)$$

This result is in agreement with those by Benbow et al. [30] regarding an exponential decrease of the yield stress along with an increase of the liquid content. On the other hand, it can be also observed from Figure 9 that the τ_b values also increase with the solid content and follow a similar relation (Equation 2) to that of the yield stress. This τ_b value may be of relevance for the characterization and processing of this sort of suspensions, since meanwhile τ_y determines the onset of deformation and flow of the suspension, τ_b determines a failure on the boundary conditions or slip, which is generally accompanied by a plug flow.

$$\tau_b = 8.99 x 10^{-6} e^{31.04\varphi} \quad (2)$$

Slip in concentrated suspensions is usually referred as "apparent slip" since it is not a true violation of the boundary conditions, but it is a flow enhancement in most cases due to a depletion layer in the neighborhood of the rheometer walls. Attempt was not made in this work to evaluate the width of the depletion layer, nor to perform any correction to the data due to slip effects (see [18]). However, evidence of slip in concentrated suspensions or pastes may be interpreted as a signal of good extrusion characteristics [19].

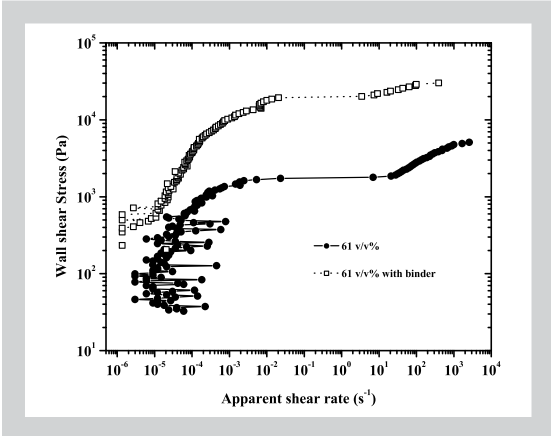


Figure 11: Flow curves for the suspensions containing ϕ = 61 v/v% of MNZ with and without binder. Continuous lines between experimental points are drawn in order to show the trend of data.

The higher the yield stress, the stronger slip and the better consistency of the suspension after extrusion.

3.4 EXTRUSION OF MNZ SUSPENSIONS

As stated in the previous paragraph, slip and plug flow in concentrated suspensions or pastes are signals of good extrusion characteristics. Following this result, extrusion tests were performed for the suspension at the highest solid load, ϕ = 61 v/v% (concentration of NHPA and pH, 0.002 (v/v%)/g of zeolite and 7, respectively). For this suspension the extrusion took place smoothly without defects on the extrudate surface. However, due to the relatively low yield stress of the paste, these tubes did not retain their shape after extrusion (see Figure 10a). To overcome this problem, a binder (methyl cellulose) in a concentration of 1.5 wt.% was added to the suspension in order to increase its yield stress and to retain the tube shape. The flow curves for the suspensions with and without binder are shown in Figure 11. The yield stress value for the ϕ = 61 v/v% suspension with binder (τ_y = 747 Pa) increased almost one order of magnitude with respect to that of the pure suspension (τ_y = 110 Pa), and may be considered as a target value for an extrudate of this kind of MNZ to retains its shape. A similar difference in the order of magnitude was observed for the breaking stress as well as for the viscosity.

The extrudates obtained by using the binder also appeared free of surface defects, but in contrast to the observed for the suspension without binder, these retained their shape after extrusion, in agreement with a higher yield stress value (see Figure 10b). The three different extrusion speeds used resulted in tubes of similar quality. Still, further work is necessary to establish the minimum binder concentration required to reach a critical yield stress that maintains the extrudate shape with the minimum extrusion pressure. At this point, however, the present study shows that the procedure followed in this work to prepare suspensions and pastes of natural zeolites allows for the production of inexpensive and free of surface defects extrudates. Further work is being carried out to evaluate the physical-chemical properties of the tubes.

4 CONCLUSIONS

The results in this work show several aspects of the rheological behavior of suspensions of natural zeolites, which are explained on the basis of their particle size distribution and morphology. The main conclusions are listed below:

- The suspensions showed Newtonian behavior for solid content up to 20 v/v% and shear thinning at higher solid loads. For solid contents above 40 v/v%, the suspensions exhibited viscoplastic behavior, hysteresis and yield stress. The appearance of a yield stress limits the slip casting processing of this sort of suspensions.
- The concept of a "breaking stress" was introduced for solid contents above 40 v/v%, which characterizes a sudden failure of the structure of the suspensions after yielding. The "breaking stress" determines the onset of slip and plug flow, which are interpreted as signals of good extrusion characteristics of the suspensions.
- Both, the yield and breaking stresses grow exponentially with the solids loading.
- Finally, the results from this work may be useful for understanding the rheological behavior of suspensions of natural zeolites and its influence during processing. A successful application of the results has been made to the extrusion of tubes made up of MNZ.

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