STUDY OF CLAY'S MINERALOGY EFFECT ON RHEOLOGICAL BEHAVIOR OF CERAMIC SUSPENSIONS USING AN EXPERIMENTAL DESIGN

Afef Jmal Ayadi[1], Julien Soro[2], Amel Kamoun[1] & Samir Baklouti[1]
[1] Laboratoire de chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax, Route de Soukra Sfax, Tunisie.
[2] Groupe d'Etudes Matériaux Hétérogènes, ENSCI, 47-73, Avenue Albert Thomas, 1187065 Limoges cedex, France.

ABSTRACT
Three clays namely Illite (I), Montmorillonite (M) and Kaolin (K) were chosen as references to study the effect of clay composition on the rheological behavior of the ceramic suspensions. A mixture design was applied to study the evolution of the viscosity of the clayey suspensions according to the proportions of the clay references in the mixture. The statistical study shows that the fitted model was adequate to describe the rheological behavior of clay suspensions. It was concluded that the rheological properties of the ceramic suspensions were mainly governed by the percentage of Montmorillonite. It was also demonstrated that to obtain low viscosities (0.20-0.40 Pa.s), as required by the ceramic industry, the clay mixture should not contain more than 16 % of Montmorillonite.

Keywords: *Clay(kaolin, illite, Montmorillonite), Rheology, Mineralogy, Mixture design.*

1. INTRODUCTION

Clays are widely used in the manufacture of many traditional clay-based ceramics. The mineralogical and chemical composition of clays determine the ceramic behavior and properties of the clays, ie their plasticity, drying and firing characteristics [M.A. MANDOUR 1989].[M Önal 2009].

In the ceramic Industry, the nature of mineral clay plays an important role in the behavior of each stage of manufacture, the rheology of slurries and sintered products [S.Ferrari, 2006L]. The clay fraction is consisting, in the most cases, of Kaolin, Illite and monmorillonite or a mixture of these three materials at different proportions.

Clay minerals are hydrous silicates or alumino silicates and they constitute the colloidal fraction of soils sediments, rocks and water [Pau.F Luckhan 1999] [Sibel Tunç 2008], [E.Tompacz 1998]. The smectite 2:1 structural units are three layer clay minerals in which one octahedral sheets entered between two tetrahedral sheets (TOT) by forming one unit layer and one tetrahedral sheet of one unit layer is adjacent to another tetrahedral sheet of another layer. Bentonites belong to smectites group are largely composed of the mineral **montmorillonite** $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2{\bullet}n(H_2O)$ and smaller amount of other clay mineral [Sibel Tunç 2008]. In every clay's category, there is a repeated basal plane distance d, between parallel silicate units, the d-spacing of a dried montmorillonite is 10 Å and the mineral swells uniformly until it reaches a spacing of 20 Å because of the weakness of connection between planes. Bentonite minerals have wide range of applications in the different industrial fields such as ceramic, cement, paints, food, drilling fluids, pharmacy and paper industries. Illite has been widely used as a fluxing material for many years in the ceramic industries. [Darunee Wattanasiriwech 2009, E.Tomback 2004]. **Illite** (micaceous mineral) is a phyllosilicate or layered alumino-silicate as smectite clay. Its structure is constituted by the repetition of Tetrahedron – Octahedron – Tetrahedron (TOT) layer. The interlayer space is about 10 Å and is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling. Structurally illite is quite similar to muscovite or sericite with slightly more silicon, magnesium, iron, and water and slightly less tetrahedral aluminum and interlayer potassium. The chemical formula is given as $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, but there is considerable ion substitution.[Mitchell JK 1993, A.C.D. Newman 1997]

It is well known that **kaolinite** is one of the most widely used clay minerals, being a major component of the raw materials used in the manufacture of ceramic, cement, and structural clay products. Kaolinite is a tow layer 1:1 silicate, $Al_2O_3.2SiO_2.2H_2O$ (TO). It is structurally formed by one layer of tetrahedral silica (SiO_4), and one layer of octahedral gibbsite ($Al_2O_3.3H_2O$), neither bearing cations nor H_2O molecules between the structural layers. [F.A.C. Milheiro 2005]. Its interlayer distance is about 7 Å.

Comparatively to Illite and kaolinite, the swelling behavior of Montmorillonite is benefic in many applications such as nanocomposits, but causes problems in ceramic process by affecting ceramic suspensions and in fired products.

Structures and ideal formulas of kaolinite, illite and montmorillonite are presented in Figure 1.

The knowledge about electrokinetic and rheological properties of clay dispersions is important for the technologic applications such as formulation of commercial products, design and process evaluation, quality control, storage stability and finally all these significantly affect the final properties of the product and economic aspects of process. [L.M. Bezerril 2006, Sibel tuç2008].[J.C. Baird 2007] [Peter B 2006]

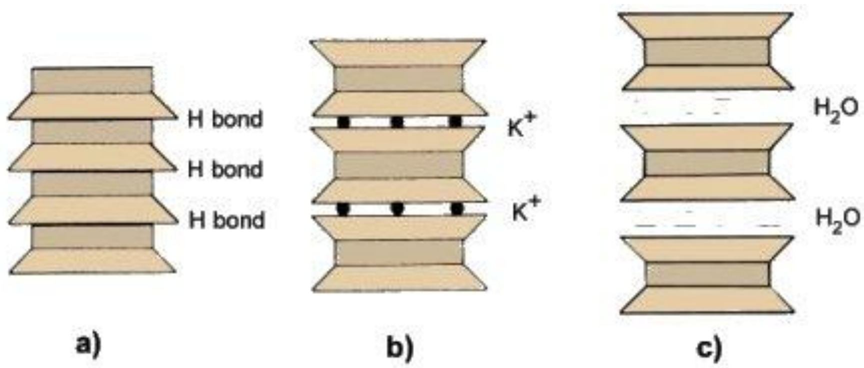

Figure 1 : Structure of the main clay minerals: (a) kaolinite, (b) illite and (c) montmorillonite, based on combined sheets [Craig, 1990]

The particle size, shape, and distribution are important physical properties, which are intimately related to the applications of the clay minerals. Other important properties are surface chemistry, surface area and surface charge.[Alessandra 2008], [koffi leon konan 2008]. These, along with color and brightness, affect many use properties such as low and high shear viscosity, absorption, plasticity, dry and fired strength, casting rate, permeability and bond strength. In almost every application the clays and clay minerals are functional and are not just inert component in the system. [Haydn 2000]

The desaglomeration and dispersion of ceramic particles is a fundamental step in the industrial ceramic processes in order to obtain an homogeneous and stable system of elementary particles. So it is necessary to understand and control the state of dispersion of particles, which will determine the structure of the mixture which is characterized by rheology. The introduction of a suitable defloculent has a beneficial effect up to a minimum concentration to reduce the viscosity of clay suspensions. In ceramic industry, chemical additives are normally used to reduce viscosity of suspension with keeping the higher dry clay concentration as possible. Inorganic substances (as silicates, phosphates and carbonates sodium salts) or organic additives, generally polyacrylates salts with different molecular structures, are commonly used. They are added in a percentage between 0,1 wt% and 0,6 wt% , to reduce the viscosity typically around 200-400 mPa.s. The mechanism of sodium silicates consists in a variation of the pH of the suspension and a specific adsorption of the negatively charged defloculent anions on the clay positive edges, being the driving force of electrostatic nature. The phosphates with more remarkable defloculent effectiveness are sodium hexametaphosphate $(NaPO_3)_6$ and sodium tripolyphosphate $(Na_5P_3O_{10})$. The phosphate anion is adsorbed onto clay particle edges, increasing their negative charge. Moreover, polyphosphate decreases the concentrations of floculant bivalent cations through their complexation performed by not adsorbed defloculant molecules [FAndreola 2006]. Polyacrylates ; sodium or ammonium salts, are defloculants with good effeciency [AJ AYADI 2011], their anions are easily adsorbed on the clay particles increasing the negatives charges and determine an electrostatic repulsion between particles [M Ramagnolie 2007, F Androella 2006].

Rheology and properties of final fired clay body that consists of these clays will depend on the composition and the homogeneity of the mixture namely on the clay minerals [Aydin Aras 2004]

The control of the rheological properties and stability of concentrated clay suspensions is determinant in the ceramic industry and several efforts have been devoted to this scoop [Fernanda Androella 2004], however there are less studies on the effect of clay's mineralogy on the rheological behavior of mixture clays.

This paper investigates the behavior in suspension of three types of mineral clays commonly found in the earth's crust: Kaolinite, Illite and Montmorillonite.

The work includes the characterization of the clay structures and a study of the rheological behavior of clay mixtures using experimental design methodology especially mixture design.

2. METHODOLOGY

The synergetic effect of a combination of two or more components on a property of interest can be easily identified by means of a mixture design approach. In a mixture experiment design, the total amount is held constant and a measured property of the mixture changes when the proportions of the components of the mixture are changed. Therefore, the main purpose of using this methodology is to verify how the properties of interest are affected by the variation of the proportions of the mixture components.[JV. NARDI 2004].

The mixture experimental design generates a map of the response over a specified region of formulation. It is possible to discover the critical variables, to define mathematical models and, by them, to optimize the product and the industrial process. [M. Romagnoli 2006]

The design of experiments with mixtures and the applied response surface analysis has been mentioned in many investigations for obtaining products compositions or formulation with optimized properties.[S.L. Correia 2003][Silvado LC 2009]. Many materials are formed by the mixture of several components, whose characteristics, such as the quality of product being manufactured, depend on the relative proportions of the components in the mixture. The mixture approach has been used, for example, in the optimization of formulations of food [I. A. Castro 2005, Aminah Abdullah 2007], paint [Shohreh Fatemi 2006], polymers [M. Muthukumar 2004], concrete [Basma Samet 2004], glass[G.F. piepel 1989], and ceramics [J.V.Nardi 2004, S.L.Correia 2004, R.R. Menzes 2008? A.A.Zaman 2003].

Recall that the purpose of this work is to study the effect of three components, namely Montmorillonite, kaolin and Illite, on the rheological behavior of clay suspensions.

The coordinate system for mixture proportion is a simplex coordinate system [Amel Kamoun 2002][Faiçal Rais 2004] [J.Goupy2000]. In the case of three components, the factorial space constituted by all the possible fractions of the components is a triangle whose vertices correspond to pure components (Figure 2).

The relationship between the clay suspension viscosity and the components composition can be represented using a polynomial mathematical model, in which the Xj represents the proportion of the j^{th} ingredient, $0 \leq X_j \leq 1$, j = 1,2, . . . , q. As the sum of the components $\sum X_j = X_1 + X_2 + . . . + X_q$ must be 1 or equivalent to 100% therefore the polynomial model, takes a canonical form. For three components, the Scheffe's canonical special cubic model takes the following form [Amel Kamoun 2002] :

$$Yi\,(cal) = b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3$$

Where Yi(cal) is the calculated response value at the ith experiment, bi are the model coefficients, X_1, X_2 and X_3 represent the proportions of Montmorillonite, kaolin and Illite, respectively.

In the present research, a mixture design with 13 experiments was carried out (Table 1 and Figureure 2). A design point (run n°7) was replicated four times (Runs n°7 to 10) in order to estimate the variance of the experimental error. Moreover, three check points (runs n° 11 to 13) were included in the experimental design, in order to check the adequacy of the fitted model.

Table 1: Three components mixture design with 13 experiments

N°Exp	X_1	X_2	X_3
Vertices			
1	1.0000	0.0000	0.0000
2	0.0000	1.0000	0.0000
3	0.0000	0.0000	1.0000
Edge centers			
4	0.5000	0.5000	0.0000
5	0.5000	0.0000	0.5000
6	0.0000	0.5000	0.5000
Centroid			
7	0.3333	0.3333	0.3333
8	0.3333	0.3333	0.3333
9	0.3333	0.3333	0.3333
10	0.3333	0.3333	0.3333
Check points			
11	0.6667	0.1667	0.1667
12	0.1667	0.6667	0.1667
13	0.1667	0.1667	0.6667

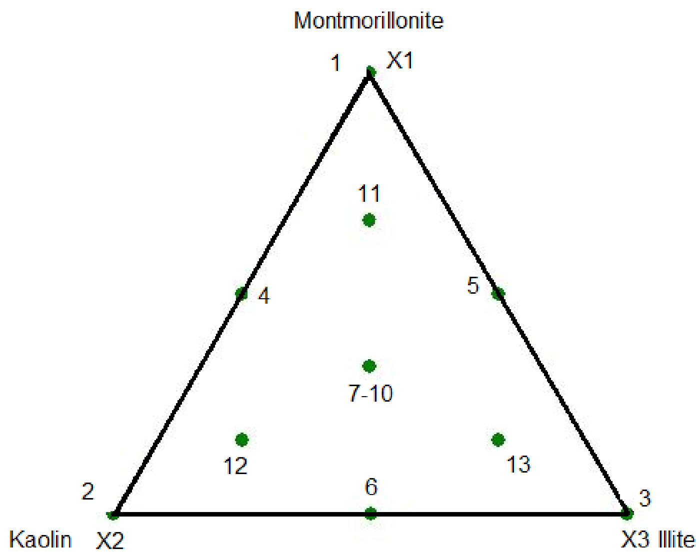

Figure 2 : Distribution of the experimental points in the studied domain

Following the experimentation program, the data were used to fit the empirical model and to test the adequacy of the fitted model. This latter was used to plot the contours of the predicted responses and to determine the optimal settings of the component proportions.
In the present work, the NemrodW software [D.Mathieu *et al.* 1999] was used to build the experimental design and to conduct all data calculations and processing.

3. MATERIAL AND METHOD:

3. 1. Raw Materials:
Three different types of clays were used as reference clays, namely a kaolinite rich sample (K), a montmorillonite rich sample (M) and an Illite rich sample (I).
Kaolin (K), a natural white clay (kaolin codex), was supplied by central pharmacy of Tunisia.
Illite (I) , a green clay nominated ARVEL was provided by Imerys (France).
Montmorillonite (M), a natural grey clay was provided by ABM (Argiles du bassin Mediterranean) .
A commercial anionic dispersant, sodium tripolyphosphate (STPP) was used as a dispersing agent for clay suspensions.
The properties of the clays (K, I and M) were determined by using various techniques of analyses. Physicochemical characteristics are summarized in table 1.
A chemical analysis using X-ray fluorescence was applied to raw materials. The results of XRF are given in table 2, data are expressed as oxides, expect loss ignition which is mainly due to the elimination of water.
Their mineralogical compositions were studied using XRD. The X-ray diffraction, especially oriented samples were analyzed with (PHILIPS-PANALYTICAL; X'PERT pro MPD) X-ray diffractometer using monochromatic CuKα radiation.
All XRD data were collected under the same experimental conditions, in the angular range $3° < 2\theta < 45°$.
The clay fractions analysis were carried out on oriented samples of (< 2µm) clay fraction to identify clay minerals. The clay fractions were separated by sedimentary and centrifugation [George William Brindley 1980] .The phases were identified from peak positions and intensities using reference data from ASTM sheets. The obtained XR spectra are shown in figure 3.

3.2. Preparation of the clayey suspensions

Sodium Tripolyphosphate was used as an anionic dispersing agent, distilled water was used to prepare the suspensions in this investigation. This deflocculent was choose since it is known as an efficacious dispersant for clays giving lower viscosity at low concentration (0.3%) [Papo 2002, Ali Assifaoui 2001]. This effect is due to an electrostatic mechanism of dispersion and to the small size of STPP.

Slurries of natural clays were prepared by mixing an appropriate amount of clay mixtures with distilled water in which the dispersant (0.3 wt% of STPP) was dissolved, followed by ultrasonification during 3 minutes and 24 hours shaking. The final solid content was 50 wt%.

Clay suspensions were prepared according to the following steps :

- Dissolution of deflocculant in a known amount of water. The amount and nature of the dispersant are held fixed for all mixtures prepared,
-Introduction of dry clays,
- Desagglomeration and homogenization of suspensions by ultrasonification and then by shaking.

The pH of suspensions were kept constant since have near pH and because the STPP dispersant not disturbs the pH of mixture according to preliminary experiments.

Sodium tripolyphosphate (NaP_3O_{14}) is one of the more remarkable effective defloculant power [M ramagnoli 2006]. The phosphate anions are adsorbed into clay particles edges increasing their negatives charges. Moreover, polyphosphates decrease the concentrations of flocculent bivalent cations through their complexation performed by not adsorbed defloculant molecules.

3.3. Measure of the viscosity of the clayey suspensions

Rheological tests were carried out on concentrated dispersions at 25°±1 C with a controlled- stress rheometre (carrimed CSL 100) equipped with a parallel-plate geometry. This sensor has been adopted due to the large range of viscosity to be explored.

Viscosity was measured under the same conditions to all samples using the same cycle. The rheological test consists of a linear increasing of the shear for 180 seconds and viscosity values are retained at a constant shear rate (100 s^{-1}).

4. RESULTS AND DISCUSSION

4.1. Characterization of the raw materials

Kaolin, Illite and Montmorillonite, referred to us as standard clay minerals, were purchased from different locations and were used as received (milled powders).

Some physicochemical characteristics are summarized in table (2).

Table 2 : Physicochemical characteristics of studied clays:

	Kaolin K	Montmorillonite M	Illite I
Density (g/cm^3)	2,77	2.71	2,23
Specific surface (m^2/g)	13,15	95,97	90, 94
Natural pH	7,8	8	8
IEP iso-eletric point	7.7	8.1	8.2

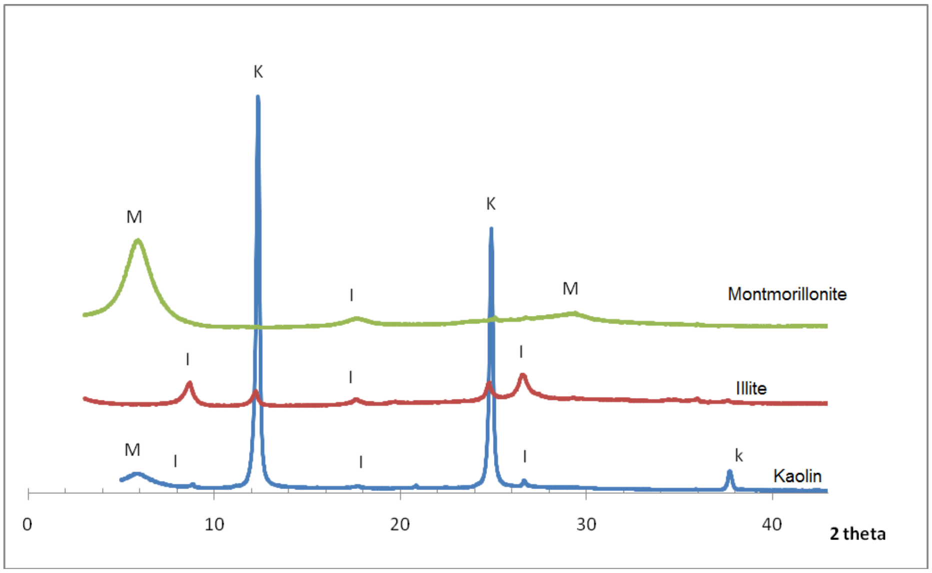

Figure 3 : X-Ray diffraction pattern of studied purified clays

The X-ray diffraction of the three samples (Figure 3) shows that:

- Kaolinite, illite and montmorillonites are the predominant phases respectively for K, I, and M.
- Kaolin (K) contains Illite and also Montmrillonite as minor constituents.
- Illite powder reveals peaks of Kaolinite as minor clay
- Montmorillonite cantains small amounts of kaolinite and illite.

These clay minerals are natural materials that cannot be considered as pure minerals since they contain some associates minerals in minor amounts.
The chemical analysis was investigated on studied clays (K,I,and M) the results are presented in table 3

Table 3 : Chemical analysis (% by weight) of different raw materials

Eléments (%)	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	Na_2O_3	*K_2O*	*TiO_2*	*MnO*	*P_2O_5*	*BaO*	*LOI*
Kaolin	48	35.3	1.8	0.2	0.3	<0.01	1	0.27	<0.01	0.08	0.01	12.7
Montmorillonite	60	15.9	6	2.6	2.2	0.2	3.9	0.8	0.04	0.09	0.03	7.8
Illite	45.5	20	6.5	6.8	3.1	0.13	5.2	0 .7	0.06	0.19	0.02	11.5

LOI : Loss on ignition

Data are expressed as oxides, expect loss of ignition (LOI) which is mainly due to the elimination of water, organic carbon and carbonate compounds.
Based on data of chemical compositions (table 2), the following comments can be deduced:

- Kaolin contains the higher amount of Al_2O_3 and small amounts of impurities (Ca, Mg, Na, Ti, Mn). The presence of 1% of K_2O can be explained by the presence of illite mineral in this clay.

  The proportion amounts of SiO_2 (48%) and of Al_2O_3 (35.3%) is nearly equal to the theoretical value in fact according to [A.C.D. Newman, 1987] the ideal composition of kaolinite is (SiO_2 45.5%, Al_2O_3 39.5%, H_2O 13.9%°.

  The presence of 0,2% of CaO and 0.3% of MgO can explain the presence of Montomorillonite showed in the DRX pattern.

  The loss ignition is basically due to the emanation of the structural water.
- Major constituents of Illite are Al_2O_3 and SiO_2.

  Illite presents the higher amount of K_2O, this explains that the major mineral constituting this sample is indeed Illite. This sample (I) contains also minor elements like (Na, Ca, Mg) and trace elements (Ti, P, Mn) as well as a large amount of water (LOI).
- Montmorillonite contains 15.9% of Al_2O_3 and a high amount of SiO_2 which are approximately in concordance to the theoretical formula of this kind of clay.

  The presence of MgO and CaO involve the substitution in octahedral positions of Mg^{2+} and Ca^{2+} for Al^{3+} ions. In this case it is possible that there is an incorporation of Fe^{2+} in octahedral positions since the amount Fe_2O_3 (6%) is important in this clay.
- The proportions of Fe_2O_3 in all cases can be explained either by isomorphic substitutions in the clay mineral structures, or by low iron oxide content which are not detected with DRX.
- The presence of high amounts of SiO_2 for the three clays explains the presence of quartz mineral which is not observed on oriented DRX pattern, it is absolutely normal because analysed fraction had a granulometry < 2µm while the grain size of quartz is higher than 2µm.
- The results provided by both chemical and mineralogical analysis are in concordance.

4.2. Study of the response "viscosity of the clayey suspensions"

Thirteen mixtures of clays were prepared according to the experimental conditions indicated in Table 4. The measured and estimated viscosity values were reported in the last columns of Table 4.

Table 4 : Experimental conditions of the mixture design with the corresponding measured and predicted viscosity values

Run	Montmorillonite (wt %)	Kaolin (wt %)	Illite (wt %)	Viscosity (meas.) Pa.s	Viscosity (pred.) Pa.s
1	100	0	0	29.50	29.50
2	0	100	0	0.15	0.15
3	0	0	100	0.55	0.55
4	50	50	0	7.20	7.20
5	50	0	50	6.00	6.00
6	0	50	50	0.16	0.16
7	33.33	33.33	33.33	3.00	3.00
8	33.33	33.33	33.33	3.20	3.00
9	33.33	33.33	33.33	2.80	3.00
10	33.33	33.33	33.33	3.00	3.00
11	66.67	16.67	16.67	12.30	12.57
12	16.67	66.67	16.67	0.40	0.84
13	16.67	16.67	66.67	0.80	0.57

Fitted to the 10 first response values in table 4, the canonical special cubic model for viscosity (η) is represented by the following equation:

$$\eta = 29.50\ X_1 + 0.15\ X_2 + 0.55\ X_3\ -30.50\ X_1X_2\ -36.10\ X_1X_3\ -0.76\ X_2X_3 + 11.28\ X_1X_2X_3$$

The good quality of the fitted model was attested with analysis of the variance (ANOVA) as shown in Table 5. Indeed, this table shows that the sum of squares related to the regression was statistically significant when using the F-test at a 99,9 % probability level, which suggests that the variation accounted for by the model was significantly greater than the residual variation. On the other hand, the validity of the model has been established by comparing the results obtained at the three check points (experiments 11–13) with the predicted values (Table 6). These results seem to confirm the validity of the model. Indeed, the differences between calculated and measured responses were not statistically significant when using the *t*-test at a 95% probability level.

Table 5 : Analysis of variance

Source of variation	Somme of square	Freedom degrees	Mean square	Ratio	Significance
Regression	685.7492	6	114.2915	4285.9327	< 0.0001 ***
Residuals	0.0800	3	0.0267		
Total	685.8292	9			

*** Significant at the level 99.9%

Table 6 : Validation of the model with the check points.

Run	y_i	$\hat{y}_i$	$y_i - \hat{y}_i$	t.exp.	Significance %
11	12.30	12.57	-0.27	-1.480	23.5
12	0.40	0.84	-0.44	-2.409	9.5
13	0.80	0.57	0.23	1.232	30.6

y_i, measured response value; $\hat{y}_i$, estimated response value; t exp., student experimental value.

Following the validation of the model, we used it for generating response surface as a contour plot or a three dimensional surface plot over the explored domain as shown in figure 4.

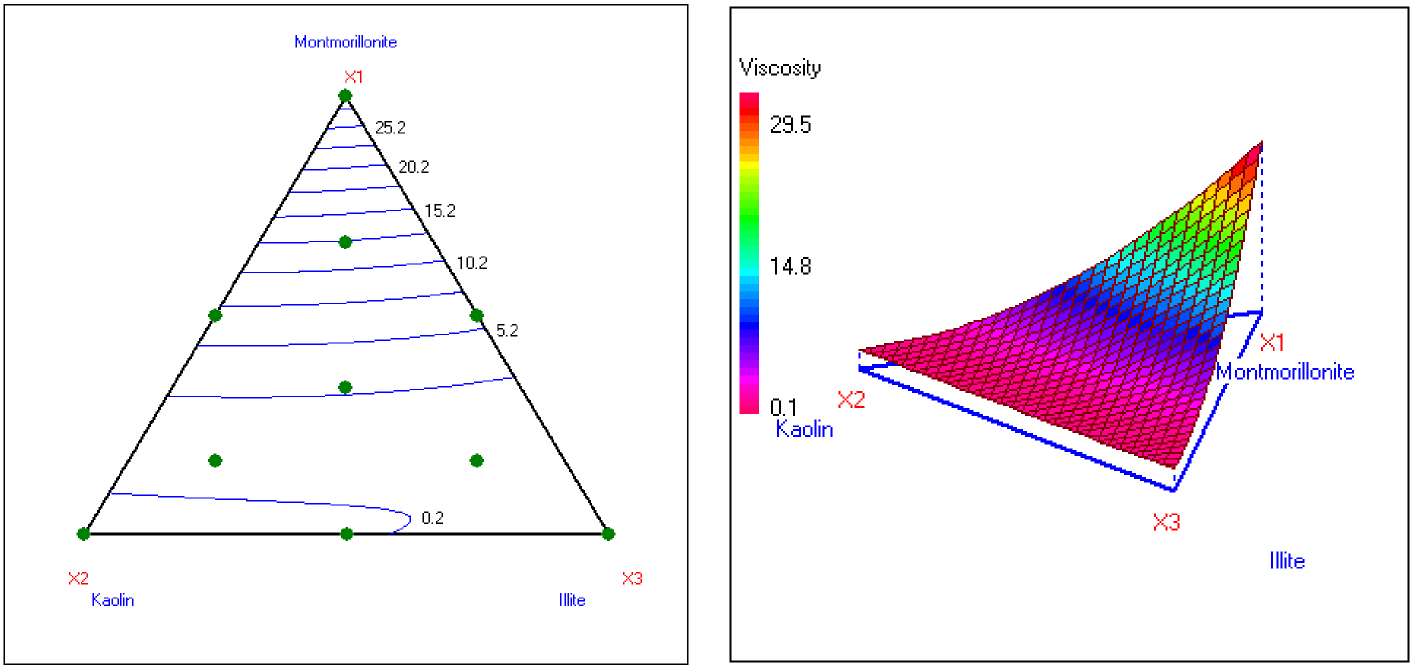

Figure 4 : Contour plot and three-dimensional surface plot of the viscosity

Moreover, in order to evaluate the contribution of each of the three components, we used the response trace technique [10 Amel kamoun 2002]. In practice, the response trace is a plot of the estimated response value as we move away from a reference mixture (in general, the centroïd of the explored region) and along the component axes. Figure 5 shows the response trace of the viscosity response using a reference mixture S the centroïd of the simplex domain (X_1=0.33, X_2=0.33, X_3=0.33). In this figure, the vertical axis is the predicted response and the horizontal axis is the incremental change in each component. The reference mixture is shown as the point 0.00 on the horizontal axis.

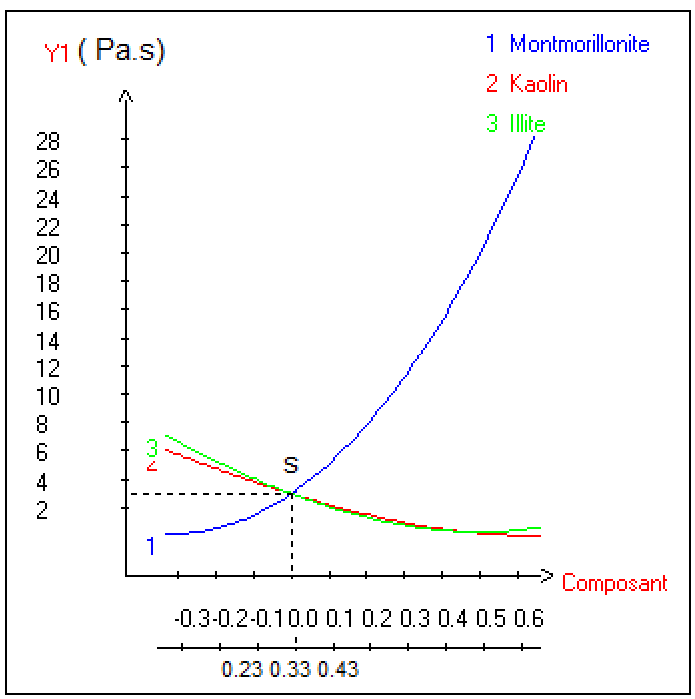

Figure 5 : the response trace of viscosity response using as reference mixture S the centroïd of the simplex domain.(effect of each clay)

From figures 4 and 5 it is very clear that viscosity increases strongly with the amount of Montmorillonite in the mixture while illite and Kaolin exhibit moderate effect on viscosity. This is an expected result since Montmorillonite is known as swelling clay [L. Heller.Kallai 1981, A.K.Helmy 1998].

Recall that in ceramic industry, clay suspension must have a low viscosity (0.20- 0.40 Pa.s). The contour plot in figure 4 indicates that formulations which correspond to this requirement are mixtures rich in kaolin and/or illite with a small amount of Montmorillonite ($\leq$ 16 %).

This result is important since Tunisia have many smectitic deposits. So it is an opportunity to value this kind of clay. Montmorillonite can be then incorporated in ceramic formulations.

In general rheological behaviour of clay suspensions depends on many characteristics such as concentration on dry clay, amount and nature of dispersant, pH of solution and clay, ionic strength, clay nature etc. For this reason and in order to understand the effect of clay nature on rheological behaviour we have worked in constant conditions (pH, Concentrations and experiment conditions).

In fact, due to the shape, the charge distribution and surface area of clay particles, clay dispersions have different rheological behaviours. Moreover chemical composition and mineralogical structure of each clay affect differently the clay suspension's viscosities.

According to noted viscosity values in our study, it is clear that kaolin and rich kaolin suspensions have the lowest viscosities, this behaviour can be explained by the little or no charge deficiencies in his structure and by its low surface area (13,15 m^2/g).[Hayden. H 1991]

In previous study, J. Longand and all demonstrated that in the presence of calcium cation, Illite particles can approach and coagulate with each others. They also showed that in the presence of magnesium cation, the electrostatic repulsion originated from the net surface charge of illite surface decreased. So the adsorption of magnesium was the major contribution to the observed attraction, as positively charged magnesium ions adsorbed on one surface could be attracted by the negatively charged sites on the other surface.

Since Illite and montmorillonite are rich on calcium and also Magnesium we can explain the higher viscosity values noted in our work.

By comparison to rich illite and rich kaolin mixtures, montmorillonite and rich montmorillonite suspensions have the higher viscosities. In fact many phenomena are present in the same time which leads to such high viscosities. In his study, karim Baccour demonstrated that rheological behaviour of montmorillonite is related to the changes occurring in the inner structure of the fluid due to the particle interaction forces like the van der waals forces which are responsible for the formation of flocks and aggregates.

According to Hydin H 1991, the high charge on the smectite or montmorillonite layers is satisfied by water layers containing cations such as sodium, calcium, magnesium, iron etc. Besides smectite are normally very thin flakes which gives the material a high surface area (95.97 m^2/g in our case). These characteristics give smectite, when mixed with water, a fluid with a high viscosity.

Moreover, in contrast to kaolinite and illite, in which the layers are strongly held together, the montmorillonite layers are held so loosely that water can penetrate between them. Montmorillonite is subject to intercrystalline swelling, a process in which the interlayer distance can increase to 1nm [Max Müller-Vonmoos 1989]. This swelling behaviour causes indeed the high viscosity of montmorillonite mixture suspensions.

5. CONCLUSION

The use of mixture design in the study of ceramic formulations and the use of multiple regressions and response surfaces is a powerful procedure in the evaluation of the individual effect of raw material in rheology of ceramic suspensions.

The mixture design, performed in this study in order to determine the effect of each of the three components(kaolin, illite and Montmorillonite) present in clay suspension shows, that :

- Kaolin and illite have a good benefit effect on the viscosity of suspension clays.
- Montmorillonite has the worst effect on the viscosity of the clay mixtures
- The presence of Montmorillonite with a small concentration can afford to get mixture clay suspensions having a low viscosity. Therefore Montmorillonite can be incorporated in ceramic formulations.
- The mineralogical nature and the structure of each clay explain the viscosity behavior of each one.

To provide a comprehensive understanding of colloidal interactions in ceramic suspensions, studies on other systems clay-clay or clay- dispersant still need to be clarified.

To date, the investigations on the rheological interactions not only help to understand the mechanisms of ceramic suspensions but also value natural raw materials which are abundant and not well exploited.

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